Structure and Property Relations Between the Polyacrylonitrile-Based Prestabilized Fibers and the Partially Carbonized Fibers

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ABSTRACT: The structure of polyacrylonitrile-based prestabilized fibers and partially carbonized fibers prepared in air and nitrogen were studied by Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD), the thermal properties were measured by differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA), and the mechanical properties and corrosion properties resistant to concentrated sulfuric acid are also tested. Oxygen functional groups form in the fibers prestabilized in air, providing active sites for dehydrogenation and intermolecular crosslinked reactions, which facilitates the formation of turbostratic graphite structure in partially carbonized fibers. The fibers prestabilized in nitrogen and their corresponding partially carbonized fibers are brittle feature, and have comparatively low tensile strength and elongation. The fibers prestabilized in air did not change the color of concentrated sulfuric acid until being etched in it for 6 h; by contrast, the fibers prestabilized in nitrogen were dissolved out only within 1 min. It indicates that the former has better chemical stability than the latter. The present work provides direct evidence that oxygen containing structure in prestabilized fibers is an essential precondition for obtaining high property carbon fibers. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 5172–5179, 2012

Key words: fibers; structure-property relations; differential scanning calorimetry (DSC); polyacrylonitrile; carbonization

INTRODUCTION

Polyacrylonitrile (PAN)-based carbon fiber is one of the most widely used high property fibers in the modern industrial fields such as aerospace, energy, automotive, and sports.[1,2] It has been well known that the high specific strength and modulus of carbon fiber are mainly depended on its turbostratic graphite structure.[3–5] To obtain high strength carbon fibers, the following conditions are popularly deemed necessary: high quality PAN precursor fibers with few defects,[6,7] prestabilization in air at proper temperature range for adequate time,[8] carbonization at rather high temperature under the protection of high purity inert atmosphere,[9] and proper stretching to maintain chain orientation during the whole manufacturing process.[10,11] Until now, the importance of precursor fibers and the processing conditions of prestabilization and carbonization have attracted much attention, but there is still little knowledge as to what kind of structure and properties are necessary and desirable in prestabilized fibers to produce high performance carbon fibers.

In this paper, PAN precursor fibers were prestabilized isothermally at 240°C in air and nitrogen, respectively. Then the prestabilized fibers are partially carbonized at 500°C in nitrogen under the same condition. Because of different environment atmospheres, the two prestabilized fibers have great difference in not only physical and chemical structure, mechanical properties, but also corrosion resistance to concentrated sulfuric acid. And the corresponding partially carbonized fibers also exhibit remarkable difference in both tensile strength and structural stability. The relationships between the prestabilized fibers and partially carbonized fibers on the aspects of structure and property were disclosed.

EXPERIMENTAL

Preparation of PAN precursor fibers

Acrylonitrile (AN) and itaconic acid (IA) with proportion of 99 : 1 (wt %) were copolymerized using α, α-azobisisobutyronitrile (AIBN) as initiator, then the copolymer solution were treated by ammonia. The molecular weight and solid content of the spinning dope is about 1.3×10^4 and 16.9%, respectively. The PAN precursor fibers were prepared by wet-spinning method using dimethysulfoxide (DMSO) as coagulation bath. The property parameters of the PAN precursor fibers are: average titer of single filament, 0.95 dtex; tensile strength, 7.0 cN/dtex; and elongation at break, 10.5%. For description convenience, the PAN precursor fibers are named as sample $0^{\#}$.

Prestabilization and carbonization process

PAN precursor fibers were prestabilized isothermally at 240°C for 2 h in air and nitrogen, respectively. The obtained samples were named as $1^{\#}$ and $2^{\#}$. Then the two prestabilized fibers were carbonized simultaneously under the same experimental condition at 500°C for 3 min under the protection of high purity nitrogen. The partially carbonized fibers were named as $1^{\#}$-CF and $2^{\#}$-CF, respectively, of which $1^{\#}$-CF is derived from the fibers prestabilized in air ($1^{\#}$), and $2^{\#}$-CF is derived from the fibers prestabilized in nitrogen ($2^{\#}$). All the fibers were kept constant length to restrain shrinkage during both prestabilization and carbonization processes.

Structure and property characterizations

Thermal properties were investigated by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) on NETZSCH DSC 404C and NETZSCH TG 209. Two steps carried out the DSC experiments. In the first step, the PAN precursor fibers were heated from 200 to 300°C at a heating rate of 5°C/min in air and nitrogen, respectively. After that, the samples that have been treated in the first step were heated from 300 to 1400°C at a heating rate of 50°C/min in nitrogen. TGA scans were also divided into two steps. First, the PAN precursor fibers were heated by different heating rate at different temperature ranges in air and nitrogen, respectively: from room temperature to 200°C, the heating rate is 20°C/min; from 200 to 300°C, the heating rate is 3°C/min. After that, the samples that have been treated in the first step were heated from 300 to 900°C in nitrogen at a heating rate of 20°C/min.

Chemical structures of the precursor, prestabilized, and partially carbonized fibers were examined by Fourier transform infrared (FTIR) using KBr disk method on Bruker Alpha FTIR spectrophotometer (Bruker Optik GmbH, Ettlingen, Germany).

Mechanical properties of the fibers were tested by XD-1 type strength and elongation tester (made by Donghua University, China) according to The People's Republic of China national standard GB 9997-1998. The testing length of each filament is 20 mm, with a tensile rate of 5 mm/min. Twenty filaments were tested for the same kind of fiber, and the average value was calculated.

Wide angle X-ray diffraction (XRD) spectra were recorded on a Rigaku D/max-rc diffractometer (Tokyo, Japan) with Ni filtered Cu K_α radiation to study the crystal structure of different fibers. The experimental conditions were as follows: applied voltage, 40 kV; current, 30 mA; and scanning rate, 4°/min with a scanning step of 0.02°. Fibers were positioned with axis perpendicular to the direction of X-ray radiation.

The prestabilized fibers were treated in concentrated sulfuric acid (98%) to examine their corrosion resistance. The surface morphologies of post-treated fibers were observed on a SU-70 (Hitachi, Japan) field emission scanning electronic microscope (SEM).

RESULTS AND DISCUSSION

Mechanical properties

Table I lists the tensile strength and elongation at break of fibers $1^{\#}$, $2^{\#}$, $1^{\#}$-CF, and $2^{\#}$-CF. There is slight difference in the tensile strength of the two prestabilized fibers, but the elongation at break is much lower for the fibers prestabilized in nitrogen ($2^{\#}$) than the ones prestabilized in air ($1^{\#}$). After carbonization at 500°C, the tensile strength of $1^{\#}$ increases from 2.9 to 3.4dtex/cN, while its elongation at break decreases from 10.46 to 3.92%. By contrast, as for $2^{\#}$-CF, which is carbonized from the fibers prestabilized in nitrogen, the mechanical properties is unable to test due to the great brittleness. The remarkable difference in the mechanical properties of these fibers is mainly attributed to the prestabilization atmosphere, and it seems to be essentially related to the different chemical and physical structures which will be analyzed below on FTIR and XRD results.

It has been universally accepted that stretching is a very important measure to keep and improve the orientation of fibers both in the prestabilization and carbonization process.[10,11] Stretching is deemed indispensable to obtain high strength carbon fibers. But if the fibers' elongation at break is too low, it is hard to apply stretching on fibers during the whole manufacturing process. From Table I, it is obvious that the elongation at break of $2^{\#}$ and $2^{\#}$-CF is very low, and is too low to measure. From it, we can

TABLE I
Mechanical Properties of the Prestabilized Fibers and the Corresponding Partially
Carbonized Fibers

Mechanical properties	1#	2#	1#-CF	2#-CF
Tensile strength (cN/dtex)	2.90 ± 0.02	3.16 ± 0.02	3.40 ± 0.02	Too brittle to test
Elongation at break (%)	10.46 ± 0.05	4.74 ± 0.05	3.92 ± 0.05	Too brittle to test

speculate that prestabilization in air is more feasible than in nitrogen for producing high strength carbon fibers, because larger stretching ratio can be applied in air than in nitrogen.

Chemical structure

The FTIR spectra of fibers 0#, 1#, 2# is shown in Figure 1. The typical absorption bands of acrylonitrle/itaconic acid copolymer precursor fibers include: 3460 cm^{-1}, due to the stretching of -OH or -NH groups; 2930 cm^{-1}, due to the stretching of C—H in CH_2 groups; 2242 cm^{-1}, due to the stretching of C≡N groups; 1740 and 1630 cm^{-1}, due to the carboxyl groups introduced by the IA comonomer; 1455 ~ 1240 cm^{-1}, due to different bending vibrations of C—H groups; and 1067 cm^{-1}, due to C—CN groups.[12]

From Figure 1, it can be seen that after prestabilized in different atmospheres, great and different changes appear in 1# and 2#. The major changes are marked out by arrows at several bands. The absorption band of C≡N at 2242 cm^{-1} becomes weaker; meanwhile, a new band appears at 1590 cm^{-1} in 1# and 2#. This is attributed to two reactions: one is the conversion from C≡N to C=N in cyclization reaction and the other is the formation of C=C caused by dehydrogenation reaction. The neighboring frequencies appear in the stretching mode region of the nitrile groups are assigned to Fermi-resonance by Varma et al.,[12] and to the conjugated and/or β-amino type C≡N by Sivy.[13] The residual absorption intensity at 2242 cm^{-1} in 1# is higher than 2#, indicating that the cyclization degree of nitrile is lower in 1# than 2#. This result reveals that nonoxidative atmosphere is helpful for intramolecular cyclization reaction. The decreasing of absorption intensity at 2930 cm^{-1} and 1455 ~ 1240 cm^{-1} bands suggests that dehydrogenation is simultaneous with cyclization reaction both in air and nitrogen atmospheres, but the dehydrogenation degree of 2# is lower than 1#.

Two shoulders at 1718 cm^{-1} and 1660 cm^{-1}, and one absorption band at 1150 cm^{-1} can be found in 1#, but these bands are absent in 2#. As suggested by Shimada and Takahagi,[14,15] the band at 1718 cm^{-1} is assigned to the free ketones in hydronaphthyridine rings, and 1660 cm^{-1} band is assigned to the conjugated ketones in acridone rings. The band at 1150 cm^{-1} is assigned to C-OH.[12] These groups are generated by the oxygen uptake reactions, so they

only appear in the fibers prestabilized in air. In addition, there are two new bands appearing around 3208 and 740 cm^{-1} in 2#. The former absorption band is attributed to -NH groups, and the latter to conjugated C=C or C=N groups.[16] Based on the analysis of Figure 1, the chemical structure of the prestabilized fibers may be like in Figure 2, of which structure (a) belongs to the prestabilized fibers in air, and structure (b) belongs to the prestabilized fibers in nitrogen. Because the chemical structure of prestabilized fibers is very complicated, it is hard to determine the exact one only with FTIR spectra. The structures in Figure 2 are merely the proposed structures.

Figure 3(a,b) compares the FTIR spectra of 1# and 2# before and after carbonization at 500°C, respectively. The same changing trend is that the absorption intensities of C≡N groups and of C—H stretching in CH_2 groups continuously weaken due to the secondary cyclization and dehydrogenation under elevated temperature.[9,17] In Figure 3(a), the bands at the range of 1580 ~ 450 cm^{-1} become broaden and stronger from 1# to 1#-CF. The oxygen containing groups become weak and even disappeared in 1#-CF because of dehydrogenation by releasing of H_2O. The bands at 1360, 1260, 960, and 800 cm^{-1} assigned to different variations of = C—H groups increase also due to dehydrogenation. It is worthy to note that a new broad band centered around
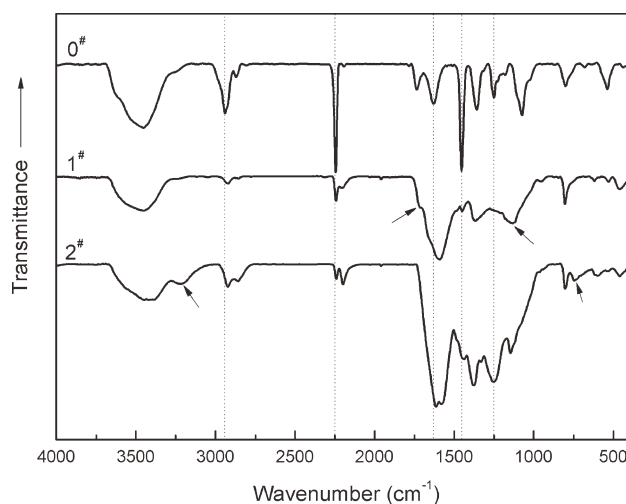

Figure 1 FTIR spectra of PAN precursor fibers (0#), the fibers prestabilized in air (1#), and the fibers prestabilized in nitrogen (2#).
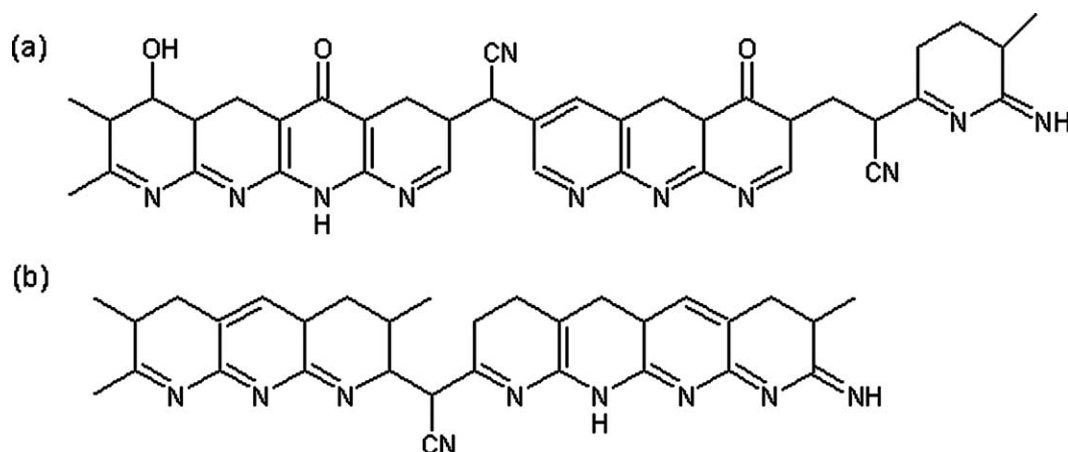
Figure 2 Possible structures of prestabilized fibers at 240°C in (a) air; (b) nitrogen.

1840 cm^{-1} appears in 1$^{\#}$-CF. It may be assigned to conjugated double bonds and is the characteristics of the formation of intermolecular crosslinked structure.

Comparing Figure 3(a,b), the spectra of 2$^{\#}$-CF are quite different from 1$^{\#}$-CF, because the two fibers are derived from different prestabilized fibers in different atmospheres. The band at 3460 cm^{-1} is almost unchanged in 1$^{\#}$-CF, but it obviously weakens in 2$^{\#}$-CF. The band at 3208 cm^{-1} is disappeared in 2$^{\#}$-CF. In Figure 3(b), it can be seen that with the decreasing of —NH, several new bands appear in the low frequency fingerprint region, as marked by the vertical arrows. A new band is also found around 1840 cm^{-1} in 2$^{\#}$-CF, but its intensity is much weaker than that in 1$^{\#}$-CF. These results probably indicate that large amounts of NH$_3$ and trace of HCN are eliminated during the low temperature 500°C carbonization process in 2$^{\#}$-CF, which can be further confirmed by DSC data. Many heterocyclic aromatics like pyridines or aridine form in 2$^{\#}$-CF, but the intermolecular crosslinked structure is relatively few. The possible structures of the partially carbonized fibers derived from different prestabilized fibers may be like in Figure 4.

Thermal properties

Most of the reactions during prestabilization and carbonization are exothermic.[18,19] DSC and TGA were used to investigate thermal stability of the prestabilized and carbonized fibers, and the relation between them. Figure 5(a) shows the DSC exothermic curves of PAN precursor fibers in air and nitrogen at the temperature range of 200 $\sim$ 300°C. There is a broad exothermic peak in air and a sharp one in nitrogen, indicating the cyclization reaction in nitrogen is more intense.[20] In air, the exothermic initiation temperature and peak temperature is at about 200 and 275°C, respectively; while, in nitrogen, the initiation temperature (250°C) is much higher but
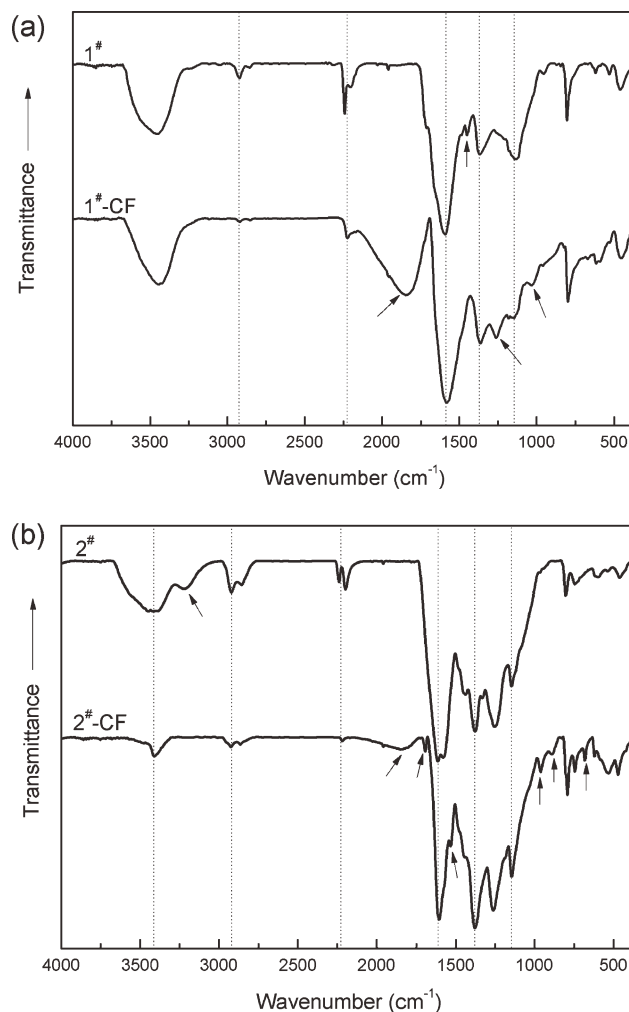

Figure 3 FTIR spectra of prestabilized fibers and their corresponding partially carbonized fibers. (a) prestabilized fibers in air (1$^{\#}$) and the corresponding partially carbonized fibers in nitrogen (1$^{\#}$-CF); (b) prestabilized fibers in nitrogen (2$^{\#}$) and the corresponding partially carbonized fibers in nitrogen (2$^{\#}$-CF).
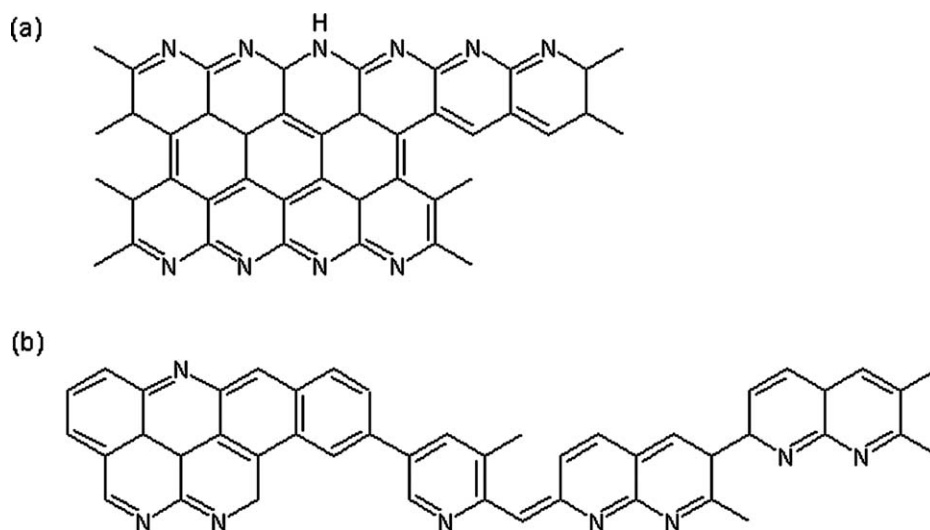
Figure 4 Possible structures of partially carbonized fibers at 500°C derived from fibers prestabilized in (a) air; (b) nitrogen.

the peak temperature (267°C) is a little lower. These results which are consistent with many previous studies can be well explained by the different reaction mechanisms in oxidative and nonoxidative atmospheres.[21,22] Fitzer found that the activation energy and the frequency factor are greater in air than in nitrogen. Oxygen acts in two opposite directions: on the one hand, oxygen is an initiator for the formation of activated centers for cyclization. On the other hand, the consecutive cyclization of these centers is inhibited by oxygen because of the increase of the activation energy.[21] The study of Beltz and Gustafson also indicated that the presence of oxygen decrease the induction period of cyclization reacton.

Based on the first DSC experiment mentioned above, the treated samples were heated successively from 300 to 1250°C in nitrogen, obtains DSC curves shown in Figure 5(b). It can be seen that the exothermic characteristics in the carbonization temperature range are remarkably influenced by the prestabilization conditions. The exotherm of lower than 400°C is due to the evolutions of CO_2, H_2O, and some HCN.[23] There is no resoluble exotherm between 500 and 700°C for the sample after prestabilized in air, but there is an obvious exothermic maximum presents between 450 and 600°C for the sample after prestabilized in nitrogen, which may be attributed to the evolution of H_2, NH_3, and HCN. An endothermic peak occurs at 800°C in the sample after prestabilized in air, indicating some fragments of graphite basal plane come into beings by crosslinking. Then, another obvious exothermic maximum which is caused by the evolution of N_2 and some H_2 appears at about 960°C in this curve. The similar exothermic maximum appears much later at about 1160°C for the sample prestabilized in nitrogen.
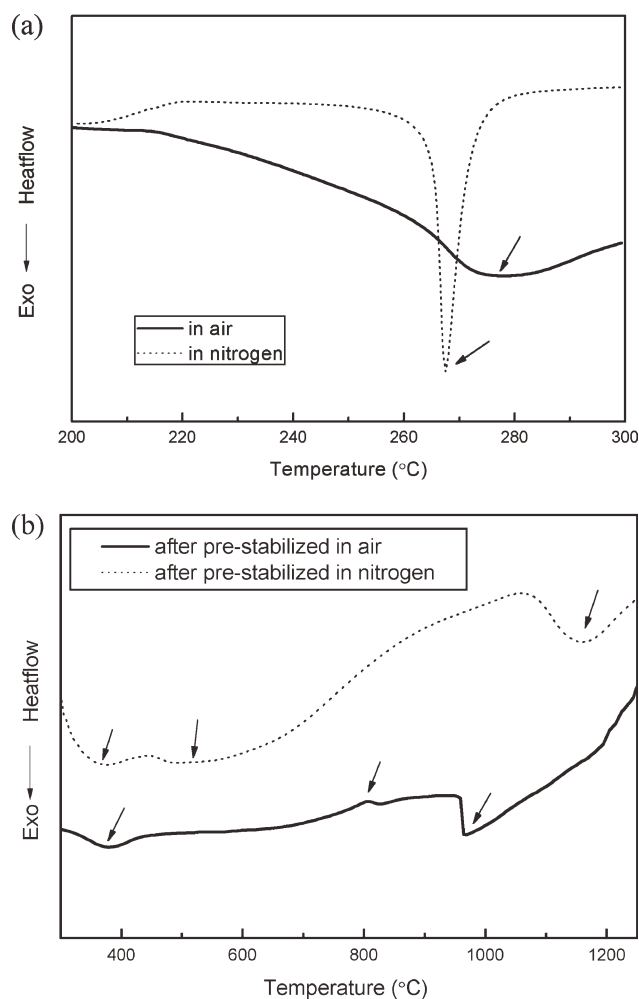

Figure 5 DSC curves under different conditions (a) PAN precursor fibers were heated in air and nitrogen, respectively, at a rate of 5°C/min from 200 to 300°C; (b) the samples after prestabilized in air and nitrogen were heated successively in nitrogen at a rate of 50°C/min from 300 to 1250°C.
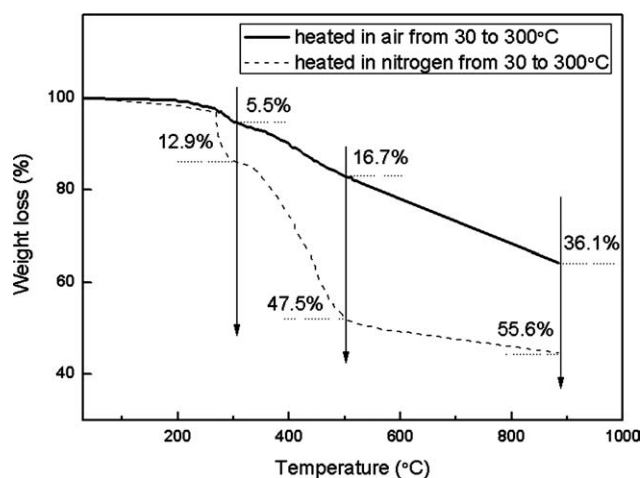
Figure 6 TGA curves under different conditions: PAN precursor fibers were first heated from 30 to 300°C in air and then from 300 to 900°C in nitrogen (the solid line); the same PAN precursor fibers were first heated from 30 to 300°C in nitrogen and then from 300 to 900°C also in nitrogen (the dashed line).

It has been known that the formation of hexagonal carbon layers is strongly depended on the cross-linking reactions by dehydrogenation and the elimination of N_2.[23,24] Accordingly, the DSC results indicate that graphitizing is much easier during the subsequent carbonization process for the PAN precursor fibers prestabilized in air than those prestabilized in nitrogen.

Figure 6 shows the TGA curves in the temperature range of 30 ~ 900°C. The heating process is consisted of two steps: previously, the PAN precursor fibers were heated from 30 to 300°C in air and nitrogen, respectively. Then, the medium gas was changed to or maintained nitrogen after 300°C in each experiment. The total weight loss is 36.1% when preheated in air and is 55.6% when in nitrogen. As the dashed line is concerned, the weight loss from 300 to 500°C accounts for the main part of the total weight loss, and its weight loosing rate is very fast. This result agrees with the DSC exotherm maximum between 450 to 600°C, as shown by the dotted line in Figure 5(b). Two speculations can be drawn from TGA: (1) the fibers prestabilized in air have higher thermal stability than those in nitrogen; (2) when the fibers are prestabilized in nitrogen, intense chemical reactions occur around 300 ~ 500°C along with much mass losing, which will inevitably destroy the structure of fibers and decrease the carbon yield for carbon fibers.

Crystal structure

The XRD pattern of the PAN precursor fiber used in the present work, as shown in Figure 7(a), shows two diffraction peaks at $2\theta = 17°$ and 29.5°,[6] which are corresponding to (110) and (200) planes of PAN crystal structure.[25,26] After prestabilization and carbonization, remarkable changes take place in the crystal structure, as shown in Figure 7(b). As for $1^{\#}$ and $2^{\#}$, the diffraction peak at $2\theta = 17°$ become weaken and broaden, the diffraction peak at $2\theta = 29.5°$ disappears, and a new maximum relevant to the (002) plane diffraction of graphite structure appears around $2\theta = 25.5°$.[27–30] The position of the first peak is unchanged in $1^{\#}$, but it moves to lower angle in $2^{\#}$, which indicates the crystal structure of PAN has been changed more severely in nitrogen than in air during prestabilization process. This also reflects that the cyclization degree in $2^{\#}$ is higher than that in $1^{\#}$. As for $1^{\#}$-CF, the diffraction peak of PAN precursor is nearly vanished, and the diffraction peak around $2\theta = 25.5°$ become sharper and stronger, indicating the formation of turbostratic graphite structure. As for $2^{\#}$-CF, a broad diffused diffraction appears around $2\theta = 21°$. It means that
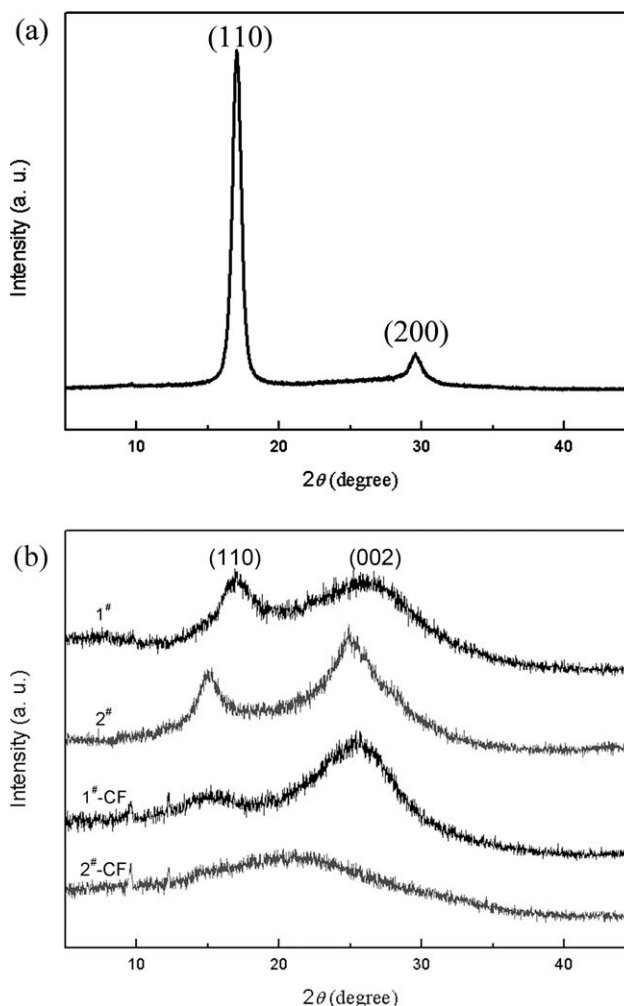

Figure 7 XRD patterns of (a) PAN precursor fibers; (b) the prestabilized fibers in air ($1^{\#}$) and in nitrogen ($2^{\#}$); the corresponding partially carbonized fibers ($1^{\#}$-CF and $2^{\#}$-CF).
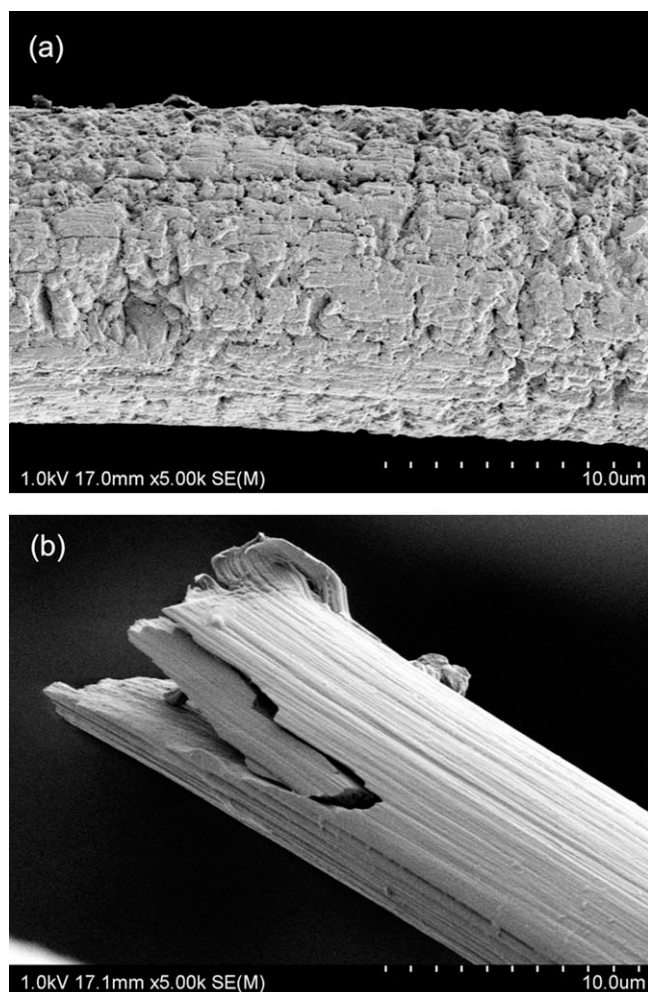
Figure 8 Morphology of fibers prestabilized (a) in air and etched in concentrated sulfuric acid for 7 h; (b) in nitrogen and etched in concentrated sulfuric acid for only half minute.

when prestabilization is carried out in nonoxidative atmosphere, the PAN crystal structure will be thoroughly destroyed, and almost no turbostratic graphite structure are formed after 500°C partially carbonization. As a result, the mechanical properties of $2^{\#}$-CF is quite bad, as shown in Table I.

Morphology after etched by concentrated sulfuric acid

The prestabilized fibers were etched by concentrated sulfuric acid to investigate their resistance to strong oxidant. Before the experiment, we expect that the fibers prestabilized in nitrogen ($2^{\#}$) may have better resistance because of the higher cyclization degree. But against the expectation, the fibers are corroded immediately as soon as they are put into the sulfuric acid, followed by the solution color turning from colorless into yellow. By comparison, the fibers prestabilized in air ($1^{\#}$) exhibit more stable quality. They did not make the solution change

color until being etched in sulfuric acid for 6 h. Figure 8(a) shows surface morphology of $1^{\#}$ after etched in concentrated sulfuric acid for 7 h. Because the fibers prestabilized in nitrogen will be dissolved out within 1 min, they are etched for about only half minute so as to maintain their fibrous shape. Its surface morphology is shown in Figure 8(b). It can be seen that the original smooth fiber surface has been changed to fragments and holes on $1^{\#}$. Though the surface of $2^{\#}$ seems unchanged, the decreasing in diameter from about 13 μm (the diameter of untreated sample) to 8.7μm is obvious. It reveals the fibers prestabilized in nitrogen are corroded layer by layer, indicating that it is the whole molecular chains but not the chain segments are removed off during the etching process. In addition, the brittleness increases in fibers $2^{\#}$ after etching, as shown by the neat fracture surface in Figure 8(b). The results further confirm that the chemical stability of the fibers prestabilized in air is much better than that of in nitrogen. The dehydrogenation and oxygen uptake reactions in air may account for this.

CONCLUSIONS

Through the studies on the chemical structure, crystal structure, thermal properties, and mechanical properties of PAN-based prestabilized fibers and the corresponding partially carbonized fibers, we find that environment atmospheres have great effects on the structure and properties of PAN-based prestabilized fibers. Those effects will successively influence the partially carbonized fibers even they are prepared under the same carbonization parameters. The main conclusions are as follows:

1. When PAN fibers are prestabilized in air, oxygen plays in two roles: one is dehydrogenation agent; the other is forming oxygen containing functional groups. Therefore, the fibers prestabilized in air have higher thermal stability in the chemical structure than the ones prestabilized in nitrogen. But nonoxidative atmosphere is more helpful for intramolecular cyclization reaction than oxidative atmosphere.

2. The oxygen containing structure within the fibers prestabilized in air facilitates intermolecular crosslinking reactions during carbonization process; while when the fibers are prestabilized in nitrogen, much less intermolecular crosslinked structures form, and intense chemical reactions will occur around 400 ~ 500°C along with large amounts of weight lost. It indicates that graphitizing is much easier for the fibers prestabilized in air than in nitrogen. The carbon yield is as well.

3. The PAN crystal structure has been changed more severely in nitrogen than in air during prestabilization process. After 500°C partially carbonization, there is obvious diffraction peak around 2θ = 25.5° in the fibers prestabilized in air, indicating the formation of turbostratic graphite structure. By contrast, almost no turbostratic graphite structure is formed in the fibers prestabilized in nitrogen.

4. The concentrated sulfuric acid corrosion experiment further confirms that the chemical stability is much better for the fibers prestabilized in air than the ones in nitrogen.

5. The elongation at break is higher for the fibers prestabilized in air than the ones in nitrogen, so does their corresponding partially carbonized fibers. It can be speculated that prestabilization in air is more feasible than in nitrogen for producing high strength carbon fibers, since larger stretching ratio can be applied on the former fibers than the latter ones.

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