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Microstructural evolution during thermal stabilization of PAN fibers

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Abstract Thermally stabilized polyacrylonitrile (PAN) fibers were produced by multi-stage thermal stabilization between 190 and 270 °C. X-ray diffraction (XRD) and Fourier Transform infrared (FT-IR) spectroscopy were used to investigate the structure of PAN fibers and the stabilized fibers. A new diffraction peak appears at $2\theta = 23.2°$ in XRD pattern of the stabilized fibers besides the peaks in that of PAN fibers. The distinct structural changes were also observed from FT-IR spectra, the intensities in the 2,936–2,918, 2,244–2,236, and 1,451–1,446 cm^{-1} regions decrease remarkably, and new peaks occur at 1,594 and 1,700 cm^{-1} (shoulder-like peak) which correspond to the stretching vibration of C=N and C=O groups, respectively. The ultramicrotomy to prepare samples of PAN fibers and the stabilized PAN fibers was explored to characterize their microstructures by high-resolution transmission electron microscopy (HRTEM). The HRTEM images further verified the microstructural changes of PAN fibers during thermal stabilization, and the detailed information was given that thermal stabilization is accompanied by a new structure forming inside the crystallites in PAN fibers, and the (110) plane of PAN fibers transforms preferentially.

Introduction

High strength carbon fibers are the ideal reinforcing material for advanced composites [1], which show increasingly wide applications in high-tech aerospace and defense areas, and also in civil engineering (e.g., sporting, transportation industry, architecture industry, and medical sectors). Carbon fibers are dominantly manufactured from rayon, PAN, and pitch precursor fibers [2]. Due to the lower cost and the mature technology, PAN fibers are presently believed as the most suitable and important precursors for making high-performance carbon fibers [3, 4].

Conversion of PAN fibers to high-performance carbon fibers acquires a critical thermal stabilization stage which has great influence on the final properties of carbon fibers [5, 6]. The process was primarily conducted in air medium [7] by heating the PAN fibers for an hour or so [8] between 200 and 300 °C [9], so that the PAN fibers transform into non-melting structures prior to carbonization up to 1,000–1,500 °C in an inert atmosphere. A lot of investigations have been devoted mainly to the basic understanding of the reaction kinetics [6, 8, 10] such as cyclization and cross-linking of the molecular chains as well as the surface morphology and the core-sheath structure of the thermally stabilized PAN fibers [11]. And the examinations were generally confined to scanning electron microscopy [12], X-ray diffraction [13], transmission electron microscope [11, 14], optical microscopy [15], Fourier transmittance infrared spectroscopy [16, 17] and differential scanning calorimetry [18]. So far, few investigations are available concerning the microstructural evolution during thermal stabilization of PAN fibers, although the work [19, 20] by Deurbergue and Oberlin involved in the HRTEM characterization of the thermally stabilized PAN fibers and PAN-based carbon fibers.

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It has been popularly accepted that the physical properties of materials depend greatly upon the structures, particularly on the microstructures. However, it is difficult to obtain HRTEM microstructures of PAN fibers and the thermally stabilized fibers owing to the scarcity of method to prepare samples retaining their virgin structures unchanged. In this work, the HRTEM samples were prepared by the method similar to biological ultramicrotomy. The information obtained from HRTEM examination may provide new clues to understand the structural evolution of PAN fibers during thermal stabilization. At the same time, XRD and FT-IR spectroscopy were also employed to analyze the structural changes more perfectly.

Experimental

Materials

PAN fibers were prepared by wet spinning from a 20 wt.% free-radical polymerization solution which was synthesized in solvent dimethylsulfoxide by using a copolymer of acrylonitrile/itaconic acid. The solution was extruded through a spinneret and drawn in coagulation bathes of various dimethylsulfoxide concentration and water steam with a total drawing ratio up to 1,200%, the stretching rate was negative in the first bathes. Each single tow consists of 1,000 filaments with the titre of 1.15 dtex.

Thermal stabilization of PAN fibers was carried out in two self-designed furnaces. Each furnace has five separate zones with their respective temperatures controlled by computer programs. PAN fibers were thermally stabilized about 40 min between 190 and 270 °C as shown in Fig. 1, with a total stretching ratio of 10% in the flowing purified hot air medium. In addition, for comparison, the PAN fibers were also stabilized about 60 min between 190 and 270 °C and about 60 min between 190 and 290 °C, respectively.

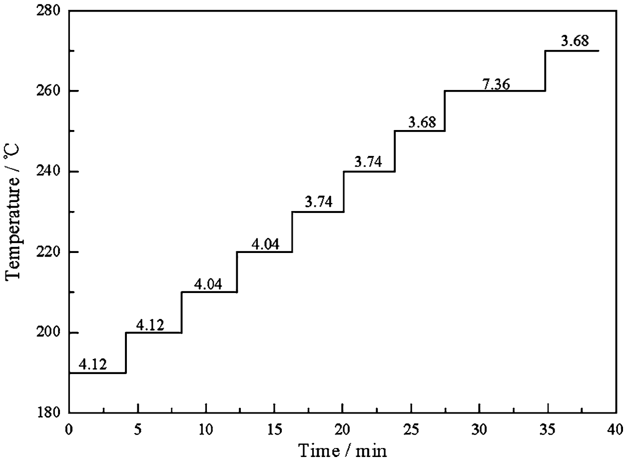

Fig. 1 Thermal stabilization of PAN fibers by successive maintenance at different temperatures for various durations

Ultrathin section preparation of the stabilized fibers

Appropriate volume of epoxi-aquivalentgewicht, methyl-norbornen-2, 3-dicarboxylic anhydride, dodecenyl succinic anhydride and 2, 4, 6-tris-dimethylaminomethyl-phenol were mixed together to obtain epoxy resin solution. A tow of fibers was cut and embedded in the solution along the direction parallel to and perpendicular to fiber axis, respectively. When the resin was solidified at 60 °C for 24 h in a small oven, both the transverse and the longitudinal ultrathin sections with the thickness of 3–4 nm were cut on an Ultracut E Model Reichert-Jung ultramicrotome (made in Austria) using a glass knife. The sections were put on different microgrids coated with amorphous carbon thin film for HRTEM examinations.

Measurements

The samples of PAN fibers and the stabilized fibers were examined by PHILIPS TECNAI20Π-TWIN high-resolution transmission electron microscopy (made in America) at an accelerating voltage of 200 kV.

A Rigaku D/MAX-rA X-ray diffractometer (made in Japan) with Ni-filtered CuK$_\alpha$ (λ = 0.1541 nm) radiation was used to determine the structures of PAN fibers and the stabilized fibers at various stages with a voltage of 40 kV and an electric current of 60 mA. The samples were prepared by compressing the randomly aligned short fibers into thin disc. The scanning speed was 6°/min with the scanning step of 0.02°.

FT-IR spectra were obtained on the Nicolet710 model spectrometer (made in America) by KBr pellet method. The wavelength was in the range of 4,000–500 cm^{-1}.

Results and discussion

X-ray diffraction analysis

The X-ray diffraction patterns of PAN fibers and the stabilized fibers at various stages were shown in Fig. 2. Two strong characteristic peaks in Fig. 2a can be observed at 2θ = 17.1° and 29.4°, which correspond to (100) and (110) planes of PAN fibers, respectively. The intensities of the two original peaks weaken after thermal stabilization, and a new peak at 2θ = 23.2° corresponds to (002) plane of the stabilized fibers as shown in Fig. 2b. Figure 2c indicates that the intensities at 2θ = 17.1° weakens further with

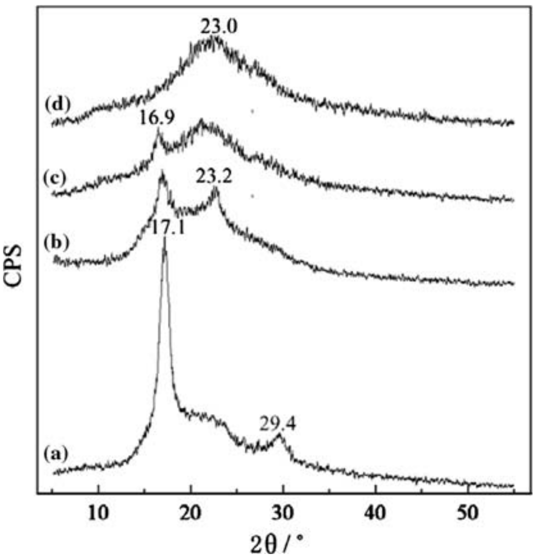

Fig. 2 X-ray diffraction patterns: (**a**) PAN fibers; (**b**) the thermally stabilized fibers (about 40 min between 190 and 270 °C); (**c**) the thermally stabilized fibers (about 60 min between 190 and 270 °C); (**d**) the thermally stabilized fibers (about 60 min between 190 and 290 °C)

stabilization duration for about 1 h. Figure 2d implies that the two original peaks of PAN fibers disappear with increasing stabilization temperature and prolonging stabilization time, the new peak at $2\theta = 23.0°$ is still present.

According to Bragg equation, $2d\sin\theta = n\lambda$ (where $n = 1$, $\lambda = 0.1541$ nm, d is the lattice spacing, and θ is the half of the diffraction angle.), d values of the two characteristic diffraction peaks of PAN fibers at $2\theta = 17.1°$ and 29.4° are $d_{17.1} = 0.5183$ nm and $d_{29.4} = 0.3036$ nm, respectively, which were coherent with the reported values [21, 22]. The new peak at $2\theta = 23.20°$ during the stabilization corresponds to $d_{23.2} = 0.3831$ nm, which was different from the value in Ref. [13], indicating the occurrence of a new structure in the stabilized PAN fibers.

FT-IR spectra analysis

Figure 3 shows the FT-IR spectra of PAN fibers and the stabilized fibers (about 40 min, 190–270 °C), giving information related to the structural changes during stabilization. Three prominent peaks at 1,451, 2,244, and 2,936 cm^{-1} in the spectrum of PAN fibers shown in Fig. 3a result from the bending vibration of methylene groups (CH_2), the stretch vibration of nitrile groups (C≡N) and methylene groups, respectively. In comparison Fig. 3b with 3a, a distinct difference is that the intensities in the 2,936–2,918, 2,244–2,236, and 1,451–1,446 cm^{-1} regions decrease remarkably, and two new peaks appear at 1,594 and 1,700 cm^{-1} (shoulder-like peak) which can be attributed to the stretching vibration of C=N and C=O groups, respectively. In spite of the structural changes observed in the stabilized fibers, C≡N and CH_2 groups have not yet thoroughly transformed into other structures. Further conversion will continue with increasing stabilization temperature and/or prolonging stabilization time.

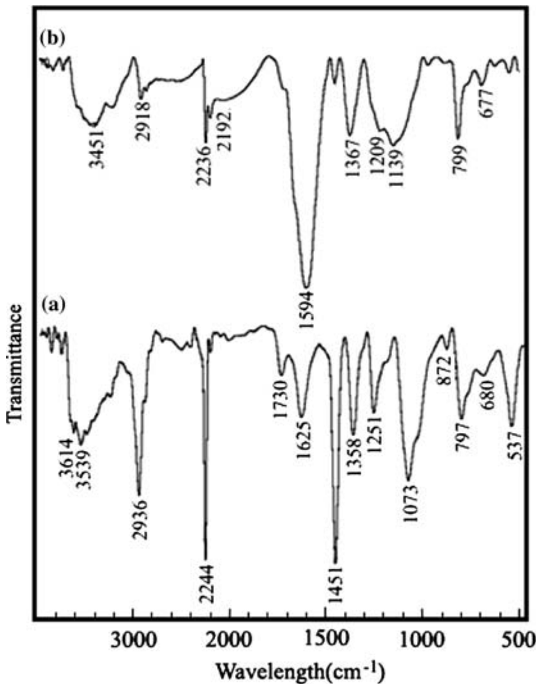

Fig. 3 FT-IR spectra: (**a**) PAN fibers; (**b**) the stabilized fibers (about 40 min between 190 and 270 °C)

HRTEM Microstructure analysis

Figure 4 is the HRTEM images from the transverse sections of PAN fibers. Figure 4a is a low magnification image, where crystallites with the dimension of 50–150 nm are visible in spite of the amorphous matrix. Figure 4b is the lattice-fringe image resulted from grain A in Fig. 4a, the spacings of 0.529 and 0.308 nm are consistent with those obtained from the XRD pattern shown in Fig. 2a, which correspond to the (100) and (110) planes of PAN fibers, respectively. These microstructures are the real evidence for the coexistence of crystalline and amorphous phases in PAN fibers. The circular section crystallites are owing to the formation of the spherical crystals under the negative stretching rate at the first step, where the crystalline PAN fibers are coagulated from high concentration polymerization solution. Although drawn up to 1200% at the later steps, samples were prepared in the relaxation state of PAN fibers, the anamorphic spherulites were reverted to their original shape.

HRTEM images from the longitudinal section of PAN fibers are shown in Fig. 5. Figure 5a is low magnification

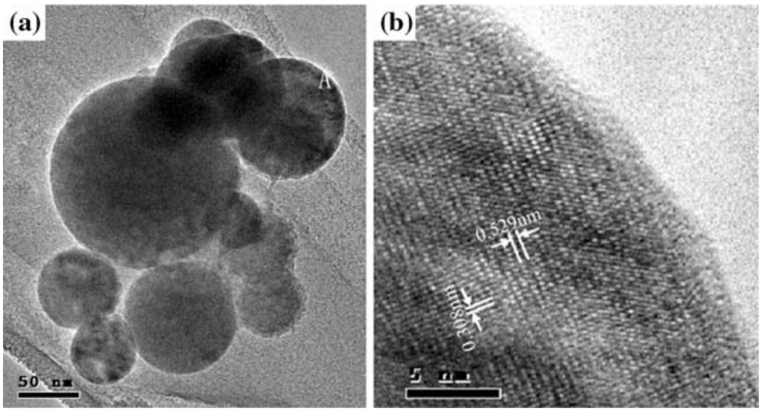

Fig. 4 HRTEM images from the transverse section of PAN fibers: (**a**) low magnification image; (**b**) lattice fringe image from grain A in (**a**)

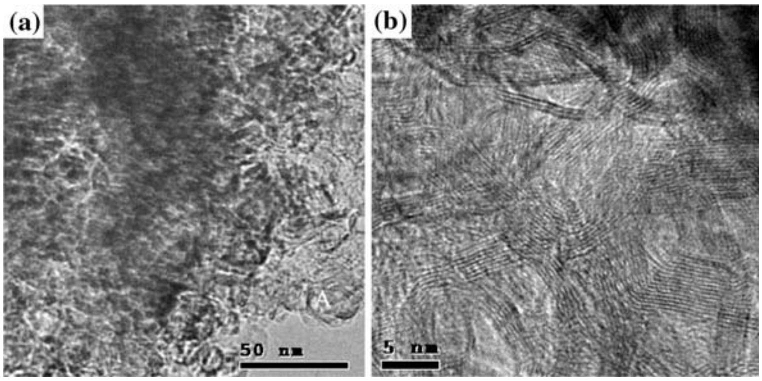

Fig. 5 HRTEM images from the longitudinal section of PAN fibers: (**a**) low magnification image; (**b**) lattice-fringe image from zone A in (**a**)

image, revealing the existence of both lamellar structure with different orientations and defects such as voids. Figure 5b is the magnification image from zone A in Fig. 5a, taking on the interpenetrating order strips with various breadths. This differs from the structural model of oriented PAN fibers in Ref. [14], where PAN molecules were assumed a contorted helical shape to form the ordered rods with a diameter averaging about 0.6 nm and the length approximately 8 nm, interspersed with the amorphous regions about 4 nm between the rods along the length of the fiber. It is clear that great structure differences between the transverse sections and the longitudinal section of PAN fibers are ascribed to the orientation along the fiber axis.

Figure 6 is the HRTEM image from the transverse section of the stabilized PAN fibers. A large numbers of grains with an average dimension of 6–7 nm were observed. These grains distribute homogeneously in the matrix except for a cluster of grains at the upper left section resulted from the continuous attack of electron beams operated at 200 kV during photographing. Some distinct interfaces are visible between the grains and the matrix, where the matrix is amorphous phase and the grains are crystallites. Figure 7 is magnification image of the grains in the square frame shown in Fig. 6. A transforming grain can be obviously observed which can be separated into three zones marked as A, B, and C. Zone A is the transformed part of the grain. The spacing between adjacent lattice planes is 0.322 nm, in agreement with the distance between two (002) crystal planes of the stabilized fibers. Part transformation has happened in Zone C, and the two dimensional fringes correspond to the spacings of 0.533

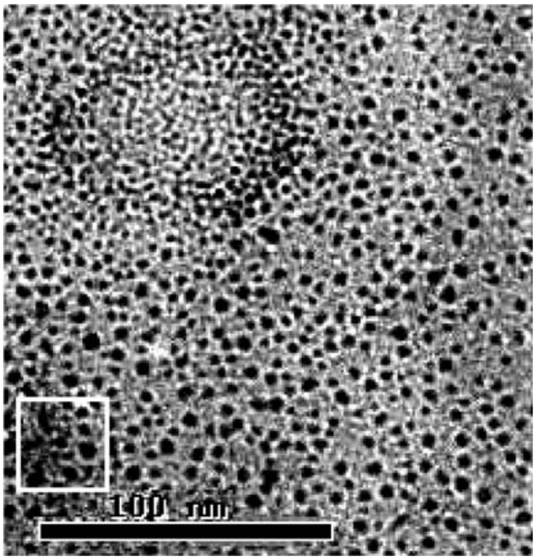

Fig. 6 HRTEM image from the transverse section of the stabilized PAN fibers (about 40 min between 190 and 270 °C)

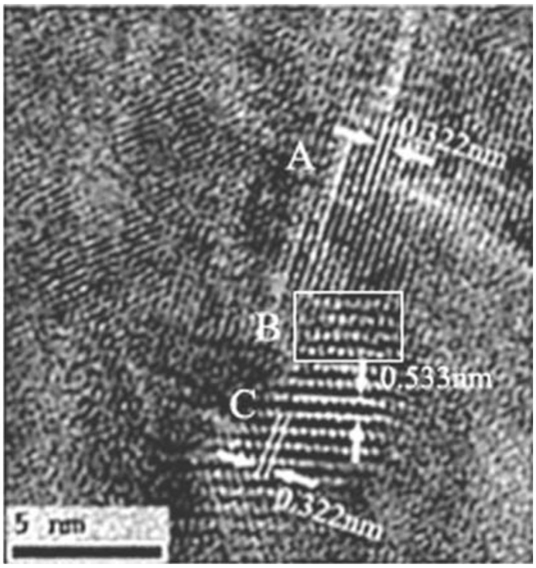

Fig. 7 Lattice-fringe image from the transverse section of the stabilized PAN fibers. Zone A is the transformed part, Zone C is the transforming part, and Zone B within the rectangular frame is the transition part

and 0.322 nm, respectively, which are close to the (100) plane of PAN fibers and the (002) plane of the stabilized fibers. This result is consistent with that obtained from XRD pattern where the (110) plane of PAN fibers almost disappear after the stabilization, accompanying with the appearance of the (002) plane of the stabilized fibers. Both results imply that the formation of new structures is based on the original structures, and the (110) plane of the PAN fibers transforms preferentially, because the spacings of the (110) plane of the PAN fibers are close to that of the (002) plane of the stabilized fibers, and only small amount of energy is needed to initiate the structural transformation. Zone B, between Zone A and C, is a transition zone, where the fringes have low order because of the strain resulted from the mismatch of the two different crystal planes.

Figure 8 displays the HRTEM image from the longitudinal section of the stabilized PAN fibers, which is very similar to that observed from the transverse section. The corresponding diffraction pattern shown at the top left corner of Fig. 8 reveals that multi-crystals distribute in the amorphous matrix. Further careful observation gives more detailed information that the grains are in transformation and the larger grains are composed of several smaller ones, which is particular true in the magnified image of grain A as shown in the inset at the bottom right corner. The nucleuses of the new structure form and grow inside the crystallites in PAN fibers and usually initiate at different sites in the same grain.

As stated above, it is obvious that the stabilization of PAN fibers is insufficient during the given treatment. However, the result provides some significant microstructural information associated with the conversion of PAN fibers to the stabilized fibers. Meanwhile, HRTEM is a cogent tool to study the microstructures of PAN fibers and the stabilized fibers, and is advantageous over the other measurement methods in elucidating the microstructural evolution during thermal stabilization of PAN fibers. The precondition is to prepare samples readily and feasibly.

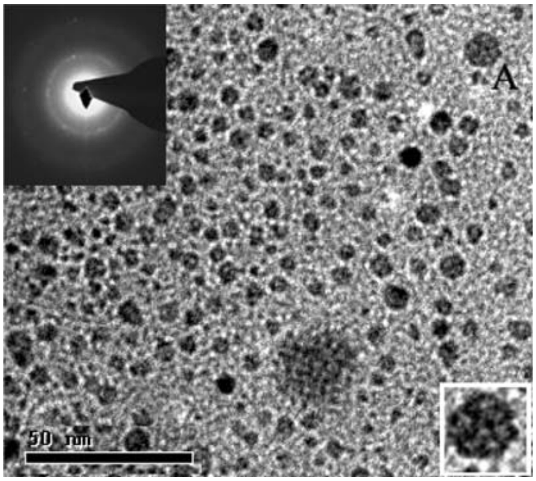

Fig. 8 HRTEM image from the longitudinal section of the stabilized PAN fibers. The inset at the top left corner is the corresponding electron diffraction pattern, and that at the bottom right is the magnification by 2 times of grain A

Conclusions

(1) The results obtained from HRTEM, XRD and FT-IR all confirmed that the conversion of PAN fibers to the stabilized fibers was underway during the given treatment in this work. However, the former one provided more detailed discernable microstructure information than the latter two.

(2) The nucleus formation of new structures is based on the original structures and begins at several sites inside the original crystallites in PAN fibers during thermal stabilization. The (110) plane of PAN fibers transforms preferentially.

(3) The ultramicrotomy to prepare HRTEM samples of PAN fibers and the stabilized fibers was proposed to characterize their microstructures and study microstructural evolution during thermal stabilization of PAN fibers. The experiment results verified the feasibility of the method.

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