

Surface structural evolvement in the conversion of polyacrylonitrile precursors to carbon fibers



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ABSTRACT

Surface structural evolvement in the conversion of polyacrylonitrile (PAN) precursors to carbon fibers was investigated through scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). SEM results showed that the characteristic striated topography of PAN precursors resulted from the wet spinning process could pass down to carbon fibers. The fiber diameter gradually decreased from 11.3 μm to 5.5 μm and the corresponding density increased from 1.18 g/cm^3 to 1.80 g/cm^3 in the conversion of PAN precursors to carbon fibers. The ridges and grooves monitored by AFM became much more well-defined after the thermo-oxidation. However, the original longitudinal grooves were destroyed and both the depth and the width of longitudinal grooves decreased after the carbonization. XPS results revealed that carbon, nitrogen, oxygen and silicon were the governing elements on the fiber surface. The $-\text{C}-\text{C}$ functional groups was the dominant groups and the relative contents of $-\text{C}=\text{O}$ and $-\text{COO}$ groups gradually increased in the process of thermo-oxidation and carbonization.

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1. Introduction

Owing to light weight, good compressive strength, high tensile strength and modulus, good temperature and chemical resistance, excellent electrical and thermal conductivity, carbon fibers are emerging as important construction in advanced composites [1–5]. Based on the precursors, carbon fibers can be roughly classified into polyacrylonitrile (PAN)-based carbon fibers, pitch-based carbon fibers and rayon-based carbon fibers. However, the majority of carbon fibers are made from PAN precursor because of its higher melting point and greater carbon yield, and meantime the properties of PAN-based carbon fibers are also better than other precursor-based carbon fibers [6–8].

Generally speaking, the manufacture of PAN-based carbon fibers consists of thermo-oxidative stabilization (or pre-oxidation) in air, low-temperature carbonization and high-temperature carbonization in an inert atmosphere. Great changes in physical and chemical structures happen to the fibers in the conversion of PAN precursors to carbon fibers, which also leads to significant changes in the mechanical properties of the fibers. In the process of thermo-oxidation, chemical reactions such as cyclization, dehydrogenation and oxidation take place which results in the

formation of a conjugated ladder structure [9,10]. At the same time, an obvious change in the color from white through yellow and brown to ultimately black due to the formation of ladder ring structure also happens to PAN precursor during the thermo-oxidation [11]. Typical graphite layer or ribbon structure consisting of three hexagons in the lateral direction and bounded by nitrogen atom is formed and increases in the process of carbonization.

During the past few decades, much work has concentrated on studying the physical–chemical structural changes especially the intrinsic chemical structural evolvement of PAN precursors [12–14], thermo-oxidized fibers [10,15–17] and carbonized fibers [6,18–20]. There are few studies on the surface structural analysis in the conversion process. In the present work, surface structural evolvement in the conversion of PAN precursors to carbon fibers was investigated. Changes in surface morphology and fiber diameters were investigated at the micrometer scale by scanning electron microscopy (SEM). Surface roughness analysis was monitored at the nanometer scale by atomic force microscopy (AFM). Chemical functionality measurements were also carried out by X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Materials

PAN precursors and PAN-based carbon fibers used in this work were produced in our laboratory. The production processes of PAN

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precursors were composed of polymerization, spinning, water bath and oiling finish. Oiling finish was a necessary process in the preparation of PAN precursors which could prevent friction and adhesion between monofilaments. Because the following conversion processes were under high temperature, silicone oil agents were usually chosen in the oiling finish. The conversion of PAN precursors to carbon fibers is according to a continuous process including thermo-oxidative stabilization (180–300 °C), low-temperature carbonization (300–800 °C) and high-temperature carbonization (1000–1600 °C). There were 6000 filaments in per tow. The samples received in different processes were correspondingly named PAN precursors (PF), thermo-oxidized fibers (TF), low-temperature carbonized fibers (LCF), high-temperature carbonized fibers (CF).

2.2. Characterization of surface physicochemical structure

A Quanta FEG250 model scanning electron microscopy (SEM) operated in the scanning mode with 20,000 times magnification was employed to characterize the morphological changes on the surfaces of PF, TF, LCF and CF fibers. The samples were secured on a metal mount by conducting tape, and then they were coated with gold prior to examination. The acceleration voltage was 5 kV.

Dimension 3100 V atomic force microscope (AFM) operated in the tapping mode with a silicon nitride probe was utilized to analyze changes in surface roughness of PF, TF, LCF and CF fibers. In the test, the single-fiber samples were secured on a glassy board with double-sided tape. The received surface topographical images were in $3\ \mu\text{m} \times 3\ \mu\text{m}$ area and $1\ \mu\text{m} \times 1\ \mu\text{m}$ area, respectively. Groove depths and widths were also investigated through AFM

in a $1\ \mu\text{m} \times 1\ \mu\text{m}$ area. In surface roughness analysis, the value of surface roughness was the average of five single-fiber samples.

Surface chemical components of PF, TF, LCF and CF fibers were analyzed by AXIS UTLTRADLD X-ray photoelectron spectrometer (XPS) using Mg $K\alpha$ X-ray as the source. The emission current was 30 mA and the voltage was 15 kV. Curve fitting was carried out using a non-linear least squares fitting program with a Gaussian/Lorentzian sum function. The carbon 1s electron binding energy corresponding to graphitic carbon was referenced at 284.6 eV for calibration.

3. Results and discussion

3.1. SEM analysis of fiber surface morphology

Fig. 1 shows surface SEM photographs of PAN precursors (PF), thermo-oxidized fibers (TF), low-temperature carbonized fibers (LCF) and carbon fibers (CF). It could be observed that PAN precursors showed a characteristic striated topography which attributed to the wet spinning process in the production of PAN precursors (shown in Fig. 1a). It is well known that obvious chemical reactions take place in the process of thermo-oxidization and carbonization. However, the striated topography was retained in the process of thermo-oxidization and carbonization (Fig. 1b–d) which indicated that the striated topography of PAN precursors could pass down to carbon fibers.

Although the striated topography on the fiber surface was reserved in the conversion of PAN precursors to carbon fibers, slight differences were also detected. Compared with PAN

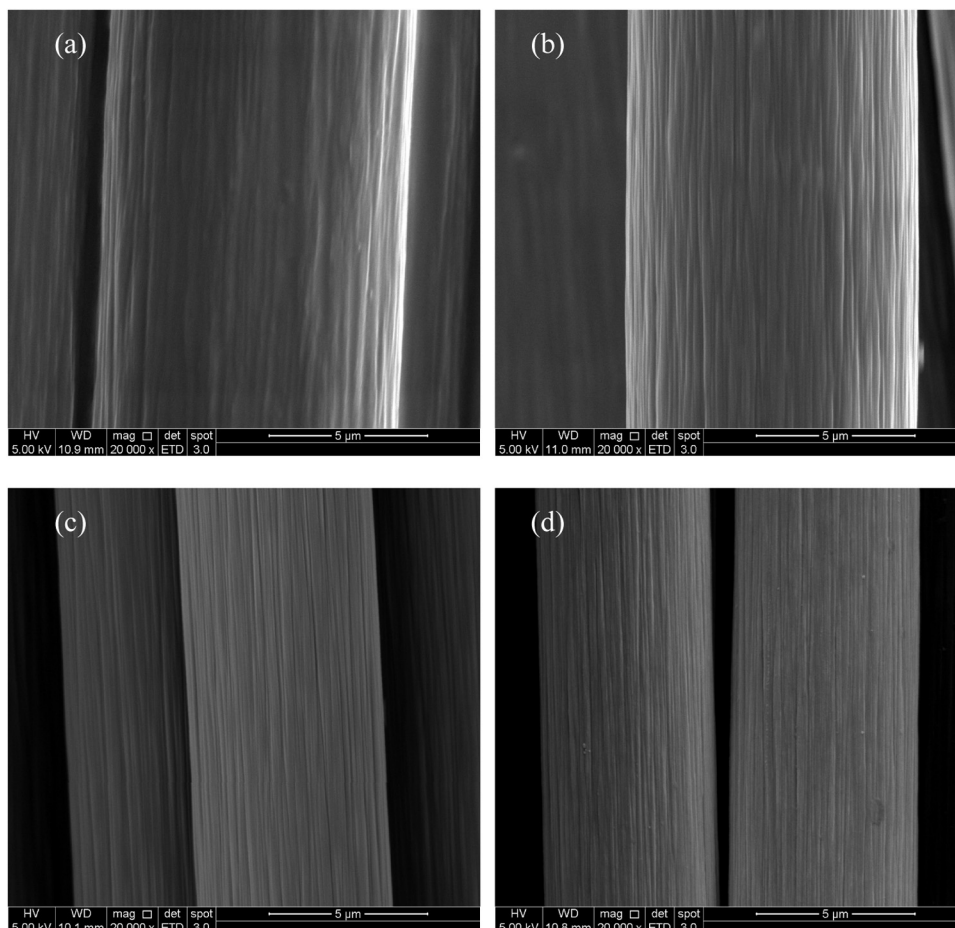


Fig. 1. Surface SEM images of (a) PF, (b) TF, (c) LCF and (d) CF; PF: PAN precursors; TF: thermo-oxidized fibers; LCF: low-temperature carbonized fibers; CF: carbon fibers.

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