Scanning Tunnel Microscopy Study of Rayon-Based Carbon-Fiber Surfaces

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ABSTRACT: Because of its atomic resolution, scanning tunnel microscopy (STM) was applied to the study of the surface topography, in air, of rayon-based carbon fibers (RCF) that were not previously studied. By a variety of larger scales, RCF exhibits some rugosities with "peaks" and "valleys." The surfaces are characterized by stripe-form crystallite stackings with the diameter of about 10 nm aligned at an angle between 45 and 60° to the fiber axis. A graphitelike structure was first observed on the surface of RCF examined at an atomic resolution scale. Distances between two adjacent carbon atoms of RCF and that between the closest centers of hexagonal carbon rings were estimated. It was also concluded that the hexagonal structure of RCF is deformed graphene (graphitelike) compared with that of highly oriented pyrolytic graphite. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 754–758, 2003

Key words: high-temperature materials; structure; surfaces; fibers; thermal properties

INTRODUCTION

Based on their low thermal conductivity, low density, low alkali metal ion content, and high flexibility, rayon-based carbon fiber (RCF)/matrix composite materials have been used extensively in military aerospace and other high-technology industries. In such composites, the RCF is expected to have good interfacial adhesion. Because the mechanical behavior of this interface depends to a great extent on the carbon-fiber surface, more detailed and precise information concerning the RCF surface is required for understanding and controlling the mechanism of the adhesion and the fibers themselves. To fit the requirement, several techniques such as high-resolution optical microscopy (HM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were variously applied to probe the structure and the microtexture of carbon fibers. However, the local nature of the carbon-fiber surface structure has not yet been described because of the difficulty of making the required unambiguous, high-resolution observations.

Scanning tunnel microscopy (STM), first used in 1982,[1,2] has proved to be an extremely powerful procedure because it is capable of resolving the surface structures with atomic resolution.[3–5] According to the literature,[6–11] PAN-based and pitch-based carbon fibers have been the object of extensive studies by this technique. However, an STM study of the surface of rayon-based carbon fibers is still lacking. The aim of this study was to evaluate the surface nature of RCF at an atomic dimensional level by STM in air.

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EXPERIMENTAL

Materials

Rayon-based carbon-fiber samples were taken directly from the carbonization manufacture line (at 1300°C) without any surface treatment and coating, and were solvent extracted systematically by acetone to eliminate possible contaminants before the specimens were prepared for STM observation.

STM observation

A scanning tunnel microscope (Multimode Nanoscope IIIa type; Digital Instruments, Santa Barbara, CA) was applied at ambient conditions. The tips [Pt(80)/Ir(20) type of size $0.010 \times \frac{1}{4}$ in. ($\sim 0.03 \times 0.6$ cm)] were checked with a sample of highly oriented pyrolytic graphite (HOPG) to ensure their quality. In all experiments, the constant tunnel current mode, which provides superior images of the morphological features of the surface, was employed. The parameters adopted were: set-point current 1.0–4.0 nA and bias voltage 10–100 MV, depending on the sample analyzed and scan size.

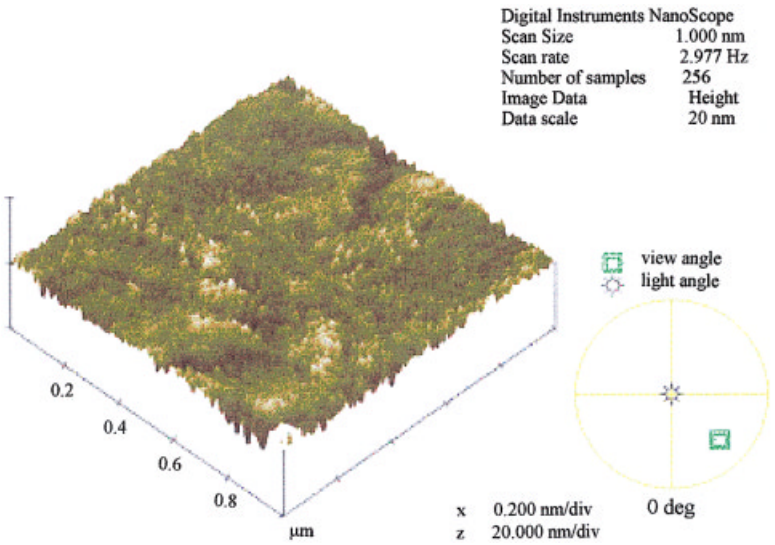

Figure 1 STM 3D image of the RCF surface (1 μm $\times$ 1 μm $\times$ 20 nm).

RESULTS AND DISCUSSION

STM at micrometer scales

SEM micrographs show that the surface of the rayon-based carbon filament looks rather smooth except for a few cracks. However, with increasing magnification, down to the micron scale using the STM, the surface roughness is unmistakably revealed, as can be seen in Figure 1. Obviously, the rugged surface seems to be composed of a number of nodular microstructures without obvious orientation along the fiber axis. Moreover, the fibers exhibit some rugosities with "peaks" (the bright aspects in the 3D image) and "valleys" (the dark ones), up to about 20–50 nm deep. A similar observation was obtained in an isotropic pitch fiber treated at 900°C.[8]

STM at nanometer scales

From the left STM top-view image (200 $\times$ 200 nm) of RCF shown in Figure 2, the ribbon structure, different from the screw structure in PAN-based carbon-fiber surfaces,[8] can clearly be seen. These ribbons, aligned with an angle between 45 and 60° to the fiber axis, have a width of about 90 nm and length of 60–80 nm. They are further constituted of the smaller stripe-form stackings, which are thought to be the crystallites. The sizes of crystallites in two directions $La_{\parallel}$, parallel to the fiber axis, and $La_{\perp}$, perpendicular to the fiber axis, will be determined in further STM investigations on rayon-based carbon fiber.

In addition, the surface defects are clearly visible. One can find a crack with a size of 50 $\times$ 25 $\times$ 20 nm^3

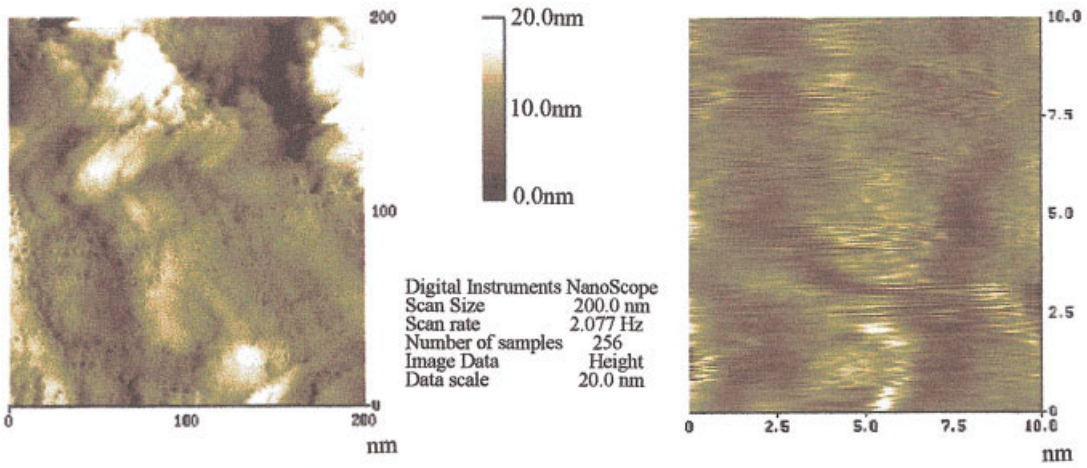

Figure 2 STM 2D image of the RCF surface (left: 200 $\times$ 200 nm; right: 10 $\times$ 10 nm).

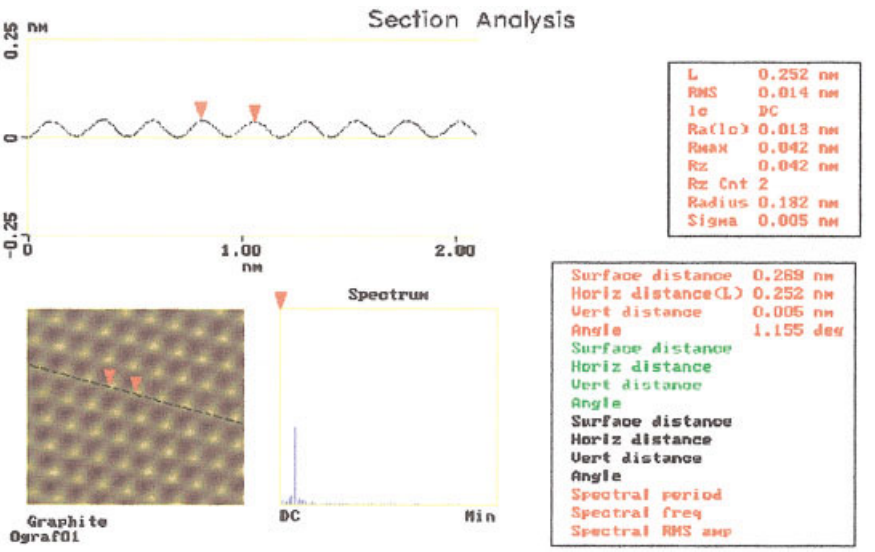

Figure 3 STM image of highly oriented pyrolytic graphite (HOPG) (2 × 2 nm).

at the right upper corner and other smaller defects scattered across the surface. As a matter of fact, the defects—especially those of larger size—undoubtedly decrease the tensile strength of RCF.

It is interesting to find that the surface still presents remembering rugosities with "peaks" and "valleys" when the observation scale down to 10 × 10 nm (the right image shown in Fig. 2). It is reasonable to propose that the surfaces at different observational scales may have the property of self-similarity. Thus, the combination of STM with the fractal theory will be a topic for future investigation. One can also find some planar hexagonal networks of carbon atoms with an irregular edge. Donnet et al.[9,11] also observed the carbon network structure in the surfaces of other carbon fibers such as PAN-based and pitch-based carbon fibers. The difference is that the net size of rayon-based carbon fibers (2–4 nm^2) is much smaller. To a certain extent, the higher quantity of graphite, which gives a larger net size of carbon, depends on the higher carbonization temperature. Thus, it is easy to understand the smaller size of the experimental rayon-based carbon fiber treated at 1300°C, lower than 2000°C for manufacturing PAN- and pitch-based carbon fibers.

STM at atomic resolution

HOPG possesses an ideal graphitic structure. In Figure 3, the bottom left inset represents the STM image of a 2D top-view mode. The bottom right figure represents the frequency of the spectral period along the line indicated in the left STM image. The top frame shows the cross section of the atomic corrugation on which the individual distance between two peaks or troughs can be measured.

Figure 4 presents the schematic pictures of the ideal graphite structure for better understanding of the graphitic basal plane. The basic structural unit is a planar hexagonal network of carbon atoms. Because of the atomic and tunneling effect, the difference in height for three different sites marked A, B, and C has been discussed. At site A, the atoms in the top layer coincide with those in the underneath layer (dashed hexagon), whereas the atom at site B does not have a corresponding atom in the underneath layer. At site C there is an atom in the underneath layer, but nothing in the top layer. The atom location at site A is 0.01 nm higher than that at site B and 0.1 nm higher than that at site C.

It has been determined that the distance between two A sites, equal to the distance between the closest centers of hexagonal carbon rings, is 0.246 nm and the spacing of the two adjacent carbon atoms is 0.142 nm

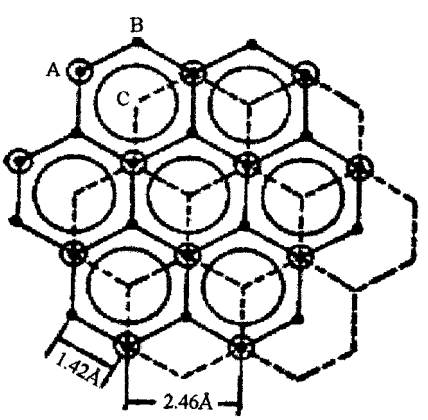

Figure 4 Surface structure of the graphite basal plane stacking parallel to the fiber axis.

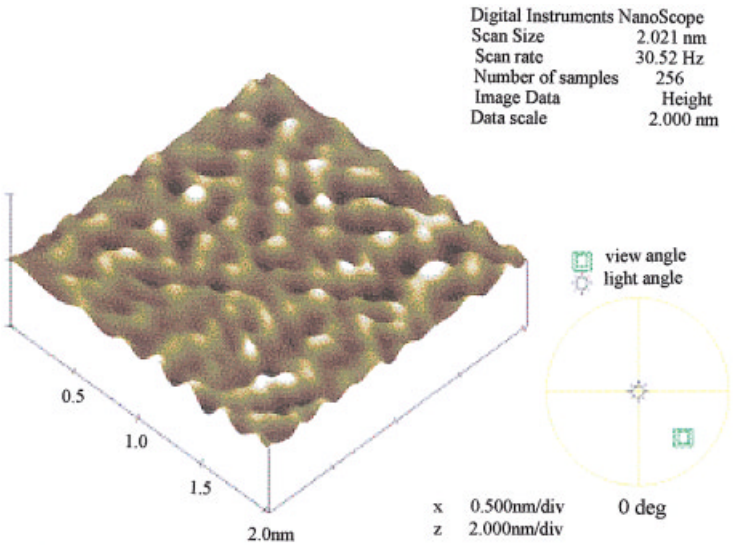

Figure 5 STM 3D image of the RCF surface (2 × 2 × 2 nm).

in the ideal graphite structure (in Fig. 4).[7] In addition, it is generally accepted that only atoms at site A, of the hexagonal rings on a graphitic basal plane, can be observed as the brightest points in the STM experiments.[6–11] Thus the actual hexagonal symmetry rings of six carbon atoms, as expected, are not directly seen. Nevertheless, as can be seen, the top frame of HOPG (shown in Fig. 3) is a sine wave and the peak-to-peak spacing of atomic corrugation was found to be 0.252 nm, indicating that regular hexagonal rings exist in HOPG.

Remarkable results on rayon-based carbon fiber were obtained at atomic resolution scales as well in this study. In a 3D STM image of RCF (shown in Fig. 5), it is difficult to find a zone of very symmetric triangle pattern (usually representing the perfect surface structure of graphite), as can be observed easily on HOPG and graphitized fibers.

Because STM image reflects the charge density of the surface atoms, these diverse corrugation patterns can be interpreted as the result of the basal plane shift (dislocation) invoked by the imperfection of crystal-

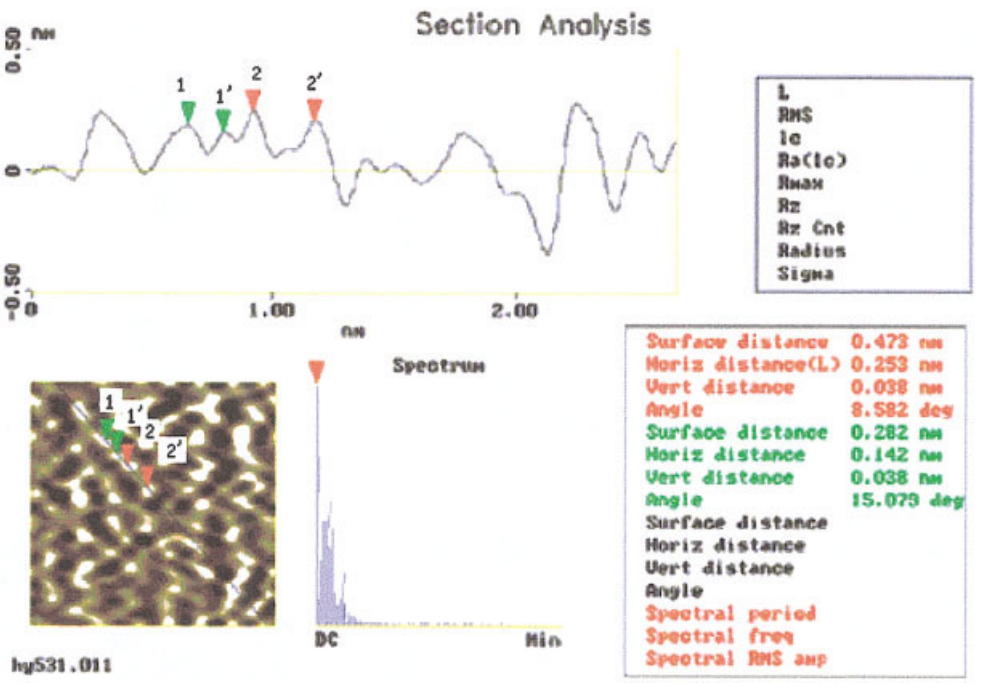

Figure 6 Section analysis of RCF at atomic resolution (2 × 2 nm).

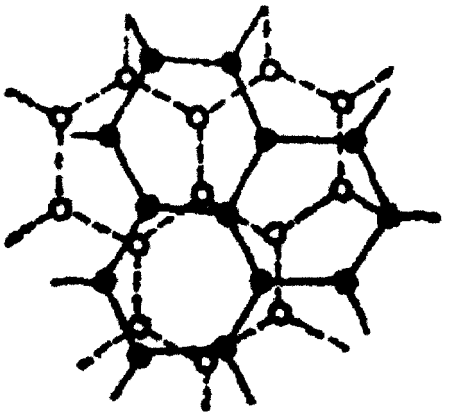

Figure 7 Turbostratic graphite structure of RCF surfaces.

lites. The phenomenon of dislocations is very common on carbon materials. The STM observations offer direct evidence for the above results. The top frame for rayon-based carbon fiber (shown in Fig. 6) showing the cross section of the atomic corrugation is not a regular sine wave, which is an obvious difference from that of HOPG. Concerning peaks 1 and 1′, the surface distance is 0.282 nm and the vertical distance is 0.038 nm; thus the horizontal distance is estimated as 0.142 nm, which is same as the spacing of the two closest atoms in the ideal graphite structure. The spacing of peaks 2 and 2′ was measured to be 0.253 nm, close to the data of HOPG. The results compared with HOPG reveal that the carbon hexagon structure of RCF is deformed graphene. Considering that carbon fibers are generally composed of two-dimensional turbostratic graphitic crystallites (seen in Fig. 7), one can easily understand the dislocation and the deformed graphene structure existing in RCF. It is believed that the poor mechanical properties of RCF are related to the deformed graphene structure. In addition, the structure is related to the low carbonization temperature at which the crystalline order is still poor and the in-plane defects such as the heteroatoms are not eliminated. It has also been demonstrated that the turbostratic structure begins to disappear and the three-dimensional order begins to increase above 1700°C, whereas above 2100°C, the crystalline size and order improved rapidly and the perfect domains began to appear. Meanwhile, RCF is believed to be characterized by improved properties through higher temperature carbonization or even graphitizing. Furthermore, surface treatment that reduces the defects may be another helpful way to improve both the tensile strength and the adhesive property.

CONCLUSIONS

The STM observations at both micron and atomic resolution scales were carried out on rayon-based carbon fibers in this study. RCF exhibits some rugosities with “peaks” and “valleys” at different scales of observation, which suggest that the surfaces may have the property of self-similarity. RCF surfaces are characterized as ribbonlike and the smaller stripe-form crystallite stackings. The distance between the two closest carbon atoms of RCF was evaluated as 0.142 nm, whereas that between the closest centers of the hexagonal carbon rings was 0.253 nm. The results reveal that the carbon hexagon structure of RCF is deformed graphene compared with that of HOPG.

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