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Study of structure–mechanical heterogeneity of polyacrylonitrile-based carbon fiber monofilament by plasma etching-assisted radius profiling

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ABSTRACT

We present a feasible method, named as radius profiling, to study the structure–mechanical heterogeneity of polyacrylonitrile (PAN)-based carbon fibers (CFs). CF monofilaments were peeled layer by layer by plasma etching, and their electrical resistances and mechanical properties were measured by a multimeter and a single-filament tensile tester, respectively. The method allows the structure and mechanical properties of CF monofilament to be explored with high spatial resolution. The measurement results show that the modulus distribution along the fiber radius direction is highly dependent on the local crystallinity, and the maximums of both modulus and crystallinity appear at approximately 1.1–1.6 μm beneath the surface. The observation is used to explain the high modulus of PAN-based CFs.

1. Introduction

Carbon fibers (CFs) are high-modulus, high-strength, and low-density structural materials that are widely used in many fields, such as aerospace and aircraft industry [1]. It is well known that CF monofilament possesses heterogeneous skin–core structure, which causes nonuniform stress distribution, concentrating stress in certain regions, accelerating the formation and the growth of microvoids, and eventually leading to fracture [2,3]. Therefore, it is more important to study the relationship between the heterogeneous structures and the corresponding heterogeneous mechanical properties [4]. To achieve this, the structure and the mechanical properties of monofilament need to be measured simultaneously with high spatial resolution. Several methods, such as wide-angle X-ray diffraction [4–8], small-angle X-ray scattering [7,9], micro-Raman spectrum [4,6,10,11], and nanoscale dynamic mechanical analysis [12,13], were used to characterize CF monofilament during in situ tensile or compression test and for studying stress heterogeneity [6], microvoid evolution [9], and structure change [7]. Although these methods gave fruitful information, they all have some limitations. X-ray diffraction is based on the microbeam generated by synchrotron source, which is complicated and expensive; therefore, only a small number of monofilaments can be characterized, which is insufficient for studying CFs whose dimensions and properties are quite scattered [14]. The Raman spectra have a limited spatial resolution of submicrometer and can only detect about the skin part accurately [4]. Nanoscale dynamic mechanical analysis requires specially prepared samples with the cross-section exposed [12], and the sample preparation process tends to modify the structure of the exposed surface. Therefore, a simple and efficient method is highly desired to characterize the structure–mechanical heterogeneity of CFs in detail.

From a geometric point of view, CF monofilament is roughly a cylinder, and both its structure and properties show center symmetry along the direction of the axis. Therefore, the study of structure–mechanical heterogeneity can be safely reduced to the measurement of structure and mechanical property distribution along the fiber radius direction. The situation can be easily handled by a well-developed destructive method, named as depth profiling, which is widely used in X-ray photoelectron spectroscopy (XPS) [15,16] and secondary ion mass spectrometry (SIMS) [17,18] for measuring the material properties along depth direction by continuously removing surface layer using ion beam.

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In this work, a new method, named as radius profiling, was developed to study the structure–mechanical heterogeneity of polyacrylonitrile (PAN)-based CF monofilaments. Plasma etching was used to peel off the surface materials layer by layer, and the electrical resistances and mechanical properties of the etched monofilaments were measured by a multimeter and a single-filament tensile tester, respectively. The radius distributions of crystallinity and Young's modulus were calculated from the measurements and compared with each other to discuss the relationship between the structure and mechanical properties of CF monofilaments.

2. Experimental

2.1. Materials

PAN-based CFs used in the measurements were standard fibers (T700) produced by Toray Industries, Inc., Japan. The bundles are composed of 12,000 filaments of approximately 7-μm diameter. From the datasheet offered by the manufacturer,[2] tensile strength, Young's modulus, and electrical conductivity of the CFs were 4.9 GPa, 230 GPa, and 6.25×10^4 S m^{-1}, respectively.

2.2. Plasma etching-assisted radius profiling

Depth profiling has been widely used in XPS and SIMS for etching layers of the surface or surface contamination to reveal subsurface information. Recently, a similar destructive method was successively applied to study the mechanical properties of CFs. For instance, focused ion beam was used to cut a groove on the monofilament to study the intrinsic strength and interface shear strength of CFs in liquid [19,20]. Radius profiling follows the same idea, in which the surface layer is removed from monofilament uniformly by plasma etching. In plasma, the monofilament is attacked by high-energy ions from all directions, resulting in homogenous etching on all surface area exposed.

A CF monofilament was removed from the filaments, placed on a glass plate across a U-shaped groove, and glued on both ends by conductive silver adhesive, leaving a piece of approximately 10-mm-long monofilament suspended, as schematically illustrated in Fig. 1. Two pieces of copper foil of 0.1-mm thickness were placed on top of the adhesive and cured together with it to work as electrodes for further electrical measurement. The copper foils need to be pressed down gently to ensure that a good contact is formed between the foil and monofilament. It should be noted that the CF monofilament needs to be kept as straight as possible but not pulled too tight. Otherwise, the CF will be broken easily under tiny vibration. The contact resistance is calibrated to be less than 10 Ω, which is much smaller than the resistance of the monofilament itself (about 5 kΩ) and thus can be ignored. The glass plate with the CF specimen was placed into the quartz tube chamber (φ75 mm × 165 mm) of the plasma cleaner (MTI, PDC-36G), which was operated at a frequency of 13.56 MHz and a power of 18 W (720 V, 25 mA). During the plasma etching, dry air gas with a pressure of 1 Torr was fed into the reactor. The etching speed was calibrated to be 10 nm/min. Therefore, during etching, the radius of the monofilament can be controlled to a resolution of less than 10 nm, which corresponds to the spatial resolution of the structural and mechanical distribution measurement of this method, exceeding the methods mentioned above. In practice, the etching was conducted for 10 min each time and is capable of removing a surface layer of 100 nm accurately. The surface morphology change and the diameter (D) of each CF monofilament were monitored by a field emission scanning electron microscope (FESEM, FEI, Helios NanoLab 600i).

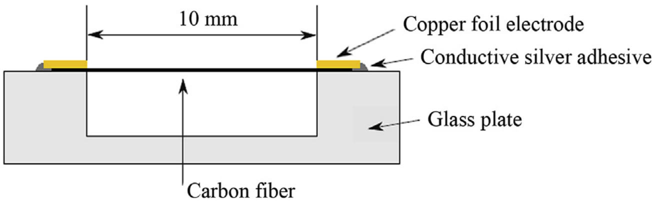

Fig. 1. Schematic of the specimen of CF monofilament for plasma etching. (A colour version of this figure can be viewed online.)

2.3. Electrical resistance measurement

After each etching step, the specimen was removed for electrical measurement. The surface layer of both the CF and the copper electrodes were etched off. However, because the thickness of the electrode is much greater than the diameter of the CF, the lost mass of the electrodes will not cause obvious contact resistance variation. The electrical resistance of CF monofilament was measured by a digital multimeter (Victor, VC9806$^+$).

2.4. Single-filament tensile test

Single-filament tensile test was performed for CF monofilament on a nanomechanical testing instrument (Agilent Technologies, T105 UTM) at room temperature according to ASTM D3379-75. The specimen is schematically shown in Fig. 2. The etched CF monofilaments were carefully removed from the etching specimen and bonded at both ends to a cardboard template with a rectangular window in center using epoxy resin. The gauge length and strain rate were 15 mm and 5×10^{-4} s^{-1}, respectively. The specimen was gripped firmly with the chucks of the tensile testing machine, and the template was cut vertically using a scissor along the cutting lines as shown in Fig. 2. The modulus (E) of the CF was calculated as follows:

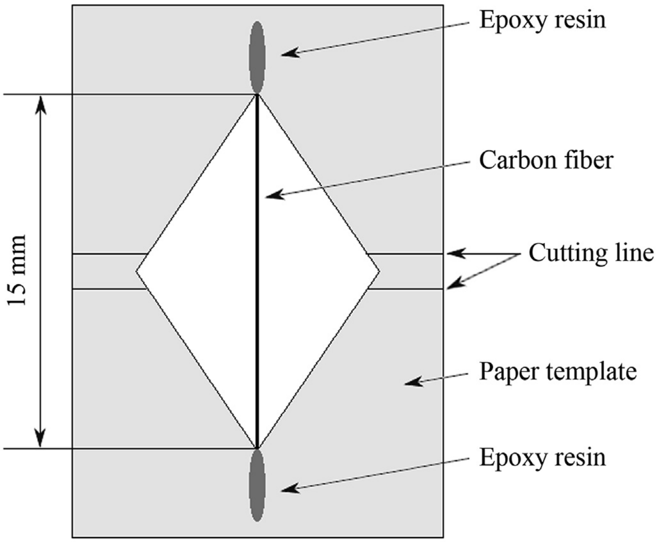

Fig. 2. Schematic of the CF monofilament tensile test specimen.

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[2] http://www.toraycfa.com/pdfs/T700SDataSheet.pdf.