Synchrotron X-Ray Diffraction of a Single Filament and a Bundle of Poly (*p*-Phenylene Terephthalamide) Filaments

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INTRODUCTION

The highly oriented high-tenacity/high-modulus *para*-aramide fibers of poly (*p*-phenylene terephthalamide) (PPTA) have been studied using X-ray diffraction (for examples, see Refs. 1–5) in bundle form and light diffraction[6] while stressing a single filament. Based on X-ray diffraction, electron diffraction, sonic and polarizing microscopic techniques, as well as macroscopic mechanical measurements of PPTA fibers, Schaefgen[7] wrote an informative review on the structure, properties, and applications of PPTA fibers, known as Kevlar (a DuPont trademark) or Arenka (an Enka trademark) fibers.

According to Schaefgen, lamellar structures of high crystallinity are formed by extended molecular chains. The defect zones, as confirmed by glazing incidence of soft X-rays,[8] which are between the ordered lamellae, can be visualized by plasma etching or hydrolysis in dilute hydrochloric acid. Alternating ordered lamellae and defect zones (of $\sim$ 30 nm spacing) form microfibrils with a diameter of $\sim$ 600 nm. The microfibrils are tied together by crystalline material to form filaments of $\sim$ 12 μm diameter. X-ray diffraction has been used to measure the lattice strain along the chain axis as a function of temperature and tensile stress for PPTA fiber bundles.[5] In a more refined experiment in which we plan to make a comparison of lattice tensile properties with macroscopic tensile properties, we report, to our knowledge, the first X-ray diffraction measurements of a single PPTA filament using synchrotron X-ray radiation

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EXPERIMENTAL

The X-ray diffraction experiments were performed at the State University of New York (SUNY) X3A2 beamline, using a modified Kratky block collimator[9] with $\lambda = 0.154$ nm at the A-2 hutch. The modified Kratky block collimator defined the X-ray beam cross section in a vacuum chamber. Two position sensitive detectors were used: a Braun linear position sensitive detector and a Siemens/Nicolet two-dimensional position sensitive area detector. The wire detectors were selected for their low background and high counting efficiency. As X-ray diffraction from a single fiber filament was very weak even with synchrotron radiation, the high incident X-ray flux would no longer be a problem for those wire detectors with very low dynamic ranges.

A schematic diagram of the geometrical arrangement for the X-ray setup is shown in Figure 1, which also depicts an actual 2-D X-ray diffraction pattern of a bundle of ~ 25 filaments using the Siemens/Nicolet area detector. The shades show different intensity zones, with the darkest shade having the highest intensity.

RESULTS AND DISCUSSION

Figure 2 shows the equatorial X-ray diffraction pattern of a bundle (~ 25 filaments) of PPTA filaments (solid line), each with a diameter of ~ 28 μm and the equatorial X-ray diffraction pattern of a *single* PPTA filament with a

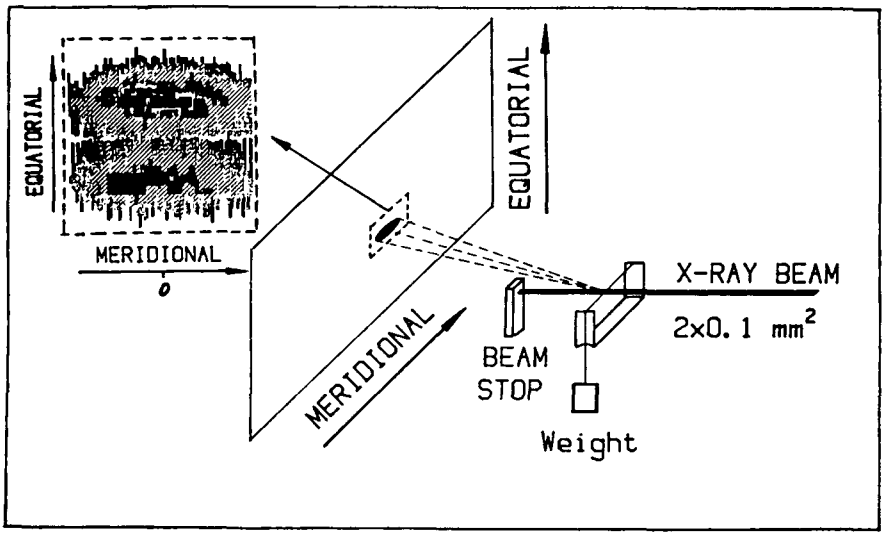

Fig. 1. Schematic diagram of the geometrical arrangement for the X-ray setup. The diffraction pattern inside the dashed lines on the upper left corner was measured on a bundle of ~ 25 filaments by using a Siemens/Nicolet 2-D position-sensitive area detector over a 300 s time period.

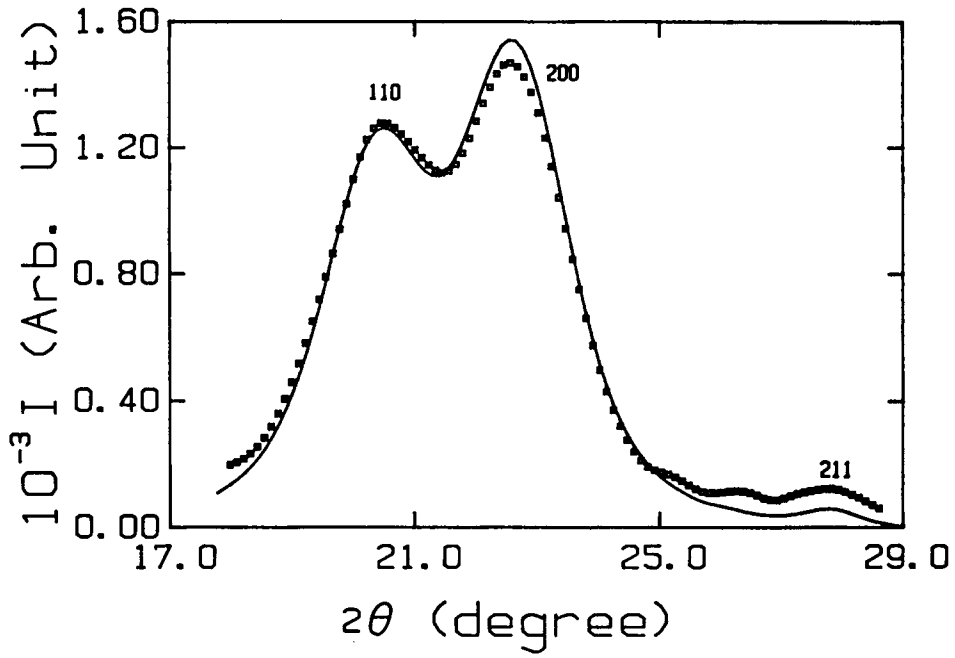

Fig. 2. Equatorial X-ray diffraction patterns obtained by using a Braun linear position sensitive detector. Solid line represents the measurement of 200 s on a bundle of ~ 25 PPTA filaments. Hollow squares represent the measurement of 3000 s on a single PPTA filament with a diameter of 28 μm.

diameter of ~28 μm (hollow squares). The synchrotron was operating at ~ 75 mA and 2528 MeV. Unfortunately, the focusing mirror at the SUNY X-3 port could not be optimized at the time, and we obtained only ~ 1/10 of the normal X-ray power density. So the measurement time for the bundle was 200 s, and for the single filament, 3000 s. By integration of intensity over 1° in the meridional direction that corresponded to the incident X-ray beam length of 2 mm, the X-ray intensity profile from a single filament had extremely good signal-to-noise ratio, as shown clearly in Figure 2. The X-ray patterns from a filament and a bundle of filaments are comparable, as to be expected. However, in lattice tensile experiments, a single filament can have better-defined stresses and avoid averaging over filaments of different orientations.

Figure 3 shows equatorial X-ray diffraction patterns at fixed meridional angles computed from the Siemens/Nicolet 2-D area X-ray detector. To insure accurate measurement of intensity and positional information, the area detector was calibrated on site using both ^{55}Fe flood-field source and the 0.154 nm X-rays from the beamline. The flood-field correction uses the uniform intensity distribution of the ^{55}Fe source to create a set of intensity and positional mapping arrays. These arrays, when loaded into the detector's computer memory, correct the incoming data for any intensity or positional anisotropy that may occur due to wire irregularity or preamplifier gains. The detector electronics were also optimized for the 0.154 nm synchrotron beam energy by adjusting the detector anode bias so as to insure maximum electron detection from the gas mixture. For the 2-D X-ray diffraction pattern, we used an incident X-ray beam

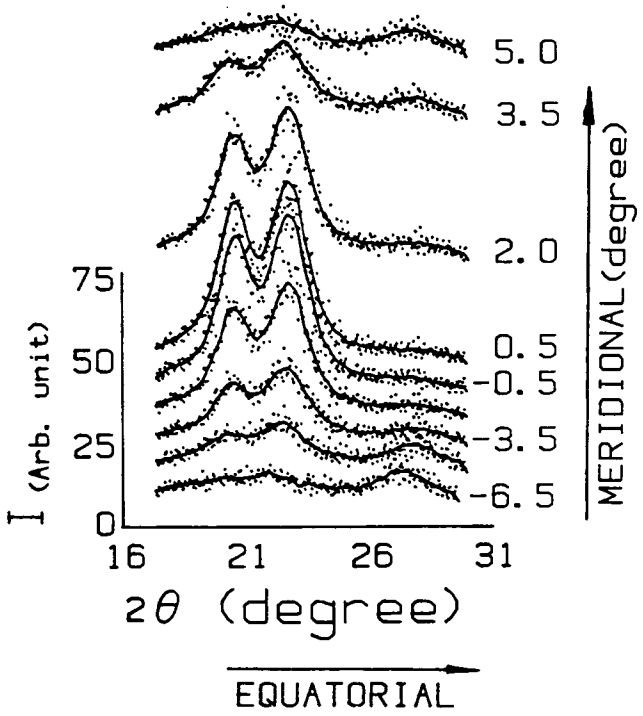

Fig. 3. Equatorial X-ray diffraction patterns of a bundle of ~ 25 PPTA filaments at fixed meridional angles computed from the Siemens/Nicolet 2-D area X-ray detector. Each curve was integrated over 1.5° in the meridional direction. Dots denote real experimental data, and the solid lines are constructed by smoothing the actual data 10 times.

cross section of 0.5 × 0.5 mm^2. Each curve was integrated over 1.5° in the meridional direction. The measurement for the entire 2-D X-ray pattern took 300 s. The diffraction data as denoted by the dots were noisier. The solid curves were constructed by using 3-point smoothing of data 10 times. From Figure 3, we see the 110 and 200 reflections at $2\theta = 20.50°$ and 22.57°, respectively, as well as the 211 double "spots" at 29.29°, with θ being the Bragg angle. If a bundle of 25 filaments can be measured over a 300 s time period with 1/10 the optimal X-ray power density, a single PPTA filament of 28 μm diameter should take ~ 1000 s, which is easily within reach in our experimental setup. The spread of the 110 and 200 reflections in the meridional direction covers an angular range of ~ 10°. The PPTA fibers have not shown noticeable structure damage by the synchrotron X-ray beam after short exposures of tens of minutes.

The stress dependence of strain in the *a* (square) and *b* (triangle) directions of the unit cell is shown in Figure 4. As the filament is being stretched, the stress is in the *c* direction. The deformation in the *a* direction was found to be greater than that in the *b* direction.

Like all previous reports,[3,5,10,11] this type of measurement has relatively low precision, because of the small deformation involved in stretching a Kevlar filament as $\Delta L/L \leq 0.6\%$, with L being the length of the filament. Thus, the corresponding change in 2θ is very small. However, we did use a linear position-

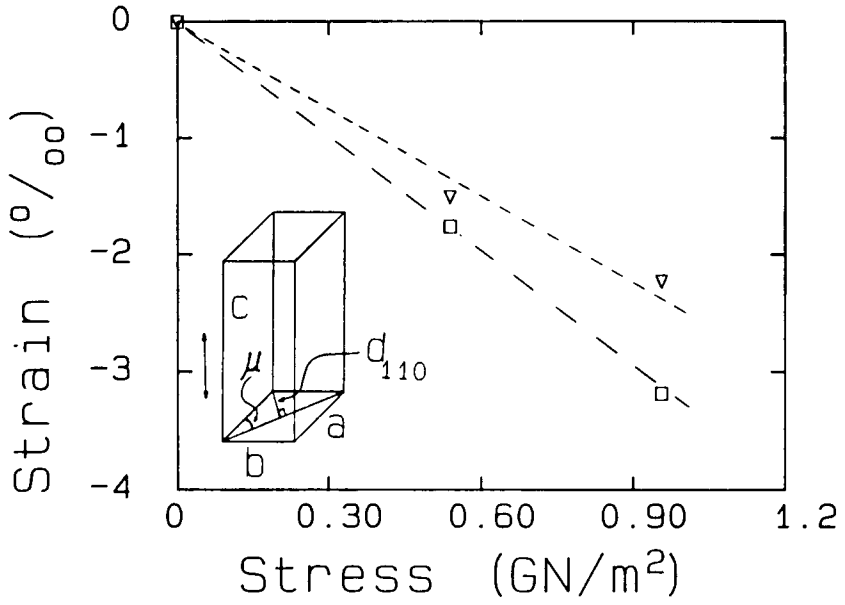

Fig. 4. Plot of strain vs. stress for a single filament of Kevlar 49, in a (□) and b (▽) directions, with $a = 2d_{200}$, $b = a \cdot \tan(\mu)$, and $\mu = \sin^{-1}(d_{110}/2d_{200})$, where d_{200} and d_{110} were calculated from the (200) and (110) X-ray diffraction patterns, respectively, using the Bragg equation. Dashed lines are for guiding the eyes only. The coordinates of the unit cell is shown in the inset.

sensitive detector with an angular resolution of 0.5 mrad. The uncertainty in the determination of the strain (ϵ) in the a direction is $\Delta\epsilon_a = (\cos\theta/\sin\theta)_a\Delta\theta \approx 5 \times 2.5 \times 10^{-4} \approx 0.13\%$, which is smaller than all the previous reported results[3,5,10,11] by a factor of ~ 5. The use of a single filament instead of fiber bundles could avoid the averaging effect in the stress distribution of fiber bundles. To our knowledge, the stress dependence of ϵ_a and ϵ_b, as shown in Figure 4, represents the first such measurements. It should be noted that even with a single filament geometry, $\Delta\epsilon_a/\epsilon_a$ (or $\Delta\epsilon_b/\epsilon_b$) remains fairly large ($\sim$ 30–60%). It is, however, possible to improve the uncertainties in $\Delta\epsilon$ by a factor of $\sim$ 3–5, corresponding to an overall improvement in $\Delta\theta$ by a factor of $\sim$ 15–25, when compared with reported literature values. Then, we could determine the Poisson ratios from fiber bundles and determine the modulus from ϵ_c in a single filament. Further study is underway.

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