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Spatially resolved nanomechanical properties of Kevlar® fibers

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Abstract

The nanomechanical properties of Kevlar® 49 fibers are quantitatively evaluated using the interfacial force microscope (IFM). The IFM is capable of differentiating the skin/core structure of the fibers and selectively probing each area. The core and skin regions were found to possess an elastic modulus of 60.8 and 13.4 GPa, respectively. The difference in modulus is attributed to an increased amount of order and hence intermolecular bonding in the core region. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Nanomechanical properties; Interfacial force microscope; Kevlar® fibers

1. Introduction

Poly(*p*-phenylene terephthalamide) fibers, such as DuPont's Kevlar® aramid fibers, exhibit exceptional mechanical properties especially considering their light weight. As a result of these favorable properties they are routinely found in such diverse applications as ballistics resistance, helicopter blades, and recreational accessories [1]. The exceptional mechanical properties of the aramid fibers are undoubtedly a result of their microstructure. A wide variety of techniques, from diffraction and electron microscopy [2–6] to modern scanning probe techniques such as atomic force microscopy (AFM) [7–10] and scanning tunneling microscopy (STM) [11], have been used to elucidate the microstructure. A variety of models have been proposed with a common feature being the differentiation of a core and skin region within each individual fiber. The core region tends to possess a high degree of order and crystallinity, while the microstructure of the skin is generally non-crystalline. This radially anisotropic microstructure is believed to be responsible for the favorable properties of aramid fibers [10] and it would prove extremely valuable to evaluate the mechanical properties of the individual regions. However until now, due to limitations in the available instrumentation, it has been impossible to selectively probe the nanomechanical properties of these areas.

The interfacial force microscope (IFM) represents a novel scanning probe technique combining high-resolution spatial imaging and quantitative force measurements [12–14]. The IFM, is based on a differential capacitance force sensor, which eliminates the compliance-related problems that plague cantilever-based instruments such as the AFM. The IFM is an ideal tool for the quantitative study of the mechanical properties of heterogeneous polymer surfaces such as aramid fibers. In a recent publication by Graham et al. [15], the elastic modulus of nanometer-sized phase segregated domains of a semicrystalline homopolymer surface were quantitatively measured. In the present paper, we report IFM measurements of the mechanical properties of the skin and core regions of Kevlar® 49 fibers. An understanding of a material's properties on a nanometer-scale, provides insight and understanding into that material's performance on a macroscopic scale.

2. Experimental

The poly(*p*-phenylene terephthalamide) fibers used were Kevlar® 49 from E.I. Dupont de Nemours and Co. They were embedded in an epoxy matrix with the final Kevlar® fiber–epoxy composite possessing a volume fraction of 0.50. The composite was cut into two pieces with each half being prepared by different methods. One half was hand polished in order to provide a relatively smooth exposed surface, while the other half was microtomed perpendicular to the fiber axis, with the bulk sample being used for the experiments and the microtomed sections discarded.

We used the IFM to directly determine the nanomechanical properties of the core and skin regions of the

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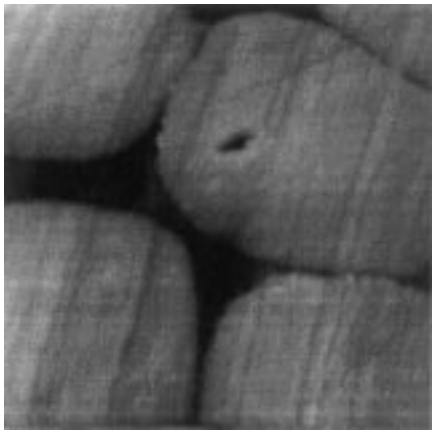

Fig. 1. A $15 \times 15\ \mu m^2$ contact mode IFM image of the polished Kevlar® fibers (height range = 1 μm). The fibers are clearly non-circular with numerous polishing grooves evident in the image.

Kevlar® fiber. As mentioned above, the IFM differs from conventional scanning force microscopes in that the cantilever has been replaced with a differential capacitance force sensor. The force feedback prevents any torsional displacement in the sensor, and absolute calibration of the *z*-piezo drive motion (through an inductance detector) and the force sensitivity (by direct measurement on a compliant microbalance), together provide true force and displacement axes. This design allows one to image with nanometre spatial resolution, select the features of interest and then measure their mechanical properties with nano-Newton force resolution. The electrochemically etched tungsten tips used for these experiments were characterized by scanning electron microscopy (SEM). Several IFM sensors and tips were used in these experiments in order to ensure reproducibility.

3. Results and discussion

Fig. 1 is a $15 \times 15\ \mu m^2$ contact mode IFM image of the polished Kevlar® fiber. The height difference between the topographical minima and maxima is 1 μm. One rather disconcerting feature of the image is the lack of symmetry in the individual fibers. They should be round, with an average diameter of 12 μm [9]. It appears that the polishing procedure has severely disrupted the surface and near-surface regions and caused the exposed fiber to become splayed. This will inevitably disrupt the highly ordered microstructure of the core region and subsequently severely reduce the amount of intermolecular bonding (i.e. hydrogen bonding). The disruption in the order and hence the intermolecular bonding will influence the mechanical properties [16] measured by the IFM, since the data obtained originate solely from this perturbed region.

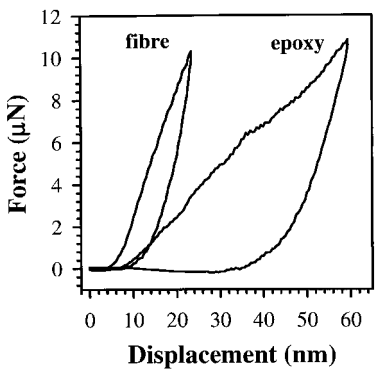

Fig. 2. Force vs displacement curve of a polished Kevlar® fiber and the epoxy matrix. The radius of the tip used was 110 nm. The fiber and epoxy possessed an elastic modulus of 10.1 ± 1.5 and 2.5 ± 0.5 GPa, respectively.

Fig. 2 shows force vs displacement (*f*–*d*) curves for the two components in the polished Kevlar® fiber–epoxy composite. In an *f*–*d* experiment, a probe of known geometry is pushed into the surface, while the load is recorded as a function of tip-sample deformation. The probe used for the *f*–*d* curves shown was a paraboloidal tungsten probe with a tip radius of 110 nm. The *f*–*d* curves in Fig. 2 exhibit an elastic (reversible) response at low initial loads, followed by a yielding event which indicates the onset of plasticity (irreversible response). Upon unloading, the curve is hysteretic indicating a considerable amount of plastic flow. A small attractive regime, attributed to a capillary interaction, is present on the final portion of the unloading curve. It should be noted that the curves shown were chosen as representative curves and a minimum of 30 experiments were performed on each region in order to ensure reproducibility.

The initial portion of the loading curves can be analyzed using Hertzian contact mechanics for a non-interacting, parabolic probe deforming an elastic half-space. The Hertzian model predicts that upon contact, the applied load will scale as the three-halves power of the displacement [17]. Hertzian analysis of the initial portion of the loading curves yields an elastic modulus of 2.5 ± 0.5 GPa and 10.1 ± 1.5 GPa (assuming a Poisson's ratio of 0.35 for the fiber [18]) for the epoxy and the Kevlar® fiber, respectively. The value for the epoxy is well within the range of the literature values, 1.2–4.1 GPa [19]. However, the modulus for the fiber is much lower than was expected based on the literature value for the modulus in compression (63 GPa) [1]. Another interesting observation from the polished sample was that the recorded elastic modulus was independent of the location of the indent on the fiber (i.e. no radially anisotropic structure was observed).

Since the parabolic probe used for these experiments is not an uniaxial indentor, the recorded modulus for an anisotropic material will be a weighted average of the different elastic modulii. Our measurements may therefore be slightly influenced by the inferior off-axis mechanical properties of the fibers. In compression and tension, the modulus is considerably higher since it involves deforming covalent bonds, while in transverse loading the weaker hydrogen bonds are disrupted. However, this discrepancy between

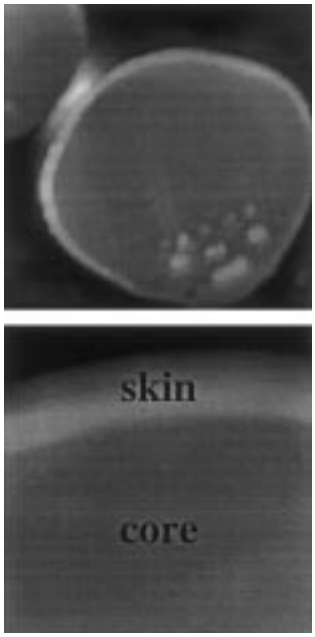

Fig. 3. (a) A $12 \times 12\ \mu m^2$ contact mode IFM image of the microtomed Kevlar® fibers. The skin/core structure of the fiber is clearly visible. (b) A $3 \times 3\ \mu m^2$ contact mode IFM image of the edge of the microtomed fiber. Once again the skin/core structure is clearly visible and labeled in the image. The height difference between the skin and the core region is ~20 nm.

the recorded and literature values is too large to be solely attributed to the influence of the off-axis properties on the data. A discrepancy of this magnitude eludes to a severely altered or damaged sample.

It is our interpretation that the polishing procedure caused the fiber ends to become splayed and thus severely reduced the degree of order and intermolecular bonding. This reduction in intermolecular bonding results in recorded values, which are much lower than the literature values. It seems that polishing the fibers to obtain a smooth surface has caused considerable sample damage. This would explain why no skin/core microstructure was observed on the polished sample. It should be noted that no attempts were made at refining the polishing procedure. Since the goal of this work was to prepare a smooth, unperturbed surface, it was anticipated that microtoming the composite should be far less damaging.

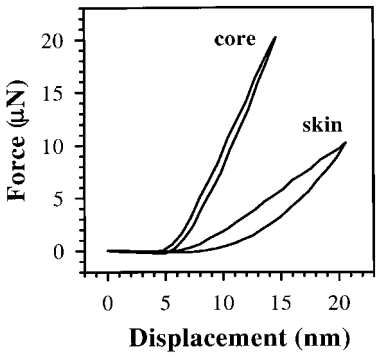

Fig. 4. Force vs displacement curve of the two regions, skin and core, of the Kevlar® fiber. The radius of the tip used was 140 nm. The core and skin possessed an elastic modulus of 60.8 ± 6.7 and 13.4 ± 2.7 GPa, respectively.

Fig. 3a is a $12 \times 12\ \mu m^2$ contact mode IFM image of the microtomed Kevlar® fiber. Fig. 3b is a $3 \times 3\ \mu m^2$ contact mode IFM image of the edge of the microtomed fiber. Several scans were recorded at different angles all yielding comparable images with no preferential alignment of the features. The height difference between the topographical minima and maxima is 200 and 150 nm for Fig. 3a and b, respectively. This difference is largely due to fiber–matrix height difference. It is evident from Fig. 3a that the microtomed fibers are essentially round with a diameter of approximately 12 μm. As expected, sample preparation using a microtome seems to be far less disruptive than polishing. Interestingly, Fig. 3a and b clearly shows that the fibers possess a radially anisotropic surface which is presumably the skin/core structure. Fig. 3b is a higher resolution image of the edge of the fiber, once again clearly depicting this radially anisotropic structure. Several images were recorded on many fibers and all showed this skin/core feature. The width of the skin region varied from 500 nm to 1 μm, which is consistent with other reports [10]. This variation in width was observed between different fibers and even within an individual fiber. The asymmetry of the skin layer appears to be random and not preferentially aligned with the direction of microtoming. The skin layer seems to be elevated, on average 20 nm, with respect to the center of the core. The explanation for the difference in height is unknown at this time. However, since the IFM was able to differentiate the skin/core structure it is now possible to selectively probe each area.

Fig. 4 shows *f–d* curves for the two components of the microtomed fiber. The probe used to record the *f–d* curves shown possessed a tip radius of 140 nm. Once again the initial portion of the loading curves (up to a penetration depth of only a few nanometers) can be analyzed using Hertzian contact mechanics with the core and skin regions possessing elastic modulii of 60.8 ± 6.7 and 13.4 ± 2.7 GPa, respectively. The value recorded for the core region is consistent with the literature value of 63 GPa for the compressive modulus. Microtoming the sample has not disrupted the crystalline microstructure. The skin region, whose microstructure is non-crystalline, possesses a modulus much lower than literature values. In fact, the value recorded for the skin is comparable to the value for the entire polished fiber. This observation is consistent with both structures (skin and polished fiber) possessing a non-crystalline microstructure. The observation that crystalline regions possess a higher elastic modulus than the non-crystalline regions of the same material is consistent with previously published results [15]. The epoxy in the microtomed sample was also studied with the results being

comparable to those recorded for the epoxy in the polished sample.

The IFM was clearly capable of differentiating the radially anisotropic structure of Kevlar® 49 and selectively probing the mechanical properties of each region. The core region was found to posses an elastic modulus of 60.8 ± 6.7 GPa. The skin region possesses a much lower modulus of 13.4 ± 2.7 GPa, due to its non-crystalline microstructure. Even though the skin does not posses the same elastic modulus of the core region it may still play a crucial role in fiber performance through the termination of cracks which propagate through the crystalline core [8]. The entire surface of the polished fiber was found to possess a modulus comparable to the skin indicating a severely damaged and non-crystalline microstructure. This study not only quantified the elastic modulus of the skin and core regions of Kevlar® 49 fibers, but provides another excellent example of the capabilities of the IFM and its applicability to polymer science.

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