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Interior morphology of high-performance polyethylene fibers revealed by modulus mapping

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ABSTRACT

This work elucidates the undisturbed interior morphology of commercial ultra-high-molecular-weight polyethylene (UHMWPE) high-performance fibers through atomic force microscopy (AFM) modulus mapping of interior surfaces exposed by a novel focused ion beam (FIB)-notched sample preparation technique. The imaging shows unequivocally the presence of epitaxial crystals in the interior of highly drawn UHMWPE fibers. Overall, AFM observations and measurements were made for three different commercial fiber types, illustrating five basic UHMWPE morphologies: (i) extended chain fibrils (shish), (ii) interlocking and (iii) standalone kebab or epitaxial crystals, (iv) voids or interface between fibrils, and (v) tie chains across voids. Furthermore, microfibrils were bundled into groups separated by voids or amorphous material. Bundled groups of microfibrils group together to form macrofibrils, typically separated by larger voids or amorphous material. Additionally, stretched tie-chain bridges provide connectivity between some fibrils. Each of these five features (extended chain fibrils, interlocking and standalone epitaxial crystals, voids and tie-chains) varies across the three types of commercial fibers, and sometimes across the individual fiber interiors. AFM contact modulus values measured transverse to the fiber draw axis were found to vary considerably within different morphological domains. The distribution of morphology sizing was quantified for each of the examined fibers. The measurement of internal facets have major implications for fiber modeling and processing, such as optimization of draw ratios to affect the extent and arrangement of epitaxial crystalline morphologies and thus improve mechanical performance.

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1. Introduction

Since the pioneering work done by Smith et al., [1–3] Ward et al., [4] Pennings et al., [5] and others [6–9] in the 1970s and 1980s on the drawing of ultra-high-molecular-weight polyethylene (UHMWPE), much has been done to improve the processing in order to produce high strength, high tenacity, high modulus UHMWPE fibers and other structures [10–15]. UHMWPE fibers have become ubiquitous in the fields of composite reinforcements and soft armor, rope, sails and parachutes. However, over the past several decades, though processing technology has progressed, scientific understanding of the internal structure of these fibers and therefore the structure/property relationships of these specialty materials remains somewhat unclear. Recently, as part of the effort to improve the state of the art, there has been a renewed interest in evaluating the morphologies present on the surface and within the interior of these fibers and the resultant properties [16–21].

What is known of the general morphology of UHMWPE fibers of various processing is gathered from studies employing a multitude of techniques including: small-angle x-ray scattering (SAXS) and wide-angle x-ray diffraction (WAXD) as well as through spectroscopic techniques such as Raman and nuclear magnetic resonance (NMR) [10,22–24]. While these techniques rely heavily upon modeling or reconstruction of the microstructure, techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) have been used to observe real-space detail of the structure.

The structural rudiments of UHMWPE fibers can form an overall complex picture. Simplifying and establishing a nomenclature at the outset is therefore critical. Fig. 1 is a schematic representation showing a co-existence of the most common features previously seen in UHMWPE. Within Fig. 1, feature (i) is the extended chain

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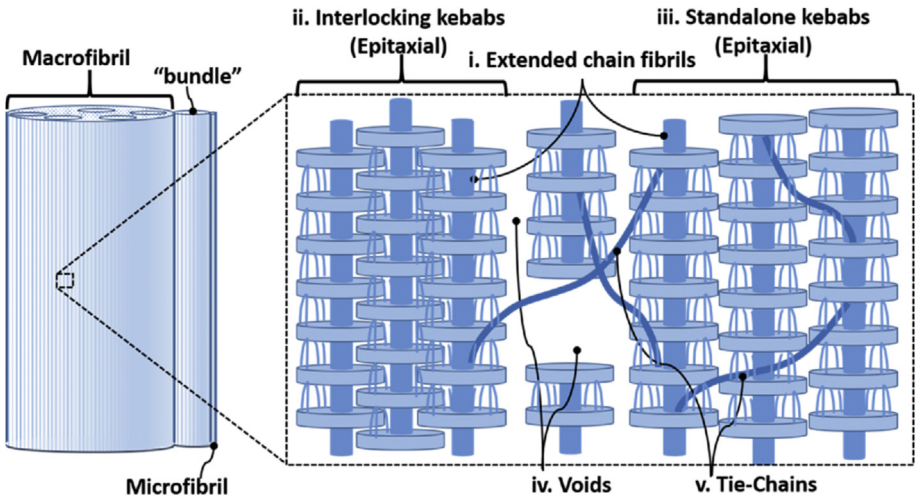

Fig. 1. UHMWPE morphology: microfibrils can bundle together and the bundles group into macrofibrils (left). The detail (right) shows the inclusion of (i) extended chain fibrils (shish), (ii) interlocking and (iii) standalone epitaxial crystals (kebab), (iv) voids, and (v) tie-chains. The epitaxial crystals (light blue disks) are connected axially by extended chain fibrils (dark blue columns), and interconnected by intrashish-kebab tie molecules of quasi-amorphous material (thin light blue lines).

microfibrils (shish), which are commonly decorated with (ii) interlocking and (iii) standalone epitaxial crystals (or, kebab). Here, kebabs are connected by quasi-amorphous material (intrashish-kebab tie molecules). Microfibrils or bundles of microfibrils are separated by (iv) voids or interface between fibrils, often with (v) tie chains across voids (intershish-kebab tie molecules). It is generally accepted that the smallest microfibrils in a fiber behave cohesively in larger sub-groups. These shall be called either 'bundles of fibrils' or 'macrofibrils', depending on void or amorphous region separating them. A fiber design approach, aimed at increasing strength and modulus may utilize finite element modeling, requiring size and properties of each structural element corresponding to constitutive fiber morphologies. Such a model might look like the left side of the schematic, Fig. 1.

Extended chain fibrils are the morphological architecture expected to provide the highest strength, highest modulus UHMWPE structure. Some works, such as Ohta et al. [12,19] have suggested from TEM observations that upon fiber drawing, the weaker epitaxial material (kebab) disappears, allowing for more extended chain crystal (shish). This is in agreement with earlier works such as Thomas et al. [8,9] who also showed TEM evidence of a decreasing epitaxial volume. However, Thomas' work did not show a *full disappearance* of the epitaxial crystal but rather an incorporation of the epitaxial crystal into the shish, where some of the epitaxial lamellae remained. Litvinov et al. [18] have shown evidence of a shifting or disappearance of a SAXS peak presumably corresponding to a long period in the fiber axis direction as a function of draw ratio. The peak disappearance was attributed to a coalescence of amorphous regions separating crystalline stems along the microfibrils resulting in an increasing crystalline long period. On the other hand, Somani and Hsaio [14,25] showed through rheo-xray observations (SAXS and WAXD) that epitaxial crystals *grow and persist* in drawn UHMWPE. Earlier, Thomas et al. [8] had noted that SAXS data suggesting long period peak shifting, disappearance, or decrease was inconclusive and that therefore it is necessary to use real-space techniques to understand how the microstructure actually looks with respect to epitaxial and extended chain crystals. It was concluded that the epitaxial crystal did not disappear but rather was incorporated into the extended chain crystal, resulting in a sharing of tie chains between microfibrils. Through drawing, such tie chains could become tight, and thereby gather microfibrils into bundles.

Whether microfibrils are pulled close together or not, there still may remain an interface between fibrils or bundles of fibrils and this is defined as the void. Solid-state nuclear magnetic resonance (SS-NMR) data was helpful in developing a schematic of UHMWPE drawn fiber where the interior has ca. 10–100 nm voids and amorphous tie molecules across these voids [23]. This view was supported by others [18], though never visualized using real-space techniques.

As for other real-space techniques that have been used, UHMWPE outer surfaces have previously been studied by atomic force microscopy (AFM) [21,26,27].More recently, others [28] have reported AFM results from room temperature microtomed samples of Spectra fiber interior with high draw ratio. Because of the very low AFM scanning forces used and low-resolution scans, the study was not able to report the existence of epitaxial structures within the fiber interior. This work clearly leaves room for further, more specific study of the interior morphology of UHMWPE fibers. On the other hand, the AFM images of the interior faces were able to provide evidence for the existence of void spaces on the order of 10–100 nm randomly spaced throughout the fiber.

The AFM and TEM observations mentioned had limitations due to instrumentation, sample preparation or technique. For example, the sample preparation techniques used in previous research efforts were performed at room temperature [19,28], much higher than the very low glass transition temperature of polyethylene (ca. −125 °C) [29], where large shear forces are in play through the use of a diamond knife during microtomy, making it more difficult to preserve fine internal structure. These same works suffered from loss of resolution through not only sample preparation but also the practical application of the imaging techniques used. Still these works provide a starting point for the current study which aims to resolve questions that remain regarding the internal structure of high draw ratio UHMWPE fiber.

Therefore it is necessary to elucidate the interior morphology of ultra-drawn UHMWPE fiber using sample preparation techniques designed to expose the interior without losing the fine structure, as well as AFM scanning parameters to provide the visualization of structural details which may only present themselves when stiffness variations are taken advantage of to provide good mechanical and topographical contrast. In our study, we chose to prepare samples using a FIB-notch technique [30], creating a shear plane within the fiber where only very low shear forces exist holding the