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Transition from shish-kebab to fibrillar crystals during ultra-high hot stretching of ultra-high molecular weight polyethylene fibers: *In situ* small and wide angle X-ray scattering studies

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ABSTRACT

The ultra-high hot stretching was conducted on four-times pre-stretched ultra-high molecular weight polyethylene (UHMWPE) fibers to the ratio of about 508% to achieve the total ultra-high stretching ratio of about 2000%. *In situ* small and wide-angle X-ray scattering (SAXS/WAXS) measurements using synchrotron radiation and Raman spectroscopy were applied to study the structural evolutions of ultra-high stretched fibers. SAXS images revealed the transition from shish-kebab to fibrillar crystals, which is believed to involve with the increasing trans-configuration ratio of C–C backbone. WAXS results demonstrate the further stretching could still be applied to the fibers to acquire the complete extended-chain crystals.

1. Introduction

High performance fibers are considered as those fibers with significant properties in stiffness, strength, conductivity, so on and so forth, designed for specifically required uses. Ultra-high molecular weight polyethylene (UHMWPE) fibers are a kind of high performance fibers in mechanical engineering application, possessing high strength of 3.8 GPa, high tensile modulus of 166 GPa, and low density of 0.98 g/cm^3, which continuously attract considerable interests. UHMWPE fibers are a typical kind of semicrystalline polymer materials, that the properties are essentially determined by the structures [1]. The studies about the relationship among the processing, structures and properties of semicrystalline polymers have been widely reported as about the processing or deformation induced the evolution of microstructures like microvoids, long period structures, microfibrils, etc. [2–14]. Polyethylene with the concise chemical structure, the vinyl repeat unit, and high-density polyethylene (HDPE) and UHMWPE with even less branched structures are the very ideal candidates for the fundamental study of structure–properties relations and other polymer physics questions. There have already been reports about the macroscopic deformation induced microstructures evolution in HDPE films by Men et al. that lamellar structure

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could transform into the micro-fibrils during uniaxial stretching through the stress-induced melting and crystallization mechanism [15,16]. More interestingly, UHMWPE precursor fibers will go through an ultra-high stretching process to achieve the high performance properties. During this process, the formation of shish-kebab and the corresponding transition have been reported early [17–20]. Our previous article also studied the relatively stretching process of UHMWPE precursor fibers at the temperature of 80 °C, and a lamellae-break induced formation of shish-kebab model was proposed by us [21]. However, the behaviors of semicrystalline polymers strongly depend on the temperature with the possible α relaxation process influenced mechanism [22]. That industrial stretching process of UHMWPE precursor fibers is conducted in a higher stretching ratio and temperature. Therefore it is worthy to further investigate the ultra-high stretching process of UHMWPE precursor fibers under higher temperature that is closer to the real industrial situation.

Small-angle X-ray scattering (SAXS) is the very effective technique for the study of about nanometer range microstructure of polymer materials. And its theory has been fully developed that can be applied for the situations of polymer lamellae, polymer microfibrils and microvoids [23–26]. Furthermore, with the awareness of the value of synchrotron radiation and continuous development, the *in situ* X-ray measurements have become available and popular for the various studies [13]. There have been reports about kinds of polymer fibers as poly (vinylidene fluoride) (PVDF), nylon 6 (PA6), polyethylene (PE), poly (oxymethylene), polybutene-1, polypropylene (PP), poly (ethylene terephthalate) (PET), etc.; the *in situ* measurements during the processing revealed the several significant evolution processes of microstructures as lamellar organization, transition and microvoids development [27–30]. And also other forms of polymer materials as polymer films or sheets have been used in some *in situ* studies by Li et al., which also effectively indicated the occurrence of the transient structures during the deformation process of HDPE and PA 12 [31–33]. As be mentioned above, our group has already established the *in situ* SAXS measurement technique to investigate the hot stretching process of UHMWPE precursor fibers [21]; moreover in this article based on the well-established technique, we conducted the further *in situ* small and wide angle X-ray scattering (SAXS/WAXS) studies about pre-stretched UHMWPE fibers at 90 °C and 100 °C temperatures, for the purpose of totally about 20-fold ultra-high stretching ratio to take a deep look into the possible transition from shish-kebab structures to fibrillar crystals.

2. Experimental

2.1. Materials

A bundle of extracted UHMWPE precursor fibers with 230 filaments fabricated by our collaborator were previously stretched at 90 °C and 100 °C to reach the effective drawing ratio of 400%. The pre-stretched fibers were used in this experiment for further hot stretching, and the main properties are listed in Table 1.

2.2. Ultra-high hot stretching and in situ X-ray measurements

Self-developed drawing apparatus was used to conduct ultra-high hot stretching of fibers, which has been described in our previous research [21], here we will not reiterate much but a brief introduction. The drawing components and a thermal sensor are incubated in a customized thermal incubator with the size of 300 mm * 100 mm * 80 mm. Heating and controlling are fulfilled by a modified heat gun and the coupling thermal sensor. To avoid the fiber samples facing the direct heating flow from the heat gun, a metal mesh was used as a turbulator. The pre-stretched fiber samples were symmetrically stretched to ensure the detecting point unchanged, the initial sample length was 44 mm, and the stretching velocity was controlled as 4 mm/min. Due to the limitation of incubator, the experimental available strain range was controlled within 510% to reach the total ultra-high stretching ratio of ~20 times. The stretching temperatures were set as 90 °C and 100 °C corresponding to the pre-stretching temperatures. SAXS and WAXS data were recorded during the stretching.

In situ X-ray measurements were performed at the beam line BL16B at Shanghai Synchrotron Radiation Facility (SSRF) with the X-ray wavelength of 0.124 nm. A two dimensional detector Mar165CCD equipped at a distance 5340 mm away from the sample calibrated by standard sample (dried cattle tendon) was used to collect SAXS images. The continuous collection method of data image [34] was used to record SAXS data in this experiment, i.e., to expose continuously without stopping stretching. The exposure time is 5 s for every SAXS image, and there is no interval between two images. The sample distance was shifted to 174 mm calibrated by standard sample (lanthanum hexaboride) to collect WAXS images. In order to keep the correspondence with SAXS data, other WAXS measurement conditions were controlled as same as the SAXS measurement. All the collected patterns were corrected by air scattering and background noise according to ionization chambers [35].

Table 1
Properties of UHMWPE precursor fibers.

Specimen	Average diameter (μm)	Density (g/cm^3)	Effective drafting ratio (%)
UHMWPE fibers	29.6 ± 0.1	0.938	400