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The effect of chitin nanocrystal on the structural transition of shish-kebab to fibrillar crystals of ultra-high molecular weight polyethylene/chitin nanocrystal fibers during hot-stretching process

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ABSTRACT

The pre-stretched ultra-high molecular weight polyethylene/chitin nanocrystal composite fibers after first hot-stretching stage were prepared. The effect of chitin nanocrystal on the structural evolution of shish-kebab to fibrillar crystals of ultra-high molecular weight polyethylene/chitin nanocrystal fibers during hot-stretching process was studied by using in-situ small-angle X-ray scattering, wide-angle X-ray diffraction measurements, and scanning electron microscopy. The results showed that the addition of chitin nanocrystal can improve the stretchability of pre-stretched fibers, and makes the elongation of amorphous layers between lamellae more uniform. The chitin nanocrystal accelerates the fragmentation recrystallization process of kebab crystals (lamellae) at 90, 100, and 110 °C and the melting recrystallization at 120 °C during hot-stretching process. Moreover, more fibrillar crystals form in UHMWPE/CNC fibers comparing with pure UHMWPE fibers at the same strain and stretching temperatures. These results suggest that the addition of chitin nanocrystal is conducive to the structural evolution of shish-kebab to fibrillar crystals of ultra-high molecular weight polyethylene fibers during hot-stretching process.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) fibers are high-performance fibers developed by Smith and Lemstra [1,2] via gel-spinning method in late 1970s, which have been widely applied in aerospace, military, medical, sports, and other fields due to their distinguished performance such as high specific strength, high specific modulus, cutting resistance, and excellent energy absorption [3–10]. The theoretical tensile strength and modulus of UHMWPE fibers are 19–26 GPa and 250–350 GPa [11], respectively, while the current reports are still well below the limit value. The high orientation and crystallinity of the extended chain crystal structure endows UHMWPE fibers with the high-performance, meaning that the formation process of extended chain crystal is very important for the improvement of fibers mechanical properties. Therefore, a number of investigations have focused on the structural evolution of UHMWPE fibers during gel spinning process, which aimed to further promote the improvement of UHMWPE fibers performance. Shish-kebab crystals were found to form after hot-stretching process with low stretch ratio, while the formation of extended chain crystals (fibrillar crystals) need to go through the hot-stretching process with very high stretch ratio [12]. The shish-

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kebab crystals could gradually transform to extended chain crystals with the increase of stretch ratio during hot-stretching process [13–17]. In addition, the spinning speed was found to have a great influence on the stretchability of gel UHMWPE fibers. The UHMWPE fibers obtained with a relatively high spinning speed composed of the uniform shish-kebab crystals and exhibited better stretchability, finally corresponded better mechanical properties [18]. The above study results suggest that the shish-kebab crystal is the most important structure for UHMWPE fibers before the formation of extended chain crystal. The basis of UHMWPE fibers obtained high-performance is that most molecules involve in the formation of extended chain crystals and constitute homogeneous and continuous matrix [19].

In recent years, the rapid development of nanocomposite technology provided a new opportunity for the improvement of the properties of UHMWPE fibers by preparing UHMWPE/nanofiller composite fibers. Therefore, many studies have been done to investigate the reinforcing effect of various nanofillers such as spherical nano-SiO_2 [20], layered attapulgite (ATP) [21] and fibrous carbon nanotubes (CNTs) [22–24] on the performance of UHMWPE fibers, and CNTs have the best effect on reinforcing UHMWPE fibers. But the actual mechanism of CNTs reinforced UHMWPE fibers is difficultly determined for the reason that CNTs have very high strength and modulus (The tensile strength and modulus of CNTs reach up to 150 GPa and 1 TPa, respectively) [25], and CNTs also can promote the orientation and crystallization of UHMWPE fibers. In addition, most of studies just limited to study the enhanced effect of various nanofillers on UHMWPE fiber and the influence on the stretchability of gel fibers, and simply analyzed the enhanced cause. Little attention was paid to the effects of nanofillers on the structural transition of UHMWPE fibers during hot-stretching process.

Chitin nanocrystals (CNC) belong to the fibrous nanofiller as CNTs, which is beneficial to the study of reinforcing mechanism of fibrous nanofillers on UHMWPE fibers. The modulus of CNC is similar to the modulus of UHMWPE fibers, which are both far below that of CNTs (The modulus of CNC is 150 GPa at longitudinal direction and 15 GPa at transverse direction [26].). Therefore, CNC affected the mechanical properties of UHMWPE/CNC fibers need to through changing the orientation and crystallization of molecular. Furthermore, the sizes of CNC (20–40 nm wide and 150–400 nm long) [27] are similar to those of fibrillar crystal in UHMWPE fibers. As early as in 1999, CNC were found to induce the formation of transcrystalline layer structure in crystalline polymer, which had an important role on the mechanical properties of composite materials [28]. Therefore, CNC might induce the formation of shish structure of UHMWPE fibers.

In our previous work, the reinforcing effect of CNC on UHMWPE fibers was studied, and we found that the ultimate tensile strength and Young's modulus of UHMWPE/CNC fibers with 1.0 wt% CNC were 14.5% and 17.0% higher respectively than those of pure UHMWPE fibers [29]. In order to obtain the actual mechanism of CNC reinforced UHMWPE fibers, we also studied the effects of CNC on the structure of UHMWPE fibers at various stages [30]. We found that the CNC could make more molecules involve in the formation of crystals, and the addition of CNC were conducive to the formation of thicker kebab and the transformation of shish-kebab to fibrillar crystal. However, the actual effect of CNC on the structural transformation of shish-kebab to fibrillar crystals of nanocomposite fibers need to be further investigated.

In this study, the UHMWPE/CNC fiber samples were cut from the stretched fibers after first hot-stretching stage in industrial production line (pre-stretched fibers). The effect of CNC on the structural evolution of shish-kebab to fibrillar crystals during hot-stretching process of UHMWPE/CNC fibers with low concentration solution at the temperatures of 90, 100, 110, and 120 °C were deeply investigated by using in situ SAXS, WAXD, and scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

The UHMWPE resin used in this study was produced by Sinopec Beijing Yanshan Company. The viscosity-average molecular weight ($\overline{M}_V$) was 2.7×10^6. The Chitin was obtained from shrimp shells, which were provided by Aladdin reagent Co., Ltd. (Shanghai, China). Moreover, the basic range of thermal degradation for the shrimp Chitin nanocrystals (CNC) was 290–420 °C [31], which suggested that CNC were not degraded in all preparation process of UHMWPE/CNC fibers. CNC were prepared by using acid hydrolysis as described in previous report [27,29,30].

2.2. Sample preparation

UHMWPE resin and CNC were dispersed and dissolved in paraffin oil to prepare 3 wt% UHMWPE/CNC gels with the twin-screw extruder at 150–250 °C, and the weight percent of CNC was 1 wt% in UHMWPE/CNC. The hot homogenized gel solutions were then used to gel-spinning through spinneret plate with 240 conical dies with an exit diameter of 1 mm at an extrusion rate of 8 m min^{-1} and an extrusion temperature of 250 °C. The gel-spinning fibers were then extracted in a dichloromethane bath, which was aimed to remove the residual paraffin oil. Finally, the pre-stretched fibers were obtained after first hot-stretching stage at the temperature of 115 °C, and the fiber samples were cut from the pre-stretched fibers.

2.3. Scanning electron microscopy (SEM)

The surfaces of stretched UHMWPE fibers were etched by using hot n-octane at 110–115 °C to remove the amorphous part. The samples were sputtered with gold before SEM observation. The SEM (S4800) was used to observe the surface morphologies of stretched UHMWPE fibers.