

The Influence of Chitin Nanocrystals on Structural Evolution of Ultra-high Molecular Weight Polyethylene/Chitin Nanocrystal Fibers in Hot-drawing Process*

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Abstract Ultra-high molecular weight polyethylene (UHMWPE)/chitin nanocrystal (CNC) fibers were prepared. Compared with the pure UHMWPE fibers, the ultimate tensile strength and Young's modulus of UHMWPE/CNC fibers are improved by 15.7% and 49.6%, respectively, with the addition of chitin nanocrystals (CNCs) of 1 wt%. The melting temperature (T_m) of UHMWPE/CNC fibers was higher than that of pure UHMWPE fibers. Pure UHMWPE fibers and UHMWPE/CNC fibers were characterized with respect to crystallinity, orientation and kebab structure by wide-angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXS) and scanning electron microscopy (SEM). It is found that the CNCs act as the shish structure in UHMWPE/CNC fibers and the kebab crystals are grown around the CNCs. There was almost no difference between pure UHMWPE fibers and UHMWPE/CNC fibers in orientation. But the degree of crystallinity of various stages of UHMWPE/CNC fibers was respectively higher than the corresponding stage of pure UHMWPE fibers. Moreover, the addition of 1 wt% CNCs improved the thickness of kebab crystals and accelerated the transformation of kebab to shish.

Keywords: UHMWPE fibers; Chitin nanocrystals; Shish-kebab; Orientation.

INTRODUCTION

UHMWPE fibers are typically high-strength fibers with flexible chain and have multiple excellent performances such as low density, high specific strength and modulus, excellent energy absorption *etc.*^[1–3], which make them widely used in high-tech fields such as aerospace, national defense and military, safety protection *etc.* However, the highest tensile strengths and modulus achieved for UHMWPE fibers are still far below the theoretical ones^[4]. Therefore, to further improve the performance of UHMWPE fibers is the goal that people unremittingly pursue. Further, many investigations on the structural evolution of UHMWPE fibers have been made. The shish-kebab crystals could be formed when gel UHMWPE fibers were gone through hot-drawing process with low draw ratio^[5–7]. Besides with the increase of hot-drawing ratio, the kebab crystals gradually are transformed into extended chain crystals, which facilitate UHMWPE fibers to acquire excellent properties^[6–10]. In addition, the drawability of gel UHMWPE fibers is found to depend significantly on the spinning speed. The UHMWPE fibers have heterogeneous cross-sectional morphology as the skin-core structure at a relatively low spinning

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speed process, while the fibers obtained at relatively high spinning speed process are composed of homogeneous alignment of the shish-kebab crystals and exhibited better drawability and corresponding better tensile properties^[11]. The basis for the excellent mechanical properties of UHMWPE fibers is that most molecules are involved in the formation of the extended chain crystals and constitute homogeneous and continuous matrix, that is, the high orientation of molecular chains and the formation of extended chain crystals are the key of high performance fibers^[12].

With the development of nanocomposite technology, people no longer simply depended on perfecting the preparation technology of fiber to improve the performance of UHMWPE fibers but began to achieve higher performance through the preparation of UHMWPE/nanofiller composite fibers. The tensile strength of UHMWPE gel-spinning composite fiber specimens filled with 5 wt% multiwalled carbon nanotubes (MWCNTs) can reach 4.2 GPa, which is 18.8% higher than that of the pure UHMWPE fibers with the same draw ratios^[13]. The nano-silicon (SiO_2) was added into the surface of UHMWPE fibers with a simple treatment approach and the tensile strength and modulus of UHMWPE/ SiO_2 fibers reached the maximum values when the nano- SiO_2 content was 0.5 wt%, which were higher than the values of the pure UHMWPE fibers by 23.2% and 76.1%, respectively^[14]. In addition, many other researches about nanofiller reinforced UHMWPE fibers also have been conducted. Carbon nanotubes (CNTs)^[15, 16], functionalized CNTs^[17, 18], nano- SiO_2 ^[19], attapulgite (ATP)^[20], original and modified bacterial cellulose (BC) nanofibers^[21] were respectively added into UHMWPE solutions to obtain the corresponding UHMWPE nanocomposite fibers, and ultimately all of them improved the tensile properties. Although they have improved the performance of the composite fibers by adding nanofiller, these studies just limited to research. But regarding the effect of nanofiller reinforced UHMWPE fiber matrix and the impact on the drawability of the original gel fiber, no reference about the influence of nanofillers on the structural evolution of UHMWPE fibers in preparation process is available.

The performance of UHMWPE fibers can be further enhanced by improving the preparation technology of fiber or adding nanofillers. But the most important thing is making as many molecules as possible to involve in the formation of the extended chain crystals. From the research results of UHMWPE/nanofiller composite fibers, it is clear that CNTs have the best effect on reinforcing and toughening the UHMWPE fibers. Since CNTs have very high strength and modulus (the tensile strength and modulus are up to 150 GPa and 1 TPa, respectively)^[22], at the same time it is possible to promote the orientation and crystallization of UHMWPE fibers, so it is quite difficult to determine the actual mechanism of CNTs reinforced and toughened UHMWPE fibers.

Chitin nanocrystals (CNCs) have the shape like CNTs, which is conducive to the research on the actual mechanism of fibrous nanofillers reinforced UHMWPE fibers. In the modulus, CNCs are similar to UHMWPE fibers that both far lower than CNTs (the longitudinal and transverse modulus of CNC are 150 and 15 GPa^[23], respectively), thus will affect the mechanical properties of UHMWPE/CNC fibers primarily by altering the molecular orientation and crystallization. Further, the size of CNC is 20–40 nm wide and 150–400 nm long (The related characterization of CNCs was presented detailedly in our previous paper)^[24], which are very similar to the size of shish in UHMWPE fibers. So CNCs can act as the shish of UHMWPE fibers that formed in the early stage, which provided nucleation sites for the formation of kebab. As early as in 1999, CNCs were found to induce crystallinity in polymer to produce the transcrystalline layer structure, which played an important role in the mechanical properties of composite materials^[25]. So it is conducive to facilitate the research on the mechanism of CNCs reinforced UHMWPE fibers matrix and to study the influence of CNC on the structural evolution of fibers. In addition, CNCs are natural renewable resources with a wide range of sources and have the nature of natural polymer such as renewable, biodegradable, non-toxic and biocompatible. Over the past twenty years, CNCs have been used to reinforce polymers such as PLA^[26], PCL^[27], PHBV^[28], PLGA^[29] and PAM^[30]. Thus, the UHMWPE/CNC composite fibers are expected to widen the application areas of UHMWPE materials.

In our previous work^[31], we have studied the effect of CNCs with different contents on reinforcing UHMWPE fibers and found that the ultimate tensile strength and Young's modulus of UHMWPE/CNC fibers have been improved by 14.5% and 17.0%, respectively, with the incorporation of 1.0 wt% CNCs. But we have

not obtained the clear mechanism of CNCs reinforced UHMWPE fibers from the structure. So we would further investigate the actual mechanism of CNCs reinforced UHMWPE fibers from the structural evolution of UHMWPE/CNC fibers. In this study, the fiber samples from different stages of the fiber preparation process at the industrial production line were selected.

EXPERIMENTAL

Materials

The UHMWPE resin used in this study has a viscosity-average molecular weight (M_v) of 2.7×10^6 , which was supplied by Sinopec Beijing Yanshan Company. The chitin used was α -chitin that was prepared from shrimp shells. The shrimp shells were purchased from Aladdin reagent Co., Ltd. (Shanghai, China). Besides, the basic range of the thermal degradation of the shrimp Chitin nanocrystals (CNCs) was 290–420 °C^[32]. So CNCs were not degraded in all processes of UHMWPE/CNC composite fibers preparation. CNCs were prepared through acid hydrolysis as described in a previous report^[33]. Chitin whisker suspensions were prepared firstly by hydrolyzing the purified chitin sample in an aqueous HCl solution (3 mol/L) under stirring at boiling temperature for 1.5 h. After acid-hydrolysis, the suspensions were diluted with distilled water followed by centrifugation. This process was repeated three times. Then, the suspensions were transferred to a dialysis bag and dialyzed for 24 h against distilled water until the pH value of the suspension was 6. The residual aggregates were subsequently removed by a filtration and the suspension was kept in a refrigerator until used. Sodium azide was added to the suspension to prevent the growth of microorganisms. Finally, the chitin nanocrystals were obtained after vacuum-drying.

Sample Preparation

1 wt% of CNCs together with UHMWPE resin were dispersed and dissolved in paraffin oil to prepare 3 wt% of UHMWPE solutions at 150 °C for 1 h. The UHMWPE, UHMWPE/CNC gel solutions prepared above were then fed into a temperature-controlled hopper and kept as hot homogenized gel solutions before spinning. The hot homogenized gel solutions were then gel-spun using a spinneret plate with 240 conical dies with an exit diameter of 1 mm at an extrusion rate of 2000 mm/min and an extrusion temperature of 248 °C. The gel-spinning fibers were then extracted in a dichloromethane bath to remove the residual paraffin oil. Finally, fibers were passed through three hot-drawing stages with 25.35 draw ratios. The draw ratio of first, second and third hot-drawing stage were 6.5, 2.6 and 1.5, respectively, while the temperatures were 120, 130 and 140 °C, respectively. The fiber samples were cut from dried gel fibers and three hot-drawing stages of pure UHMWPE fibers and UHMWPE/CNC fibers. The samples identification and CNCs content in the UHMWPE composite fibers are shown in Table 1. D0F are dried gel fibers, while D1F, D2F and D3F are drawn fibers of first, second and third hot-drawing stage, respectively. Table 1 summarizes all the drawn samples and their drawing conditions, where samples PD0F and CD0F are dried pure gel UHMWPE fibers and dried gel UHMWPE/CNC fibers, respectively. PD1F, PD2F and PD3F are drawn fibers of first, second and third hot-drawing stage of pure UHMWPE fibers, and CD1F, CD2F and CD3F are drawn fibers of first, second and third hot-drawing stage of UHMWPE/CNC fibers. The total draw ratio (TDR) can be defined as follow as previously described^[11] as:

$$\text{TDR} = \text{DR}_1 \times \text{DR}_2 \times \text{DR}_3 \quad (1)$$

where DR_1 , DR_2 and DR_3 are the draw ratio for D1F, D2F and D3F, respectively.

Tensile Test

Tensile test of pure UHMWPE fibers and UHMWPE/CNC fibers with no twisting was performed on an Instron 5567 tension testing machine at a tensile rate of 250 mm/min, and the fiber initial gauge length was 500 mm.

Table 1. Samples identification and CNC content in the fiber samples

Sample	CNC content (wt%)	First drawing stage		Second drawing stage		Third drawing stage		TDR
		DR ₁	Temperature (°C)	DR ₂	Temperature (°C)	DR ₃	Temperature (°C)	
PD0F	0	–	–	–	–	–	–	0
PD1F	0	6.5	120	–	–	–	–	6.5
PD2F	0	6.5	120	2.6	130	–	–	16.9
PD3F	0	6.5	120	2.6	130	1.5	140	25.35
CD0F	1	–	–	–	–	–	–	0
CD1F	1	6.5	120	–	–	–	–	6.5
CD2F	1	6.5	120	2.6	130	–	–	16.9
CD3F	1	6.5	120	2.6	130	1.5	140	25.35

Thermal Analysis

Differential scanning calorimetry (DSC) measurements were performed with a Mettler Toledo DSC under nitrogen atmosphere. The fiber samples were prepared by cutting into pieces. The samples were heated to 180 °C at a heating rate of 10 K/min under nitrogen atmosphere at a flow rate of 50 mL/min. Samples with the weight of 7.0 mg were placed in the standard aluminum sample pans for determination of their melting temperature (T_m).

The SAXS and WAXD Measurement

The wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) measurements were carried out at the BL16B1 beamline in the Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of the synchrotron radiation was 0.124 nm. Two-dimensional (2D) WAXD and SAXS patterns were collected by using a Mar CCD X-ray detector (MAR165), having a resolution of 2048 × 2048 pixels. The beam intensity monitor before sample is a N₂ gas ionization chamber, and the monitor after sample adsorption is a photodiode in the beam stop. Two scatter-less slits (Xenocs) were used to depress parasitic scattering. The sample holder was mounted onto an optical table^[34]. The sample-to-detector distance was 5139 mm for SAXS and 188 mm for WAXD. Both the SAXS and WAXD image acquisition time of each data frame were 2 s. All X-ray images were corrected for background scattering, air scattering, and beam fluctuations. The WAXD and SAXS measurement data analysis was carried out by the Fit2d software package^[35].

Scanning Electron Microscopy (SEM)

The surface morphologies of UHMWPE gel fibers and drawn fibers were observed by SEM (SU70). The surface of UHMWPE gel fibers and drawn fibers were etched by hot *n*-octane respectively at 105–110 °C and 110–115 °C. The samples were sputtered with gold before SEM observation.

RESULTS AND DISCUSSION

Tensile Test

Table 2 presents the tensile properties of processed fibers of pure UHMWPE fibers and UHMWPE/CNC (1 wt%) fibers. In our previous work^[31], we have studied the effect of CNC with different content on reinforcing UHMWPE fibers and found that the ultimate tensile strength and Young's modulus of UHMWPE/CNC fibers have been improved by 14.5% and 17.0%, respectively, with the incorporation of 1.0 wt% CNC. In order to further probe the influence of CNC on the structural evolution of UHMWPE fibers matrix, we have selected conditions which are not same as the conditions used in previous paper to produce pure UHMWPE fibers and UHMWPE/CNC fibers. Compared with the pure UHMWPE fibers, the ultimate tensile strength and Young's modulus of UHMWPE/CNC fibers are improved by 15.7% and 49.6%, respectively, with the incorporation of 1.0 wt% CNC. The result indicates that CNC plays an important role on reinforcing UHMWPE fiber.

Table 2. The tensile properties of pure UHMWPE fibers and UHMWPE/CNC fibers

Sample	Tensile strength (GPa)	Young's modulus (GPa)
Pure UHMWPE fibers	1.65 ± 0.15	53.2 ± 2.7
UHMWPE/CNC fibers	1.91 ± 0.17	79.6 ± 2.2

Crystallinity Change

2D WAXD patterns (Fig. 1) were analyzed to calculate the degree of crystallinity of pure UHMWPE fibers and UHMWPE/CNC fibers using Eq. (2).

$$X_c = \frac{I_c}{I_t} \quad I_t = I_c + I_a \quad (2)$$

where I_c and I_a represent the integrated diffraction intensity of the crystal phase (sum of orthorhombic 110 ((110)_o) and 200 ((200)_o) reflections) (Fig. 2) and the scattered intensity of the amorphous phase, respectively; I_t is the integrated diffraction intensity (azimuthal angle, $\phi = 0^\circ$ – 360°) due to the sum of amorphous and crystal phases. The WAXD profile was curve-fitted by applying Voigt functions.

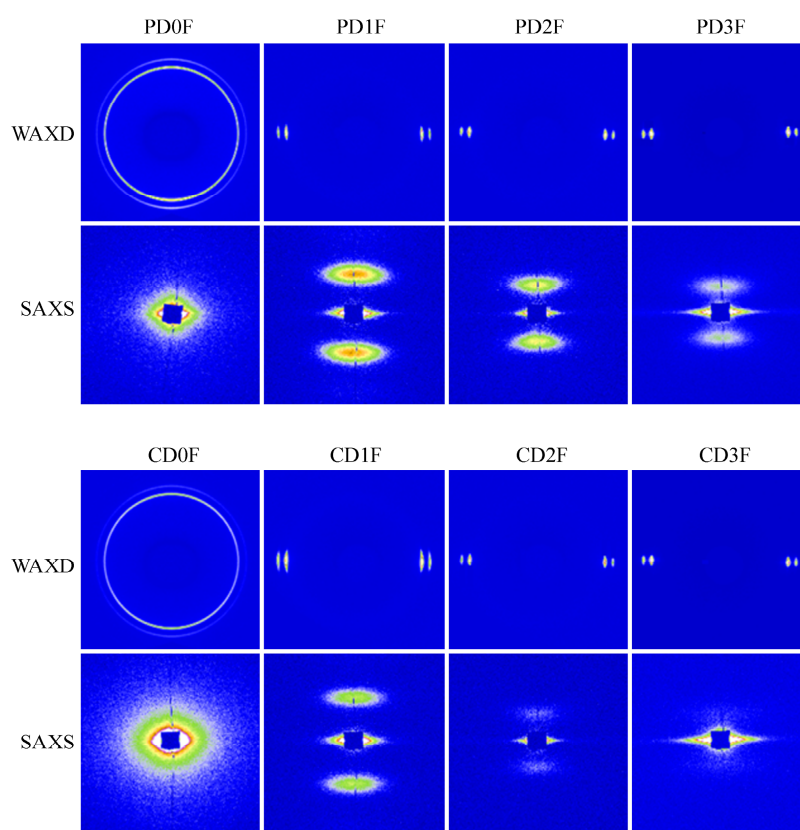
**Fig. 1** The 2D WAXD and SAXS images of PD0F, PD1F, PD2F, PD3F, CD0F, CD1F, CD2F and CD3F

Figure 2 shows the 1D WAXD intensity profiles of dried gel fibers and drawn fibers of pure UHMWPE fibers and UHMWPE/CNC fibers. The degree of crystallinity of dried gel fibers and drawn fibers of pure UHMWPE fibers and UHMWPE/CNC fibers are shown in Fig. 3. Comparing the intensity and position of diffraction peaks (110)_o and (200)_o, there is no obvious difference between various intensity profiles of drawn fibers. But compared with drawn fibers, the intensity of diffraction peaks (110)_o and (200)_o of dried gel fibers of PD0F and CD0F are much lower. The reason is that the degree of crystallinity of dried gel fibers is lower than that of the drawn fibers. The degrees of crystallinity of various stages of UHMWPE/CNC fibers are higher than

those of pure UHMWPE fibers. This result indicates that CNCs have the function of induced crystallization and involve more molecules in crystallization. In addition, CNCs are very similar to the shish in UHMWPE fibers in shape and size. So CNCs might have acted as the shish of UHMWPE fibers that formed in the early stage, which provided nucleation sites for the formation of kebab.

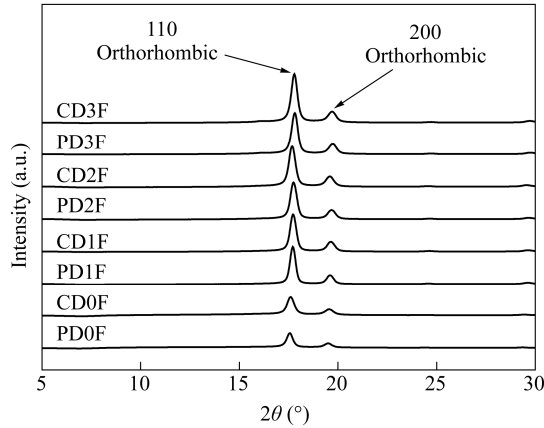


Fig. 2 1D WAXD intensity profiles of PD0F, PD1F, PD2F, PD3F, CD0F, CD1F, CD2F and CD3F

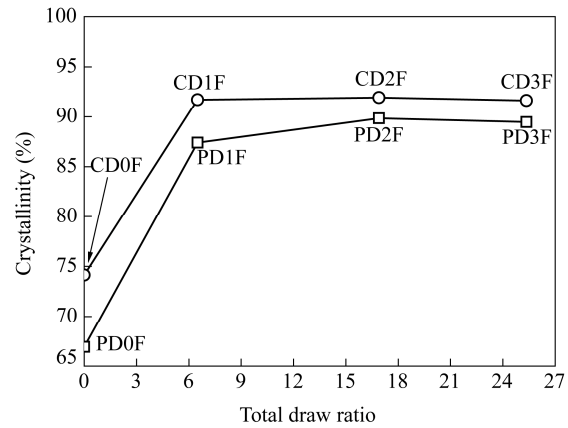


Fig. 3 The degree of crystallinity of various stages of pure UHMWPE fibers and UHMWPE/CNC fibers

Crystalline Orientation

Quantitatively, the degree of crystal orientation in pure UHMWPE fibers and UHMWPE/CNC fibers was determined by using the Herman's method^[36]. Accordingly, the crystalline orientation can be characterized by average orientation of the normal to the crystalline plane with respect to an external reference frame. Here, the fiber axis direction was taken as the reference direction. For a set of hkl planes, the average orientation, expressed as $\langle \cos^2 \phi \rangle_{hkl}$, can be calculated mathematically using the following equation:

$$\langle \cos^2 \phi \rangle_{hkl} = \frac{\int_0^{\pi/2} I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi} \quad (3)$$

where ϕ is the azimuthal angle and $I(\phi)$ is the scattered intensity along the angle ϕ . Herman's orientation function f , is defined as

$$f = \frac{3\langle \cos^2 \phi \rangle_{hkl} - 1}{2} \quad (4)$$

where f has the value of -0.5 , when the normal of the reflection plane is perpendicular to the reference direction ($\phi = 90^\circ$ or crystals are oriented parallel to the fiber axial direction), f value of 1 , when the normal is parallel to the reference direction ($\phi = 0^\circ$ or crystals are oriented perpendicularly to the fiber axial direction), and f value of 0 , when the orientation is random. The degree of orientation, f_{110} is calculated from the azimuthal intensity distribution, $I(\phi)$ of the $(110)_0$ reflection of α -crystals in various stages of pure UHMWPE fibers and UHMWPE/CNC fibers.

Table 3 shows the degree of orientation, f_{110} of various stages of pure UHMWPE fibers and UHMWPE/CNC fibers. Compared with drawn fibers, the degree of orientation of dried gel fibers is much lower because the internal structure of dried gel fibers is disorganized which is obviously shown in 2D WAXD images (Fig. 1). The orientation of the molecular chains has occurred through the hot-drawing stage, so drawn fibers have obtained better orientation. The degree of orientation of drawn fibers is slightly improved with the increase of TDR. Comparing the degree of orientation, there is no difference between pure UHMWPE fibers and UHMWPE/CNC fibers at various stages. It indicates that CNCs are well dispersed in the UHMWPE fibers matrix.

Table 3. The degree of orientation and the corresponding TDR at various stages of pure UHMWPE fibers and UHMWPE/CNC fibers

Stage	TDR	f_{110}	
		Pure UHMWPE fibers	UHMWPE/CNC fibers
D0F	0	-0.059	-0.064
D1F	6.5	0.912	0.905
D2F	16.9	0.917	0.913
D3F	25.35	0.930	0.924

Kebab Structure

The SAXS patterns of various stages of pure UHMWPE fibers and UHMWPE/CNC fibers are shown in Fig. 1. The meridional scattering in SAXS displays the patterns of kebab structure, while the equatorial streaks across the beam stop are scattering patterns of shish structure (Fig. 4a). The SAXS patterns of both PD0F and CD0F do not emerge the scattering patterns of the oriented kebab structure because both PD0F and CD0F are the dried gel fibers and their internal structure is disorganized, which corresponds to the SEM results of eroded UHMWPE fibers as shown in Figs. 5(a) and 5(e). When the fibers get into hot-drawing stage, the scattering patterns of the oriented kebab structure are exhibited in SAXS patterns. As the TDR increases, SAXS patterns exhibit significant evolution as shown in 2D SAXS images of Fig. 1.

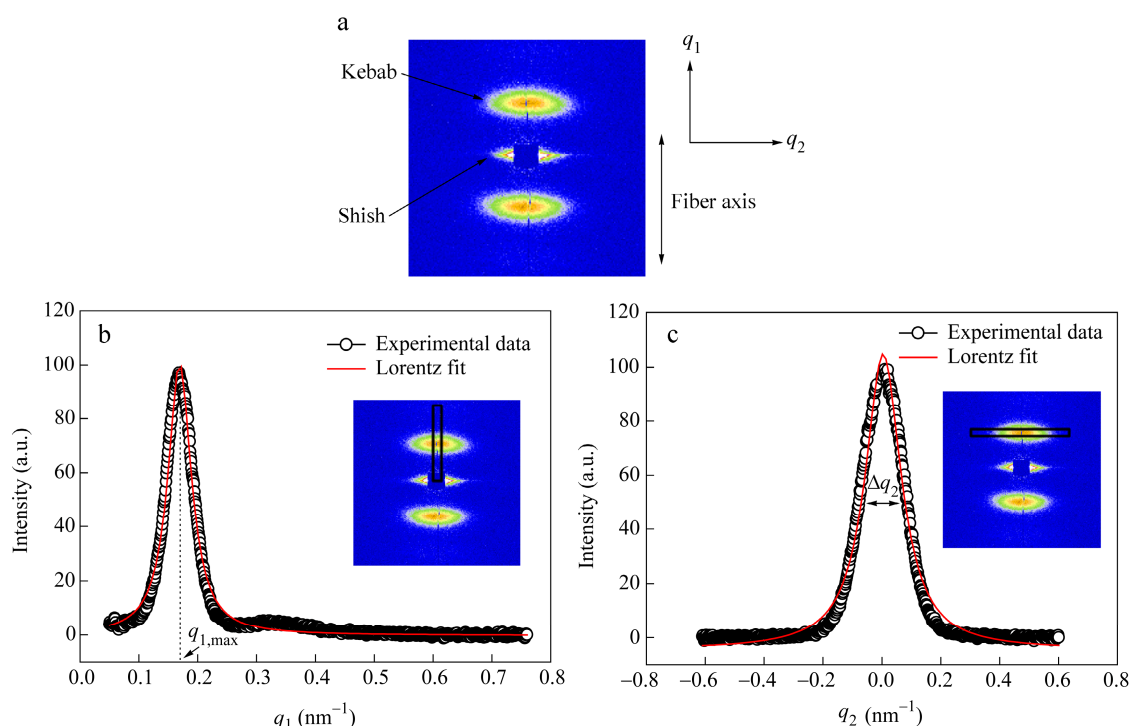


Fig. 4 (a) The scattering patterns of kebab and shish structure in 2D SAXS image and the direction of fiber axis, (b) fitting process of long period, (c) fitting process of lateral size of shish-kebab crystals

In order to further investigate the influence of CNCs on the structural evolution of UHMWPE/CNC fibers in preparation process, more detailed information from the SAXS patterns are obtained. The scattering vectors along and perpendicular to the direction of axis are designated as q_1 and q_2 , respectively (Fig. 4a). From the SAXS data measured along the equator two parameters to describe the kebab structure are derived, namely, the long period L and the lateral dimension of the kebab. The long period of stacks of kebab along direction of the fiber axis can be obtained by considering the scattering intensity distribution along the q_1 direction $I(q_1)$, which is obtained by equator scans along q_1 for certain intervals of q_2 as schematically shown in Fig. 4(b). The long period L measured along q_1 of the samples was calculated from the peak position of $I(q_1)$ according to Bragg's

law:

$$L = 2\pi / q_{1,\max} \quad (5)$$

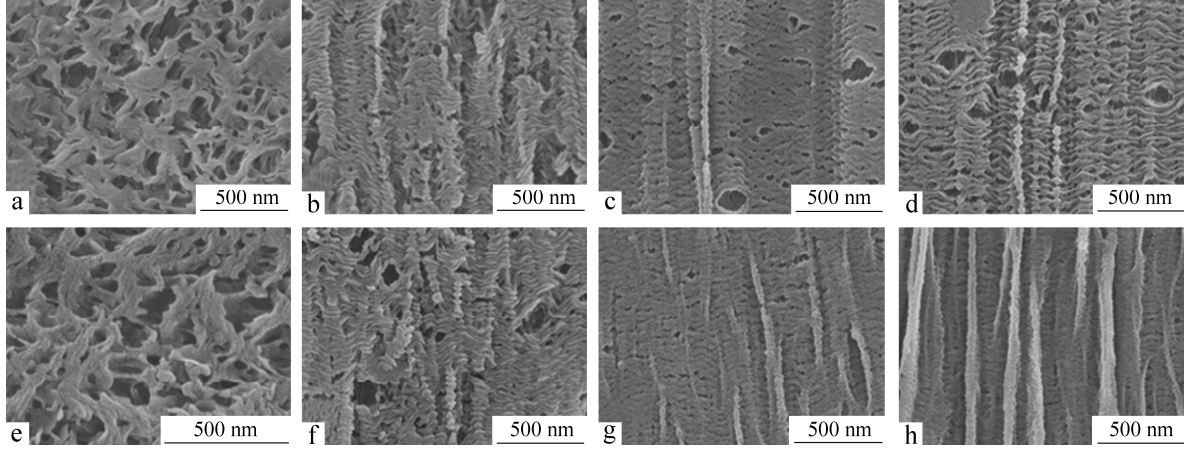


Fig. 5 SEM images of various stages of pure UHMWPE fibers and UHMWPE/CNC fibers: (a) PD0F, (b) PD1F, (c) PD2F, (d) PD3F, (e) CD0F, (f) CD1F, (g) CD2F and (h) CD3F

The lateral size, L_{SAXS} can be derived from the width Δq_2 (Fig. 4c) of the peaks at half height in the meridional direction according to the following equation^[37]:

$$L_{\text{SAXS}} = 2\pi / \Delta q_2 \quad (6)$$

The scattering intensities from shish and kebabs were integrated from Fig. 1 by using the following equations^[38–40]:

$$I_{\text{shish}} = \int_{0.03}^{0.3} \int_{70^\circ}^{110^\circ} I(q, \phi) dq d\phi \quad (7)$$

$$I_{\text{kebab}} = \int_{0.05}^{0.5} \int_{-70^\circ}^{70^\circ} I(q, \phi) dq d\phi \quad (8)$$

where q is the scattering vector and ϕ is the azimuthal angle.

At later stage of hot-drawing process, the long period does not just represent the sum of the kebab crystals thickness and the amorphous thickness. It may also include the interspace between the kebabs as shown in TEM images^[41]. To obtain the accurate kebab thickness, the shish-kebab model^[42] was used. The fitted kebab scattering patterns of drawn fibers were obtained from the shish-kebab model as shown in Fig. 6. The kebab thickness, T was estimated by fitting of 2D SAXS scattering patterns using the shish-kebab model.

The long period, L and the lateral size, L_{SAXS} of various stages of pure UHMWPE fibers and UHMWPE/CNC fibers are shown in Table 4. Further, the kebab thickness of drawn fibers of pure UHMWPE fibers and UHMWPE/CNC fibers are shown in Table 5. With the increase of TDR, the kebab thickness of drawn fibers of pure UHMWPE fibers and UHMWPE/CNC fibers obviously is increased. But the kebab thickness of drawn fibers of UHMWPE/CNC fibers is bigger than that of pure UHMWPE fibers at various stages of hot-drawing process. Moreover, the L_{SAXS} of drawn fibers of UHMWPE/CNC fibers rapidly decrease with the increase of TDR, while that of pure UHMWPE fibers has decreased slowly. At the final stage of hot-drawing, L_{SAXS} of drawn fibers of UHMWPE/CNC fibers is much smaller than that of pure UHMWPE fibers. The variation trend of L_{SAXS} decreases with the increase of TDR is in conformity with the result of TEM^[39]. It can be seen from Figs. 5(b) and 5(f) that the kebab thickness of UHMWPE/CNC drawn fibers of first hot-drawing stage is obviously bigger than that of pure UHMWPE fibers, which accords with the result from SAXS. Furthermore,

the shish number of UHMWPE/CNC drawn fibers of first hot-drawing stage is more than that of pure UHMWPE fibers.

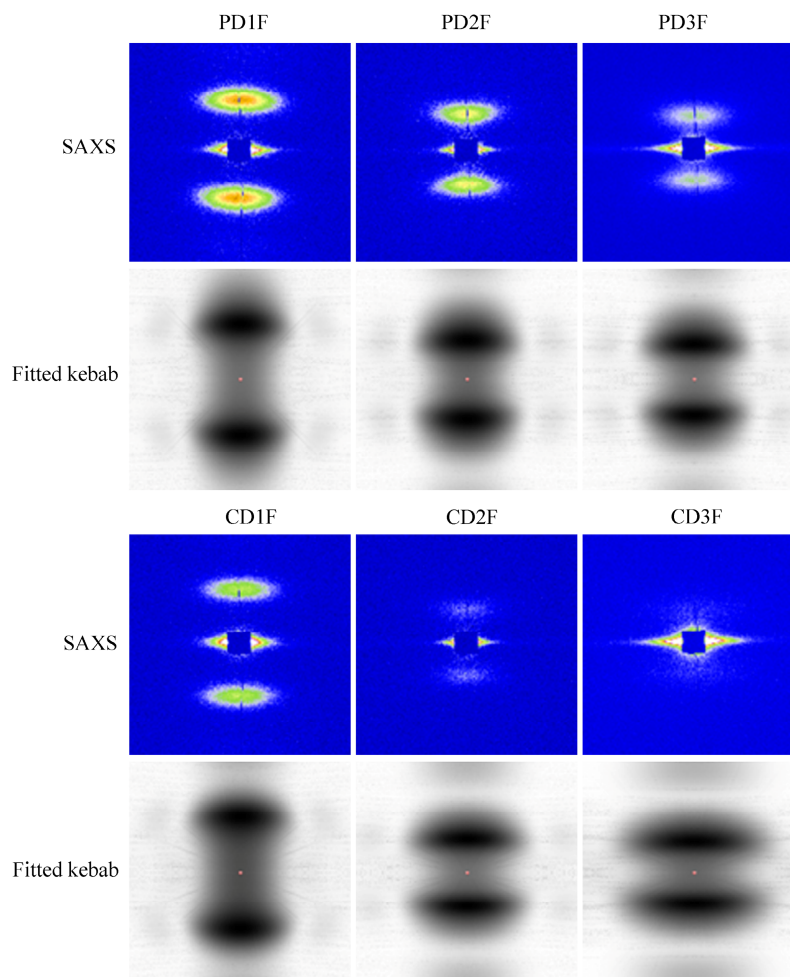


Fig. 6 The original SAXS and fitted kebab scattering patterns of PD1F, PD2F, PD3F, CD1F, CD2F and CD3F

Table 4. The long period, L and the lateral size, L_{SAXS} of various stages of pure UHMWPE fibers and UHMWPE/CNC fibers

Stage	TDR	L (nm)		L_{SAXS} (nm)	
		Pure UHMWPE fibers	UHMWPE/CNC fibers	Pure UHMWPE fibers	UHMWPE/CNC fibers
D0F	0	—	—	—	—
D1F	6.5	37.12	35.30	43.60	41.50
D2F	16.9	51.66	61.33	40.30	34.54
D3F	25.35	58.11	66.41	38.83	25.92

Table 5. The kebab thickness, T of drawn fibers estimated from the shish-kebab model

Stage	TDR	T (nm)	
		Pure UHMWPE fibers	UHMWPE/CNC fibers
D1F	6.5	17.76	21.73
D2F	16.9	22.39	26.49
D3F	25.35	23.94	27.76

Figure 7 shows the SEM images of CNCs in UHMWPE/CNC drawn fibers of first hot-drawing stage. It clearly shows that the CNCs act as the shish crystal in UHMWPE/CNC fibers and the kebabs are grown around the CNCs. Comparing the kebab grown on the shish from UHMWPE molecular chain, the kebab grown on CNCs has bigger thickness but with smaller lateral size. Moreover, it can be found that the CNCs are well dispersed in the UHMWPE fibers matrix. With the increase of TDR, the lamellae (kebab) are arranged more orderly as shown in Fig. 5. The strip structure shown in Figs. 5(g) and 5(h) is the micro-fibril structure, which is mainly composed of shish structure. It can be seen that there are many micro-fibrils in UHMWPE/CNC drawn fibers of second and third hot-drawing stage especially the third hot-drawing stage drawn fibers. But almost no micro-fibril structure can be seen in the SEM images of pure UHMWPE drawn fibers with various TDR. Only the increase of shish number can be found from the SEM of pure UHMWPE fibers. It can be obviously seen that the structural evolution of UHMWPE/CNC fibers is faster than that of pure UHMWPE fibers under the same condition, which corresponds to the results of SAXS. These results indicate that the addition of CNC in UHMWPE fibers matrix is conducive to the formation of thicker kebab and the decrease of the lateral size of kebab at hot-drawing stage, which are good to the transformation of kebab to shish. Further, the process of formation and transformation of kebab have happened simultaneously in the hot-drawing process of fibers. The changes in intensity of shish and kebab are shown in Fig. 8. It can be seen that the scattering intensity of shish structure become more obvious with the increase of TDR. With the increase of TDR, the scattering intensity of kebab of UHMWPE/CNC fibers significantly decreases, while that of pure UHMWPE fibers declines relatively slowly. In addition, the relative intensity, $I_{\text{shish}}/I_{\text{kebab}}$ of UHMWPE/CNC fibers is obviously higher than that of pure UHMWPE fibers especially when TDR is 25.35. It means that the kebab transformation of UHMWPE/CNC fibers is easier than that of pure UHMWPE fibers under the same condition. The above results suggest that the formation of kebab has taken place as the primary thing at hot-drawing process of pure UHMWPE fibers. Besides, the formation of kebab occupies the main process of first hot-drawing stage of UHMWPE/CNC fibers, while it mainly occurs to transform the kebab to shish at second and third hot-drawing stage. So the addition of CNCs is advantageous to the transformation of kebab to shish, which could make most molecules involve in the formation of the extended chain crystals. So CNCs have significantly improved the properties of UHMWPE fibers matrix.

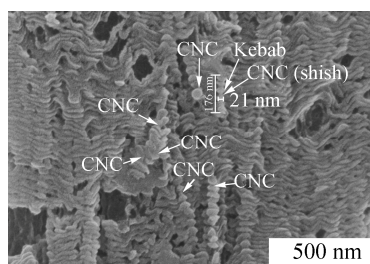


Fig. 7 SEM image of CNCs in UHMWPE/CNC drawn fibers of first hot-drawing stage

Thermal Analysis

Figure 9 shows the DSC thermograms of various stages of pure UHMWPE fibers and UHMWPE/CNC fibers. The melting temperature (T_m) of various stages of pure UHMWPE fibers and UHMWPE/CNC fibers are presented in Table 6. The increase of TDR enhances the melting temperature (T_m) of pure UHMWPE fibers and UHMWPE/CNC fibers. With the increase of TDR from 0 to 6.5, the improvement of the melting temperature (T_m) of pure UHMWPE fibers is very approximate to that of UHMWPE/CNC fibers. But with the TDR from 6.5 to 16.9, the improvement of the melting temperature (T_m) of UHMWPE/CNC fibers is very larger than that of pure UHMWPE fibers. The main reason is that when the TDR is less than 16.9, the formation of kebab occupies the main process for pure UHMWPE fibers and UHMWPE/CNC fibers. With the increase of TDR from 16.9 to 25.35, pure UHMWPE fibers still take the formation of kebab as the principal thing, while transformation of

kebab to shish is the main changing process of UHMWPE/CNC fibers and most of kebab are transformed to shish. In addition, the average kebab thickness of UHMWPE/CNC fibers is higher than that of pure UHMWPE fibers when TDR are 16.9 and 25.35.

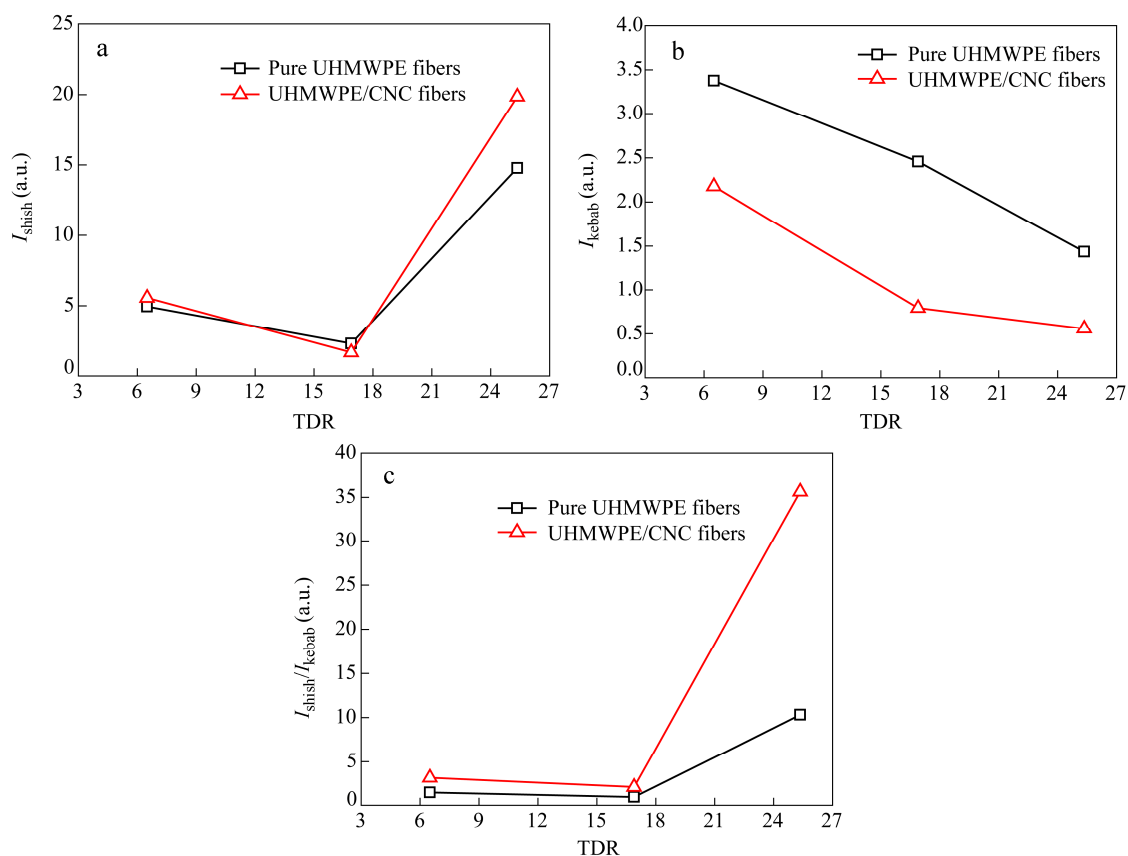


Fig. 8 The scattering intensities from shish and kebabs of pure UHMWPE fibers and UHMWPE/CNC fiber at different TDR: (a) the scattering intensity of shish, (b) the scattering intensity of kebab, (c) the relative intensity of $I_{\text{shish}}/I_{\text{kebab}}$

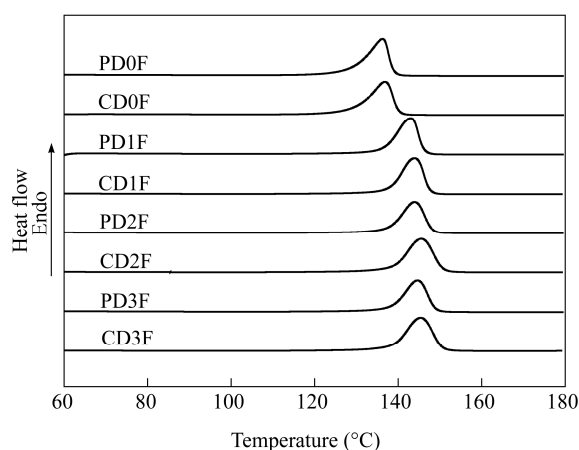


Fig. 9 DSC thermograms of various stages of pure UHMWPE fibers and UHMWPE/CNC fibers

Table 6. The melting temperatures of various stages of pure UHMWPE fibers and UHMWPE/CNC fibers

Stage	TDR	Melting temperature (T_m) (°C)	
		Pure UHMWPE fibers	UHMWPE/CNC fibers
D0F	0	136.25	136.84
D1F	6.5	143.00	143.94
D2F	16.9	143.94	145.52
D3F	25.35	144.66	145.35

CONCLUSIONS

The addition of CNCs of 1 wt% has significantly enhanced the ultimate tensile strength and Young's modulus of the UHMWPE fibers matrix with higher melting temperature (T_m) and the degree of crystallinity. CNCs have acted as the shish structure in UHMWPE/CNC fibers and many kebab crystals are formed around CNCs. So that CNC could make more molecules involve in the formation of kebab. Further, CNCs are conducive to the formation of thicker kebab and the transformation of kebab to shish, which make most molecules involve in the formation of the extended chain crystals. In addition, CNCs have no significant influence on the degree of orientation of various stages of pure UHMWPE fibers matrix. The above results suggest that CNCs have significant influence on structural evolution of UHMWPE fibers matrix in hot-drawing process and could significantly enhance the properties of UHMWPE fibers matrix. This study makes the actual mechanism of CNCs reinforced UHMWPE fibers more clear. To further investigate the influence of CNCs on the transformation of kebab to shish, the investigation of in-situ structural evolution of UHMWPE/CNC fibers is ongoing.

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