

Structure and Properties of Gel-spun Ultra-high Molecular Weight Polyethylene Fibers with High Gel Solution Concentration^{*}

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Abstract The gel-spun ultra-high molecular weight polyethylene (UHMWPE) fibers were prepared at the industrial production line with different gel solution concentrations of 15 wt%, 18 wt% and 24 wt%. The difference in ultimate structure and mechanical properties of UHMWPE fibers for different gel solution concentrations were analyzed by tensile testing, differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS). With the increase of gel solution concentration, the ultimate mechanical properties of UHMWPE fibers were decreased and the crystallization and orientation of UHMWPE fibers became inferior. Besides, both the average shish length ($\langle L_{\text{shish}} \rangle$) and shish misorientation (B_{ϕ}) of UHMWPE fibers were decreased with the increase of gel solution concentration. In addition, the appropriate increase of spinning temperature led to the further optimization of the ultimate structure and mechanical properties of UHMWPE fibers.

Keywords UHMWPE fibers; Gel solution concentration; Orientation; Crystallization; Shish structure

INTRODUCTION

Ultra-high molecular weight polyethylene (UHMWPE) fibers are produced *via* gel-spinning method^[1–7] in the current industrial production, which makes it come true that UHMWPE fiber structure is mainly composed of extended-chain crystals. The extended-chain crystals^[8] endow UHMWPE fibers with distinctive properties of high specific strength and modulus, excellent energy absorption, and high wear and cutting resistance^[9–17]. So UHMWPE fibers can be widely used in many fields such as safety protection, oceanographic engineering, aerospace, sport equipment and so on. With the expansion of UHMWPE fibers applied areas, the fibers with higher performance are needed. Furthermore, the highest tensile strengths and moduli of UHMWPE fibers, which can be achieved at present, are still far below those estimated theoretically^[18]. So there is still a great space for the improvement of UHMWPE fiber mechanical properties. To obtain higher properties of UHMWPE fibers, many studies^[19–28] on the structural evolution of fibers in hot-drawing process have been done due to the fact that the hot-drawing process is the key process to obtain high performance for UHMWPE fibers. Moreover, the hot-drawing process could make most molecules take part in the formation of extended chain crystals so that the resulting UHMWPE fibers have excellent performance^[8]. But the most important precondition is that the chain entanglement concentration in UHMWPE gel fibers is appropriate, which will make gel fibers have better drawability in hot-drawing process. The appropriate chain entanglement concentration needs proper gel-spinning

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conditions^[29]. So the gel-spinning conditions are also very important for the improvement of UHMWPE fibers properties. In addition, a number of previous studies have reported the effect of gel-spinning conditions before hot-drawing process on the structure and properties of UHMWPE fibers. Hoogsteen *et al.*^[5] investigated the effect of spinning conditions on structure and properties of UHMWPE fibers with 5 wt% gel solution concentration and found that the flaws were easily introduced in extended chain crystals under the condition of low spinning temperatures and high take-up speeds. Moreover, Hoogsteen *et al.*^[29] discovered that the reduction of chain entanglement number *via* reducing gel solution concentration could lead to the fibers with better properties, but a minimum number of entanglements was crucial to avoid premature breakage of the fiber spin line with the formation of entanglement network. Jian *et al.*^[30] also found that gel fibers prepared at the optimum concentration had good spinning and drawing properties. The previous researches have suggested that the appropriate gel solution concentration is very important to obtain high-performance UHMWPE fibers. But the actual effect of gel solution concentration on the ultimate structure and properties of UHMWPE fibers was still not clear, which is greatly important to the improvement of fibers properties. Furthermore, the gel solution concentration used in most studies was relatively low such as 1 wt%–5 wt%. Little attention has been paid to the effect of gel solution concentration higher than 8 wt% on the structure and mechanical properties of UHMWPE fibers.

In the industrial production of UHMWPE fibers, it is an effective method to enhance fiber productivity *via* improving gel-spinning solution concentration. At early stage, the UHMWPE gel solution was prepared by using general mechanical agitation so that the high concentration homogeneous gel solution could not be obtained^[2–7], which limited the production of UHMWPE fibers with higher concentration. In recent years, the gel-spinning technique has been developed rapidly. The twin-screw extruder has been successfully introduced to prepare UHMWPE gel solution, which makes it possible to produce UHMWPE fibers with higher gel solution concentration^[31–33]. Taking into account the mechanical properties and production efficiency, the gel solution concentration used in practical industrial production of UHMWPE fibers is usually 8 wt%–10 wt%. Xiao *et al.*^[34] studied the effect of UHMWPE gel solution concentration of 8 wt%–16 wt% on the extracting, drawing, and crystallizing properties of gel fibers and they found that the maximum draw ratio and tensile strength of extracted fibers decreased with increasing UHMWPE concentration. But they did not study the effect of high gel solution concentration on the ultimate structure and mechanical properties of UHMWPE fibers, which has practical significance on fibers industrial production. Moreover, in our previous work^[35], the effect of gel solution concentration of 10 wt%–18 wt% on ultimate structure and mechanical properties of UHMWPE fibers was investigated. We found that the ultimate tensile strength and Young's modulus of UHMWPE fibers decreased with the increase of gel solution concentration and the crystallization and orientation became inferior, which suggested that the properties and structure of fibers became worse with the increase of gel solution concentration.

In this study, the UHMWPE fibers were prepared from high concentration solutions of 15 wt%, 18 wt% and 24 wt% at the industrial production line. The UHMWPE gel solution concentration was further improved and the effect of high gel solution concentration on the ultimate structure and mechanical properties of UHMWPE fibers was further studied.

EXPERIMENTAL

Materials

The UHMWPE resin (GUR 4012) used in this study has a weight-average molecular weight (M_w) of 1×10^6 , which was supplied by Ticona Company. The paraffin oil of total finavestan A360B was used in this study. The flash point and the temperature of the fraction of the paraffin oil are 250 and 390 °C, respectively.

Sample Preparation

The UHMWPE gels were prepared by twin-screw extruder at 150–250 °C with 15 wt%, 18 wt% and 24 wt% UHMWPE solutions in paraffin oil, respectively. The hot homogenized gels were then gel-spinning using

spinneret plate with 240 conical dies with an exit diameter of 1 mm at an extrusion rate of 8 m/min and an extrusion temperature of 274 °C. After spinning from the spinneret, the fibers were cold drawn to different drawing ratios (DR₀) at room temperature. The gel-spinning fibers were then extracted in a dichloromethane bath to remove paraffin oil. Finally, the fibers were passed through three hot-drawing stages at the temperatures of 110, 120 and 130 °C, respectively (where the draw ratio of the first, second and third hot-drawing stages are DR₁, DR₂ and DR₃, respectively). The details are listed in Table 1.

Table 1 Various draw ratio stages of UHMWPE fibers in preparation process and the single fiber final diameter with different gel solution concentrations

Gel solution concentration (wt%)	DR ₀	DR ₁	DR ₂	DR ₃	Final diameter (μm)
15	4.0	4.8	2.0	1.4	22.48 ± 0.59
18	4.0	4.5	2.0	1.4	25.63 ± 0.89
24	4.0	3.6	2.0	1.4	34.78 ± 1.24

Tensile Test

Tensile test of UHMWPE fibers with no twisting was carried out with an Instron 5567 tension testing machine. The tensile rate of 250 mm/min was used and the fiber initial gauge length was 500 mm.

Differential Scanning Calorimetry (DSC) Analysis

DSC experiments were performed using a Mettler Toledo DSC under nitrogen atmosphere. The samples of fibers were prepared by cutting into pieces. Samples weighing about 5.0 mg were placed in the standard aluminum sample pans. The samples of UHMWPE fibers were heated to 180 °C at a heating rate of 10 K/min under flowing nitrogen at a flow rate of 50 mL/min.

Small-angle X-ray Scattering (SAXS) Measurement and Wide-angle X-ray Diffraction (WAXD)

The SAXS and WAXD measurements were carried out at the BL16B1 beamline in the Shanghai Synchrotron Radiation Facility (SSRF). The X-ray wavelength was 0.124 nm and the beam size of X-ray was 0.4 mm (*H*) × 0.5 mm (*V*). Two-dimensional (2D) SAXS and WAXD 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 was a N₂ gas ionization chamber, and the monitor after sample adsorption was 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^[36]. The sample-to-detector distance was 5070 mm for SAXS and 213 mm for WAXD. The SAXS and WAXD image acquisition time of each data frame was 15 and 2 s, respectively. All X-ray images were corrected for background scattering, air scattering, and beam fluctuations. The SAXS and WAXD measurement data analysis was carried out by the Fit2d software package^[37].

RESULTS AND DISCUSSION

Tensile Test

The tensile strength and Young's modulus of UHMWPE fibers with different gel solution concentrations are shown in Fig. 1. It can be easily found that both the ultimate tensile strength and Young's modulus of UHMWPE fibers have decreased with the increase of gel solution concentration. The UHMWPE fibers with 18 wt% gel solution concentration have an ultimate tensile strength and Young's modulus of 2.69 and 102.8 GPa respectively, which are respectively 3.9% and 9.4% lower than those of the 15 wt% UHMWPE fibers. In addition, compared with the 15 wt% UHMWPE fibers, the ultimate tensile strength and Young's modulus of the 24 wt% UHMWPE fibers are decreased by 32.1% and 40.5%, respectively. These results suggest that the increase of gel solution concentration has a great influence on the mechanical properties of UHMWPE fibers, and too high gel solution concentration leads to the decrease of mechanical properties of fibers dramatically. The decrease of mechanical properties is attributed to the fact that the number of chain entanglement increases with the increase of gel solution concentration^[29]. Then the increase of chain entanglement number leads to the increase of flaw, which will limit the strength of materials^[25]. In our previous study^[35], the ultimate tensile

strength of UHMWPE fibers with 15 wt% and 18 wt% gel solution concentration were 2.62 and 2.37 GPa, respectively, which were respectively lower by 6.4% and 11.9% than those of UHMWPE fibers with the same gel solution concentration in this study. It is worth noting that the spinning temperature used in this study was 274 °C, which was higher than that of the previous study^[35]. The appropriate increase of spinning temperature can decrease the shear viscosities of the gel solutions^[30], which leads to the chain disentanglement of screw in spinning process. So the appropriate increase of spinning temperature decreases the number of chain entanglement and then increases the drawability of UHMWPE gel fibers. The draw ratio of first hot-drawing process (DR_1) of 15 wt% and 18 wt% UHMWPE fibers as shown in Table 1 are 4.8 and 4.5, respectively, which are both higher than those of our previous study (the DR_1 of various gel solution concentration both were 4.0)^[35]. It is worth reminding that the draw ratio used in various stages was optimal in the experiment condition of this study. Moreover, the final diameters of single fiber of the 15 wt% and 18 wt% UHMWPE fibers are 22.43 and 25.63 μm , respectively, and are both smaller than those of our previous study (the single fiber final diameters of 15 wt% and 18 wt% UHMWPE fibers were 23.86 and 31.46 μm , respectively)^[35], which corresponds to that fibers with thinner diameter have better mechanical properties^[38]. So the ultimate mechanical properties of UHMWPE fibers have been further optimized and the UHMWPE gel solution concentrations have been further improved compared with those in our previous work^[35] though the UHMWPE fibers with 24 wt% gel solution concentration have worse mechanical properties.

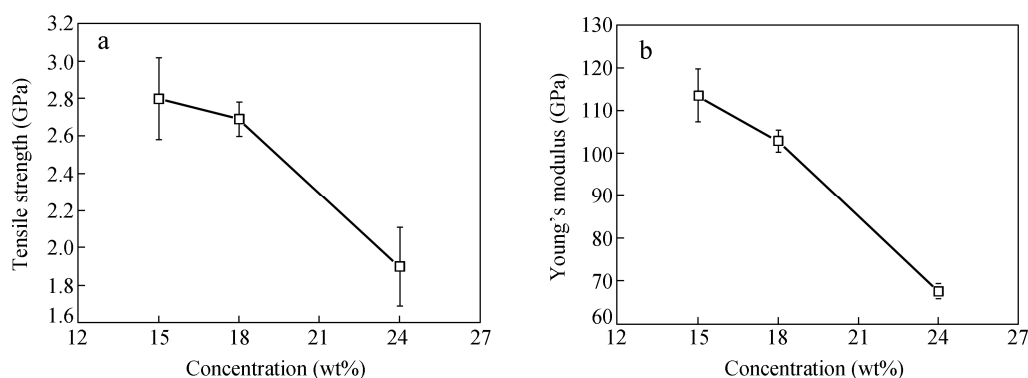


Fig. 1 The tensile strength (a) and Young's modulus (b) of UHMWPE fibers with different gel solution concentrations

DSC Analysis

Figure 2 shows the DSC curves of the UHMWPE fibers made using gel solution of different concentrations. The main melting peak located between 140 and 149 °C is thought to be caused mainly by the melting of lamellar crystals and micro-fibrils crystals. The second melting peak located between 149 and 157 °C is thought to result from the orthorhombic-to-hexagonal phase transition of highly constrained crystallites^[39–42]. It can be seen from Fig. 2 that the main melting peak position was gradually moved to the low temperature due to the fact that the content of micro-fibrils crystal in UHMWPE fibers decreases with the increase of gel solution concentration, while the content of lamellar crystal increases and the uniformity of lamellar crystal declines. The peak of UHMWPE fibers with 15 wt% gel concentration at about 146 °C is attributed to the melting of thick lamellar crystals, while a peak at about 149 °C results from the melting of shish crystals^[41, 43]. In addition, a weak peak of 24 wt% UHMWPE fibers at about 143 °C is caused by the melting of thin lamellar crystals^[41]. These results indicate that not all the lamellar crystals transform to micro-fibrils and the melting peak of lamellar crystals obviously exist in 15 wt%, 18 wt% and 24 wt% UHMWPE fibers. The main reason may be that the transformation of lamellar crystals to micro-fibrils (the micro-fibrils are composed mostly of shish structure) is hindered by the too many chain entanglements. Furthermore, it can be found that the peak located between 149 and 157 °C becomes more obvious with the gel solution concentration increasing from 15 wt% to 24 wt%, which is caused by the stress concentration due to the increase of chain entanglement number^[41]. This phenomenon can be explained in the following way. The melting of partial orthorhombic phase is limited by the defect such as

chain entanglement and then local fusion around defects leads to the development of stresses in the fiber inhibiting the melt-crystal interface to proceed further^[44]. So the transition of orthorhombic phase to hexagonal phase located between 149 and 157 °C has happened. The proportion of orthorhombic phase, which is limited by chain entanglement, increases with the increase of gel solution concentration. Therefore, the peak located between 149 and 157 °C becomes more obvious with the increase of gel solution concentration. Besides, the peak width of main melting peak becomes wider, and it suggests that the uniformity of crystal size and crystalline ability become worse with the increase of gel solution concentration. With the increase of gel solution concentration, the proportion of melting peak at high temperature increases because the chain entanglement number increases.

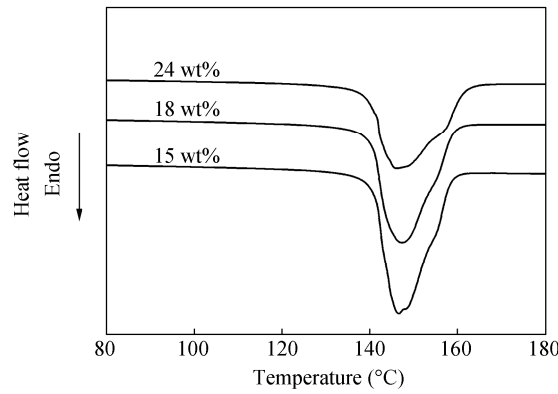


Fig. 2 DSC thermograms of UHMWPE fibers with different gel solution concentrations

The Degree of Crystallinity Change

The 2D WAXD patterns of UHMWPE fibers with different gel solution concentrations are shown in Fig. 3. It can be calculated that the 2D WAXD patterns of all UHMWPE fibers present diffraction patterns of (110), (200) orthorhombic unit cell and (010) monoclinic unit cell. The 1D WAXD intensity curves of UHMWPE fibers with different solution concentrations obtained from the 2D WAXD patterns are shown in Fig. 4(a). But the difference between the UHMWPE fibers with different gel solution concentrations cannot be clearly seen from Fig. 4(a). To find out their difference, the degree of crystallinity of UHMWPE fibers with different gel solution concentrations was calculated by Eq. (1) with 1D WAXD intensity curves (Fig. 4a).

$$X_c = \frac{I_c}{I_t}, \quad I_t = I_c + I_a \quad (1)$$

where I_c and I_a are the diffraction intensities of crystal phase (sum of (010)_{Mon}, (110)_{Orth} and (200)_{Orth} reflections) and amorphous phase, respectively. I_t is the diffraction intensity sum (azimuthal angle, $\phi = 0^\circ - 360^\circ$) of amorphous and crystal phases. The 1D WAXD profile curves were fitted with Voight functions as shown in Fig. 4(b).

Figure 5 presents the degree of crystallinity of UHMWPE fibers with different gel solution concentrations. One can see that the degree of crystallinity of UHMWPE fibers decreases with the increase of gel solution concentration because of the increase of the number of entanglements. Clearly, more molecular chains take part in entanglement with the increase of gel solution concentration so that the number of molecular chains participating in the formation of crystal decreases. The result indicates that the UHMWPE fibers with too high gel solution concentration are not conducive to obtain high degree of crystallinity though the degree of crystallinity of 24 wt% UHMWPE fibers still reaches 83.8%. In our previous study^[35], the degrees of crystallinity of 15 wt% and 18 wt% UHMWPE fibers were 74.9% and 71.8%, respectively, which were obviously lower than those of UHMWPE fibers in this study. So the degree of crystallinity of UHMWPE fibers with the same gel solution concentration has been improved compared with that in our previous study, which is beneficial to the improvement of fiber mechanical properties.

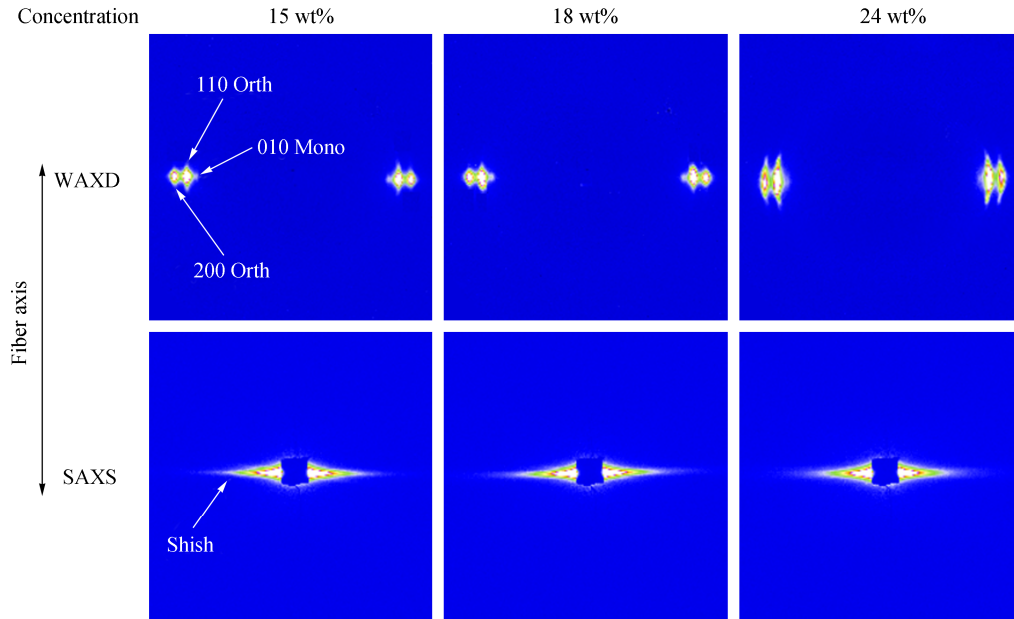


Fig. 3 The 2D WAXD and SAXS patterns of UHMWPE fibers with different gel solution concentrations

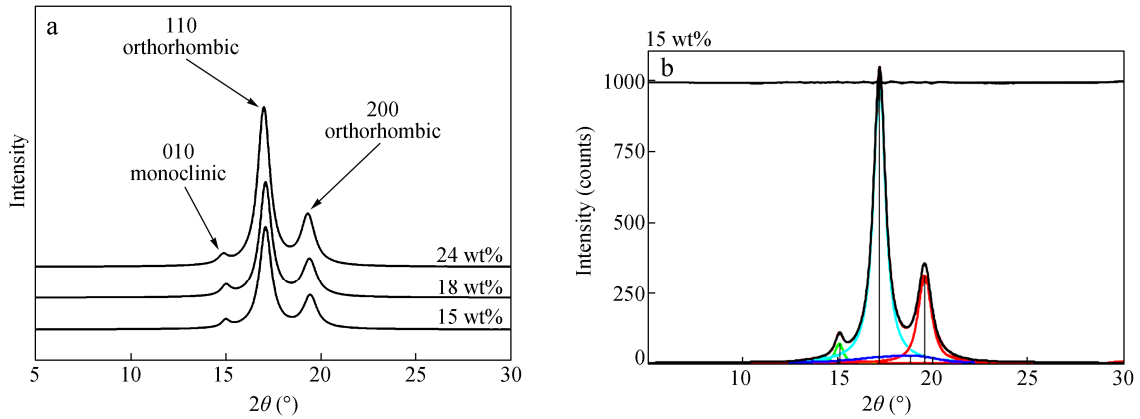


Fig. 4 (a) 1D WAXD intensity curves of UHMWPE fibers with different gel solution concentration; (b) The peak fitting process for the calculation of the degree of crystallinity

Crystalline Orientation

Herman's method^[45] was used to calculate the degree of crystal orientation of UHMWPE fibers with different gel solution concentrations. Therefore, the degree of crystal orientation can be characterized by average orientation of the normal to the crystalline plane with respect to an external reference frame. Furthermore, the direction of fiber axis was set as the reference direction. For a set of hkl planes, the average orientation, expressed as $\langle \cos^2 \phi \rangle_{hkl}$, can be calculated by using Eq. (2):

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

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

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

where f is equal to 1, when the normal of the reflection plane is parallel to the reference direction ($\phi = 0^\circ$), where f has a value of -0.5 , when the normal is perpendicular to the reference direction ($\phi = 90^\circ$) and a value of 0, when the crystal orientation is random. The degree of orientation f_{110} is calculated from the azimuthal intensity distribution $I(\phi)$ of the (110) reflection of α -crystals in UHMWPE fibers.

Compared with 15 wt% and 18 wt% UHMWPE fibers, the 2D WAXD pattern of 24 wt% UHMWPE fibers presents a wider diffraction pattern as shown in Fig. 3, which suggests that the crystalline orientation obviously becomes inferior when the gel solution concentration is 24 wt%. To know the detailed information of crystal orientation, the degree of orientation of UHMWPE fibers with different gel solution concentration was calculated from 2D WAXD patterns (Fig. 3) with Herman's method as shown in Fig. 6. The degree of orientation of UHMWPE fibers is decreased with the increase of gel solution concentration, which corresponds to the decrease of Young's modulus. The result may be caused by the increase of chain entanglement number with the increase of gel solution concentration, which introduces more defects into crystals and leads to more imperfections in the crystal structure of UHMWPE fibers. But the degree of orientation of 15 wt% and 18 wt% UHMWPE fibers are both improved compared to those of UHMWPE fibers in our previous study^[35], so the ultimate structure of UHMWPE fibers with 15 wt% and 18 wt% gel solution concentrations has been further optimized.

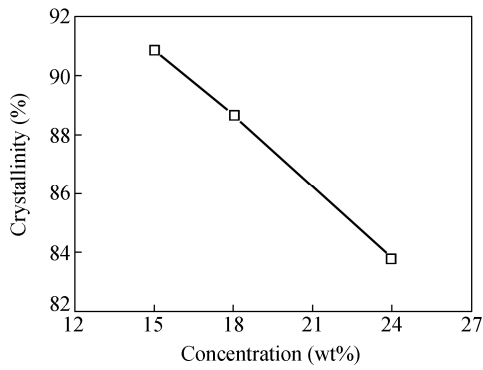


Fig. 5 The degree of crystallinity of UHMWPE fibers with different gel solution concentrations

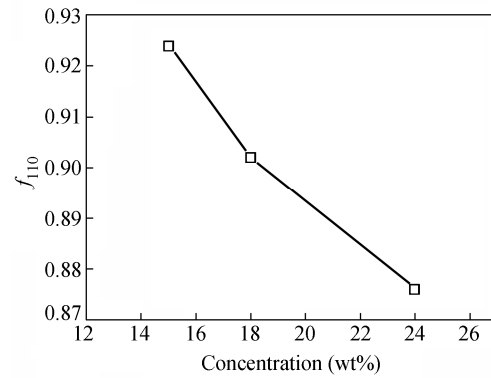


Fig. 6 The degree of orientation of UHMWPE fibers with different gel solution concentrations

Shish Structure

To better investigate the effect of gel solution concentration on the ultimate structure of UHMWPE fibers, the shish structure was analyzed. The changes of the average shish length, $\langle L_{\text{shish}} \rangle$, and the shish misorientation, B_ϕ , were calculated by using the Ruland streak method to analyze the equatorial streak feature in SAXS^[46–48]. Actually, the size and orientation distributions of longitudinal voids in polymer and carbon fibers in real space estimated from the equatorial streak of SAXS in reciprocal space have been demonstrated by Ruland. This method can also be used to separate the average length of shish and its average misorientation due to that the method is principally based on the separation of experimentally measured azimuthal breadth from contributions of scatterer length and misorientation. If it is assumed that all azimuthal distributions can be modeled by Lorentzian functions, the observed azimuthal width, B_{obs} , can be related to the length of shish, $\langle L_{\text{shish}} \rangle$, and the azimuthal width, B_ϕ , due to misorientation of shish by the following equation:

$$B_{\text{obs}} = \frac{1}{\langle L_{\text{shish}} \rangle s} + B_\phi \quad (4)$$

If all azimuthal distributions accord with Gaussian expressions, then the relationship is

$$B_{\text{obs}}^2 = \left(\frac{1}{\langle L_{\text{shish}} \rangle s} \right)^2 + B_{\phi}^2 \quad (5)$$

where B_{obs} is the integral width of the azimuthal profile from the equatorial streak at s . On the basis of Eq. (4) or Eq. (5), $\langle L_{\text{shish}} \rangle$ and B_{ϕ} can be calculated from the slope and the intercept of the plots, respectively. In this study, all azimuthal distributions had a good fit with Lorentzian functions, thus the plot based on Eq. (4) (as shown in Fig. 7) was used to determine $\langle L_{\text{shish}} \rangle$ and B_{ϕ} .

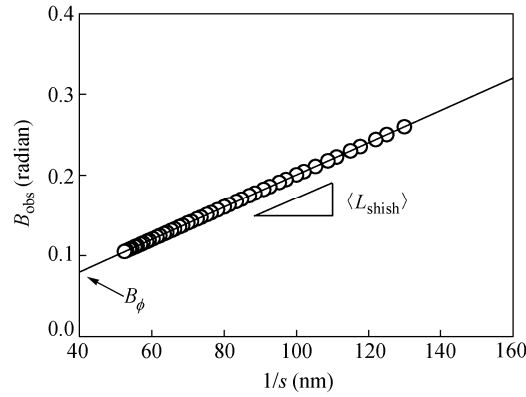


Fig. 7 The plot of azimuthal integral width (B_{obs}) versus the value of $1/s$, which was used to calculate the average shish length ($\langle L_{\text{shish}} \rangle$) and the shish misorientation (B_{ϕ}) based on Eq. (4)

The 2D SAXS patterns of UHMWPE fibers with different gel solution concentrations are presented in Fig. 3. The equatorial streaks across the beam stop, which represents the shish crystal structure, have no obvious change with the increase of gel solution concentration. The average shish length ($\langle L_{\text{shish}} \rangle$) and the shish misorientation (B_{ϕ}) of UHMWPE fibers with different gel solution concentrations are shown in Fig. 8. It can be seen that the average shish length of UHMWPE fibers decreases with the increase of gel solution concentration due to the increase of chain entanglement number. The increase of chain entanglement number limits average length of shish in UHMWPE fibers. Furthermore, the shish misorientation of UHMWPE fibers is also decreased with the increase of gel solution concentration. The reason is that too many chain entanglements limit the formation of longer shish so that average shish length decreases and short shish is easy to orient. In our previous study^[35], the average shish lengths of 15 wt% and 18 wt% were 1201 and 1127 nm, respectively, which were shorter than those of UHMWPE fibers in this study. This result suggests that the spinning condition used in this study is more conducive to the reduction of chain entanglement number compared with that in our previous study, which makes the ultimate structure of UHMWPE fibers be further optimized.

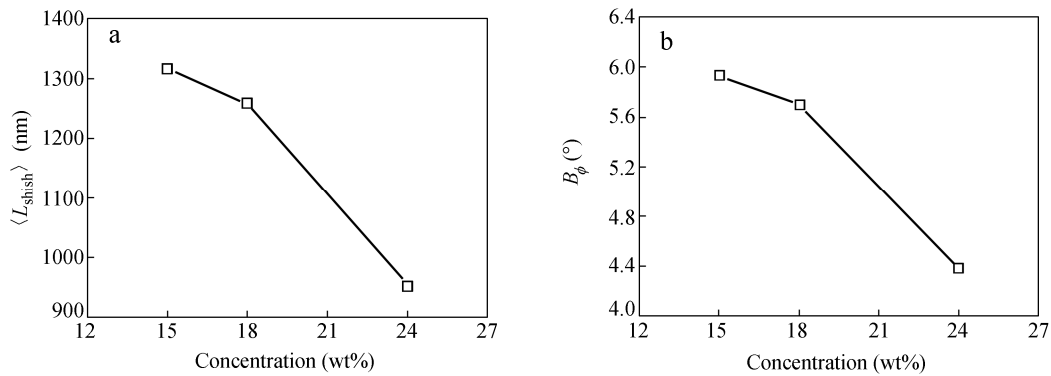


Fig. 8 The average shish length ($\langle L_{\text{shish}} \rangle$) and the shish misorientation (B_{ϕ}) of UHMWPE fibers with different gel solution concentrations

CONCLUSIONS

The UHMWPE fibers with the gel solution concentrations of 15 wt%, 18 wt% and 24 wt% were prepared at the industrial production line. The ultimate tensile strength and Young's modulus of UHMWPE fibers were decreased with the increase of gel solution concentration. Compared with the 15 wt% and 18 wt% UHMWPE fibers, the ultimate mechanical properties of 24 wt% are inferior though the UHMWPE fibers with 24 wt% gel solution concentration were successfully prepared. The DSC results show that the crystal structure of UHMWPE fibers becomes inferior with the increase of gel solution concentration. And the degree of crystallinity and orientation decrease with the increase of gel solution concentration. Furthermore, the average shish length ($\langle L_{\text{shish}} \rangle$) and the shish misorientation (B_ϕ) of UHMWPE fibers are also decreased with the increase of gel solution concentration. The above results indicate that the increase of gel solution concentration is not beneficial to the structure and mechanical properties of UHMWPE fibers when the gel solution concentration is higher than 15 wt%. Moreover, compared with those in our previous study, the ultimate structure and mechanical properties of 15 wt% and 18 wt% UHMWPE fibers have been further optimized and the spinning concentration are successfully increased to 24 wt%. This study is expected to be helpful to further improve the mechanical properties of UHMWPE fibers in industrial production.

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