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Effect of UHMWPE concentration on the extracting, drawing, and crystallizing properties of gel fibers

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Abstract In this study, ultra-high molecular weight polyethylene (UHMWPE) gel fibers were made by gel-spinning with different concentration solutions of 8–16 wt%. The solvent separation and extracting dynamics of different gel fibers were studied. The thermal and crystallizing properties of different fibers were characterized with differential scanning calorimeter and wide-angle X-ray diffraction. The morphological structure of different gel fibers was observed using scanning electron microscope (SEM). The maximum drawing ratios (DRs) of different fibers and the tenacity of ultra-drawn fibers were measured and compared. The results showed that the phase separation of different concentration UHMWPE gel fibers were severe at the first hour and reached equilibrium state after about 48 h placing. The critical extraction time of different gel fibers and the optimum bath ratios of extraction agent to gel fibers were 2 min and 10 mL/g, respectively. The melting point and the crystallinity of extracted fibers were both higher than that of gel fibers, and the crystallinity of fibers increased with increasing of UHMWPE concentration. High concentration UHMWPE fiber has more dense morphological structure while compared with lower concentration ones. The maximum achieved DRs of gel fibers were higher than that of extracted fibers. The DR and tensile strength of extracted fibers decreased with increasing of UHMWPE concentration.

Introduction

Ultra-high molecular weight polyethylene (UHMWPE) fibers have been produced by gel-spinning technique since 1980s [1–9]. The UHMWPE fibers have ultra-high strength of 38cN/dtex which are about 10 times higher than those of steel fibers, and these fibers have considerable advantages such as low density, excellent chemical, ultraviolet, abrasion and impact resistance, therefore they have been widely used in the manufacturing of a wide variety of commercial articles like towing lines, helmet reinforcement or sails and other composite applications [10].

The extracting technique is the key factor to improve the extracting efficiency and drawing ability of UHMWPE gel fibers. Maghsoud and Moaddel [11] investigated the effect of paraffin concentration on the extraction time; they prove that in a continuous process of fiber production, the extraction solvent should be continuously replaced by pure solvent. Zhang [12] investigated the phase separation of gel as-spun and spun fiber under various spinning conditions using general kerosene as the solvent and gasoline as the extraction solvent. Under normal circumstance, the concentration of UHMWPE solution for gel-spinning is about 6–8 wt%. In such low spinning concentration, fiber productivity is relatively low, 12–15 times amount of solvent and much more extraction solvent will be used for producing 1 unit of UHMWPE fibers. Some solvent and extraction solvent will be inevitably wasted during the solvent's recycling process, which is harmful to our environment. Enhancing gel-spinning concentration is an effective method to improve fiber productivity. The gel-spinning

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technique has made a great progress in recent years; the twin-screw extruder has been successfully used as the swelling and dissolving equipment, which makes it possible to produce higher concentration UHMWPE fibers [13–16].

Although many articles have dealt with qualitative investigation of the extracting, drawing process and the structure and properties changes of UHMWPE fibers [17–20], however, less of them have reported a fundamental quantitative description on the extracting, drawing process of high concentration UHMWPE gel fibers. In this study, UHMWPE gel fibers were made by gel-spinning with different concentration solutions of 8–16 wt%. During placing time, much solvent will be separated from the as-spun gel fibers, the solvent separation rates of different gel fibers were measured in this study. The effects of extraction time and extraction bath ratio on the extracting dynamics of different gel fibers were investigated. Orthorhombic crystal phases accompanied with small fractions of monoclinic crystalline phases are often found in the crystalline phases of UHMWPE fibers. The crystalline and morphological structure in fibers are usually considered important parameters influencing the drawing process, and the superior mechanical properties of UHMWPE fibers can be obtained only after ultra-drawn. The morphological structure and the melting and crystalline properties of different fibers were characterized using scanning electron microscope (SEM), differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD). The maximum DRs of different fibers and the fiber tenacity were measured by homemade drawing device and tensile tester.

Experimental

Materials

The UHMWPE used in this experiment has a viscosity-average molecular weight (M_η) of 3.8×10^6 produced by Beijing No. 2 Chemical Company. The mineral oil used in this experiment is Total finavestan A360B provided by Tecona Co., Ltd, the flash point is 250 °C and the fraction is 390 °C. The extraction agent for the UHMWPE gel fibers was xylene provided by Shanghai Lingfeng Chemical reagent Co., Ltd., which is a mixture of *p*-xylene, *o*-xylene, *m*-xylene and ethyl-benzene, the ethyl-benzene content is less than 19%. The antioxidant 1076 (*β*-(3,5-bis-tertiary butyl-4-hydroxy phenyl) propaneoic acid octadeca carbonic ester) was provided by Shanghai Jinjin Trade Co., Ltd.

Preparation of UHMWPE gel fibers

The suspension of UHMWPE and antioxidant in mineral oil was fed to a twin-screw extruder with the screw diameter of 25 mm and the length-to-diameter ratio of 40:1. After undergoing high temperature swelling and dissolving, the UHMWPE solution was extruded into a filament at a certain spinning temperature using a 1-pore spinneret. The pore diameter was 0.9 mm and the length-to-diameter ratio was 7:1. The filament was quenched into cold water of 20 °C to form UHMWPE gel fiber. In this experiment, the suspensions containing 8, 10, 12, 14, and 16 wt% UHMWPE were used to prepare gel fibers, respectively, the spinning temperature was from 290 to 315 °C and the screw rotating speed was 5.6 r/min.

The solvent separation test

After gel-spinning, the as-spun gel fibers were placed under unconstrained state, some solvent will be separated out. The solvent separation ratio (C_s, %) of as-spun gel fibers can be calculated with the following equation, where W_0 is the original weight of as-spun gel fibers, and W_t is the weight of gel fibers at certain time after gel-spinning. In this test, five samples from each composition were used in order to guarantee the quality of the results and also to calculate the standard deviation.

$$C_s(\%) = \frac{W_0 - W_t}{W_0} \times 100\%$$

Extracting dynamics of gel fibers

The gel fibers of certain weight (W_0) were extracted in the presence of different amount of xylene with ultrasonic agitation for 6 min or extracted for different time with the extraction bath ratio of 20 mL/g, then the extracted fibers were put into an oven of 105 °C to remove the xylene. After drying, the fibers were weighed as W_1. In this test, five samples from each composition were used in order to guarantee the quality of the results and also to calculate the standard deviation. The solvent removing ratio (C_0, %) of UHMWPE gel fiber can be calculated with the following equation:

$$C_0(\%) = \frac{W_0 - W_1}{W_0} \times 100\%$$

Differential scanning calorimetry analysis

The melting behavior of gel fibers and extracted fibers were investigated using a Perkin-Elmer DSC7 differential scanning calorimeter. Fiber samples were cut into small pieces and each sample weighed about 5 mg, they were placed in a standard aluminum sample pan and heated from 70 to 170 °C, the sample was kept at melting state for 3 min to completely eliminate its thermal history, and then was cooled from 170 to 70 °C, the heating and cooling rate used were 10 °C/min with N_2 flow of 40 mL/min. The percentage of crystallinity Xc of fibers can be calculated with the following equation, where ΔH is the enthalpy of fiber sample and ΔH_f is the enthalpy of wholly crystallized polyethylene, which is 293 J/g [18].

$$X_c = \frac{\Delta H}{\Delta H_f}$$

Wide-angle X-ray diffraction analysis

The fibers for WAXD analysis were chopped into lengths of less than 0.5 mm to randomize the orientation, and the WAXD patterns of fibers were collected in a 2θ scan range of 5°–35° on a Rigaku D/Max-2550 PC X-ray diffractometer (Japan) with Ni-filtered CuKα ($\lambda = 0.15401$ nm) radiation operated at 300 mA and 40 kV in the reflection mode. The amorphous and crystalline peaks were decomposed by fitting a Gaussian function to an experimental curve using a non-linear, least-squares curve-fitting program, Jade 5.0.

Scanning electron microscope observation

The UHMWPE gel fibers were extracted and dried under constrained state to remove the solvent thoroughly, after that the extracted fibers were immerged in liquid N_2 and broken off to get the cross section of fibers. The surface and cross section of fibers were coated with 5–10 nm of gold, then their morphological structure was observed using a JSM-5600LV SEM made by JEOL Co., Ltd.

Drawing property test

A certain length (L_1) of gel fiber or extracted fiber was put into a homemade drawing device, then clamped one side of the fiber and drew another side of the fiber until the fiber broke, measure the fiber's total length L_2. The drawing temperature was 100 °C and a drawing speed of 1.00 m/min was used. The drawing ratio (DR) is calculated as follows:

$$\mathrm{DR} = \frac{L_2}{L_1}$$

In order to ensure the repetition of DR measurements, the initial length of fiber (L_1) was set as 5 cm for every sample, the drawing process was performed 10 times to get the average DR.

Fiber strength measurements

The tenacity of fibers was measured with the DXLL tensile tester (Shanghai D&G Machinery Equipment Co., Ltd, China). The stress scope of the tensile tester was in the range of 0–1000 N. The fiber initial gauge length was 250 mm and a tensile speed of 200 mm/min was used until the fiber broke in the home temperature. In this test, five samples from each composition were used in order to guarantee the quality of the results and also to calculate the standard deviation.

Results and discussion

Solvent separation analysis of as-spun gel fibers

After quenched into gel fibers, the gel fibers will gradually shrink if they are placed under unconstrained state, and some solvent will be separated from the gel fibers until equilibrium is reached. Therefore, the concentration of UHMWPE in gel fiber will be higher than that in the solution [21].The changes of solvent separation ratio of different as-spun gel fibers with placing time are shown in Fig. 1.

From Fig. 1, one can see that C_s increases quickly at the beginning 60 min, and then gradually increases to a certain value after placing about 3000 min, which indicates that the phase separation of UHMWPE as-spun fiber is severe in the first hour and then gradually reached equilibrium state after about 2 days. Figure 1 also indicates that the final C_s decreases as the UHMWPE concentration increases, this is because that high concentration as-spun gel fibers contain less solvent and more entangled points than the low ones, which influence the solvent separation from the gel fibers.

By the phase separation process, much solvent is separated out, which will help to reduce the amount of extraction agent in the subsequent extraction process.

Extracting dynamics of gel fibers

When gel fibers are put into the extraction bath, the mutual diffusion of fiber solvent and extracting agent will happen. The diffusion motivity of fiber solvent is the concentration

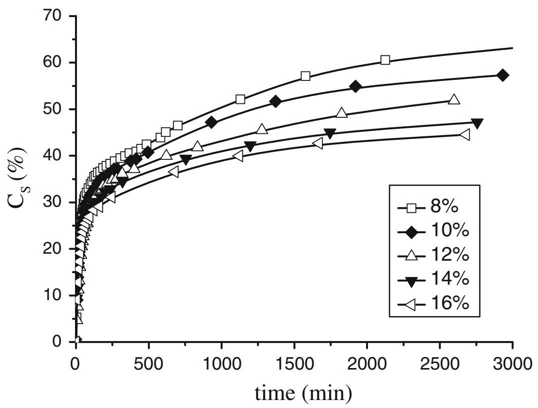

Fig. 1 C_s of as-spun gel fibers versus placing time

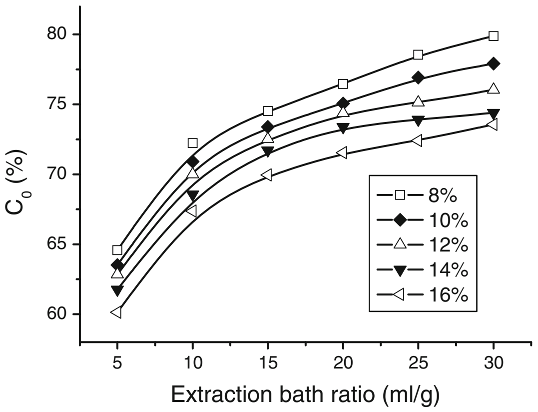

Fig. 2 C_0 of different gel fibers changes with extraction bath ratio (extraction time is set as 6 min)

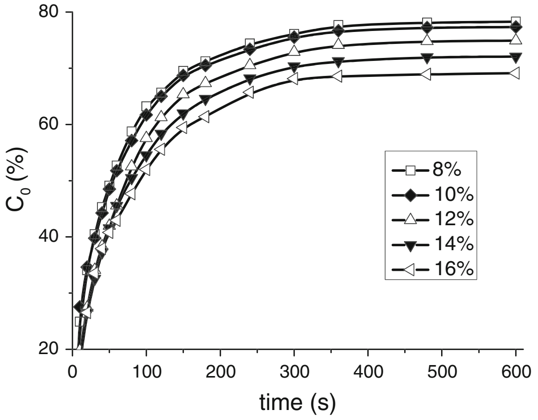

Fig. 3 C_0 of different gel fibers changes with extraction time (extraction bath ratio is set as 20 mL/g)

difference between inner and outer of gel fiber, so the C_0 of the gel fiber increases as UHMWPE concentration decreases or the extraction bath increases, as shown in Fig. 2. From Fig. 2, one can see that C_0 of the gel fiber increases quickly at the beginning and then slowly reached equilibrium.

In the same time, extraction time plays an important role in the extraction process. With the prolonging of the extraction time, the C_0 increases rapidly and then reached equilibrium state, as shown in Fig. 3. The reason is that the rate of solvent diffusion is decided by the concentration difference. At the beginning of extraction, the concentration difference is high, so the solvent diffuse rapidly, with the time passed, the concentration difference decreases and C_0 reaches an equilibrium state in the end.

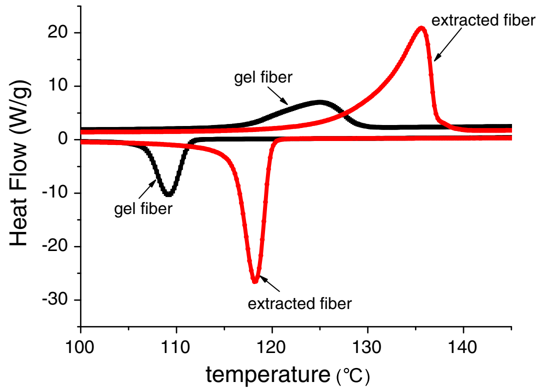

Fig. 4 Melting and cooling DSC curves of 16% UHMWPE gel and extracted fiber

From Figs. 2 and 3, one can see that there is a critical value for extraction bath ratio and extraction time, the critical extraction bath ratio is about 10 mL/g for all gel fibers and the critical time for all gel fibers are 2 min. When the extraction bath ratio and extraction time are higher than their critical values, the solvent removing rate slows down. So simply raising extraction bath ratio or prolonging extraction time is not an economical way to remove the solvent of gel fibers in extraction process. On the other hand, the final C_0 of the same gel fibers have little difference whatever prolonging extraction time or raising extraction bath ratio (as shown in Table 1). A little solvent is still remained in UHMWPE gel fibers after extracted. The remained solvent will affect the ultra-drawing efficiency of the fibers, so the gel fiber should be further extracted. The economical way for the extraction process is that the gel fibers are extracted for multi-times with the bath ratio of 10 mL/g and extracted for 2 min.

Melting behavior of UHMWPE fibers

The UHMWPE gel fibers were extracted with xylene for multiple times to completely remove the solvent from gel fibers, then the extracted fibers were dried under constrained state in a fume hood at 25 °C until the weight was stabilized. The melting and cooling DSC curves of 16% UHMWPE gel fiber and extracted fiber are shown in Fig. 4. Gel fiber contains a large amount of solvent and the solvent doesn't crystallize, so the melting and cooling peak of gel fiber are both smaller than that of extracted fiber. From the cooling curves of both fibers, one can see that the crystallizing

Table 1 Final C_0 from Figs. 2 and 3

Concentration (%)	8	10	12	14	16
Final C_0 from Fig. 2 (%)	79.89 ± 2.05	77.92 ± 1.95	76.04 ± 1.82	74.40 ± 1.78	73.56 ± 1.70
Final C_0 from Fig. 3 (%)	78.27 ± 2.02	77.34 ± 1.96	74.90 ± 1.78	72.09 ± 1.80	69.12 ± 1.75

Table 2 DSC results of different gel fibers and extracted fibers

Concentration (%)	Gel fibers				Extracted fibers			
	T_m (°C)	Crystallinity (%)	T_c (°C)	Recrystallinity (%)	T_m (°C)	Crystallinity (%)	T_c (°C)	Recrystallinity (%)
8	123.90	14.13	109.92	12.58	134.46	66.35	118.84	51.49
10	124.20	16.07	109.56	13.82	134.63	67.38	118.18	51.71
12	124.48	17.40	109.24	15.17	134.87	67.54	118.34	52.24
14	124.73	18.11	108.92	16.47	135.24	68.00	118.50	52.49
16	124.91	18.54	109.10	17.38	135.60	68.96	118.15	53.98

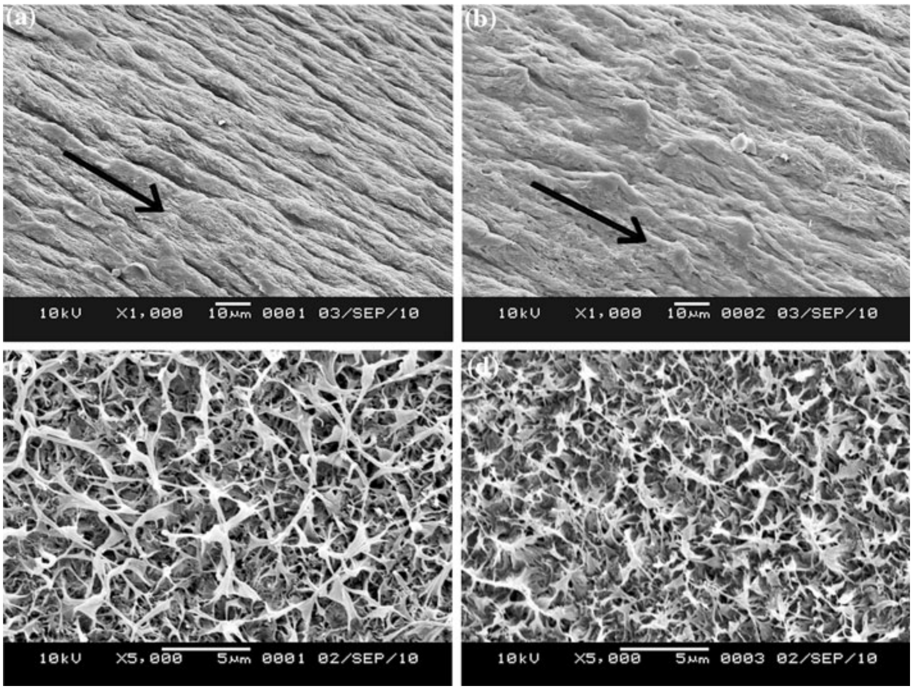

Fig. 5 SEM micrographs of extracted UHMWPE fibers of the surface of **a** 8 wt%, **b** 16 wt% fibers and the fractured section of **c** 8 wt%, **d** 16 wt% fibers (the *arrow* is along the fiber axis)

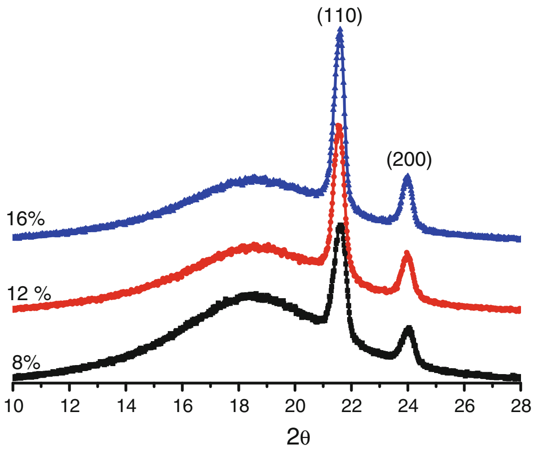

Fig. 6 WAXD patterns of gel fibers with different concentration

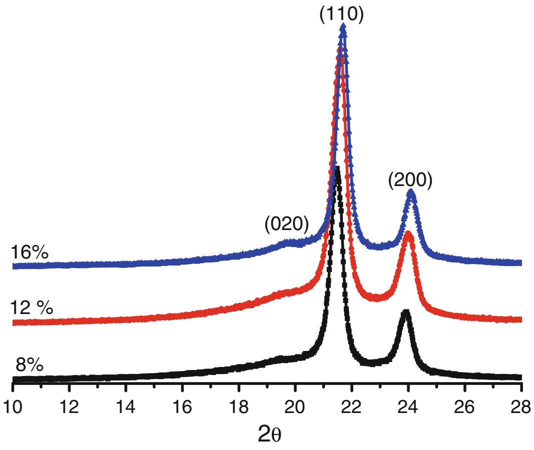

Fig. 7 WAXD patterns of extracted fibers with different concentration

temperature of gel fiber is about 10 °C lower than that of extracted fiber, it is indicated that the solvent in UHMWPE solution prevent the polyethylene from crystallizing. Therefore, the crystalline structure formed during quenching process in gel fiber is not very regular. With the removing of solvent, the polyethylene crystal becomes more regular so

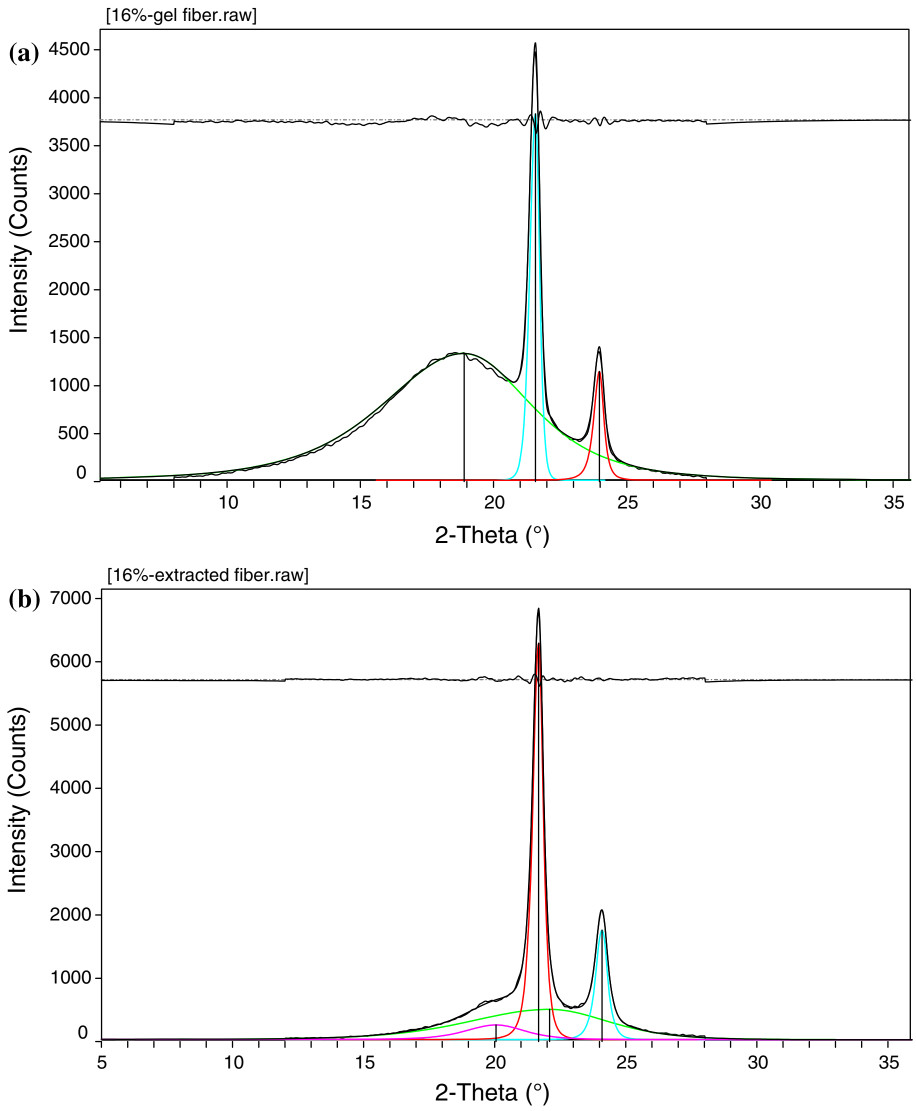

Fig. 8 Amorphous and crystalline peaks divided from WAXD pattern of 16% UHMWPE gel fiber **a** and extracted fiber **b**

the melting temperature of extracted fiber is higher than that of gel fiber.

Table 2 shows the DSC data got from the melting and cooling curves of different gel fibers and extracted fibers.

From Table 2, one can see that above phenomenon takes place for the fibers of all concentrations, the melting temperature and crystallizing temperature of extracted fibers are all about 10 °C higher than those of gel fibers, and the percentage of crystallinity of gel fibers increase significantly after extracted, the reason is almost the same. In the same time, it is observed that the melting temperature and the percentage of crystallinity of gel fibers and extracted fibers all increase with increasing of UHMWPE concentration. It is owing to the fact that more concentrated gel tends to form much more crystals and the crystalline structure becomes more regular, which contributes to such an increase in crystallinity and melting temperature. This phenomenon explains that increasing polymer content will be accompanied by an increase of number of entangled molecular chains, which will increase the interaction force between polymer chains. It is further observed in Table 2 that crystallinity of fibers almost have the linear relationship with the UHMWPE concentration.

Figure 5 shows the morphological structure of extracted UHMWPE fibers obtain from the SEM micrographs of the surface and fractured section of extracted fibers with different UHMWPE concentrations. The shish-kebab-like entities were found on the surface of these extracted fibers, which is similar to those found in the literature [16]. With the increasing of UHMWPE concentration, the shish-kebab-like entities become much denser. However, the orientation of the shish-kebab-like entities of 16% fiber(b) looks worse than that of 8% fiber(a), although its shish-kebab-like entities look even denser than that of

Table 3 Average crystal sizes for different lattice planes and the crystallinity of different fibers

Concentration (%)	Gel fibers			Extracted fibers		
	Crystallinity (%)	$L_{(110)}$ (nm)	$L_{(200)}$ (nm)	Crystallinity (%)	$L_{(110)}$ (nm)	$L_{(200)}$ (nm)
8	12.85	16.9	16.3	54.46	15.9	14.8
12	15.11	19.0	17.8	63.38	14.5	13.0
16	19.63	20.6	19.8	68.89	17.3	14.9

8%(a). On the other hand, 16% fiber (d) exhibits more compact network structure than that of 8% fiber(c). This helps to verify that crystallinity of the fiber grows as the UHMWPE concentration increases.

Wide-angle X-ray diffraction analysis of different fibers

Figures 6 and 7 show the WAXD patterns of gel fibers and extracted fibers of different concentration. There is a broad peak for amorphous region of gel fiber because it contains a large amount of solvent which does not crystallize, and this peak becomes smaller after solvent removed. The WAXD patterns of fibers display two distinct peaks at 2θ scan radian of 21.6° and 23.8° which correspond to the (110) and (200) lattice planes of the orthorhombic phase of polyethylene crystals, respectively. After solvent removed, (110) and (200) peaks become more distinct and bigger, and a small peak appears at 2θ of 19.5 °corresponding to the (020) lattice planes of the orthorhombic phase.

The WAXD patterns of fibers are dealt with the curve-fitting program, different crystalline peaks and amorphous peak are divided as shown in Fig. 8. The average crystal sizes for different lattice planes are shown in Table 3. It is observed that the crystal sizes of fibers become smaller after solvent extracted, which indicates that the crystals formed in gel fibers are not regular because of the hindering of solvent and the crystalline structure becomes regular after solvent removed. This is consistent with the DSC results of fibers. It is also observed that the crystallinity of gel fibers and extracted fiber almost increase linearly with increasing of UHMWPE concentration, which is same as the DSC results of these fibers (shown in Table 2).

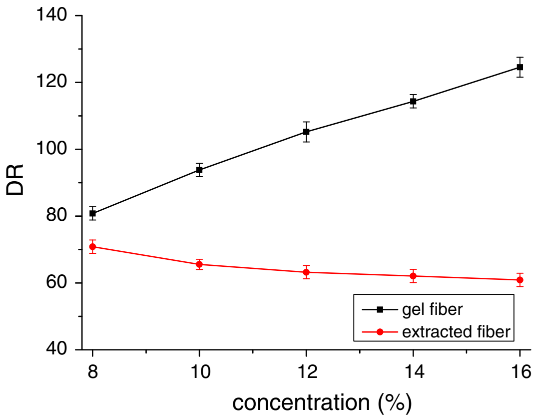

Fig. 9 Effect of DR from different concentration

Drawing ratio

The aggregation structure of fibers before drawing process may determine the drawability and hence the mechanical properties of the fiber. Figure 9 shows the maximum achieved DR of UHMWPE gel and extracted fibers spun from different concentration of solutions. The DR of extracted fiber decreases when UHMWPE concentration increases from 8 to 16%. The UHMWPE chains are much closer in higher concentration fibers, much more crystals and entanglement points are formed in high concentration fiber. The entangled chains can not be easily stretched, it also seems impossible to draw crystallized chains out from the crystals at the drawing temperature of 100 °C because the crystals begin to melt at the temperature of about 122 °C (see Fig. 4). So the fiber with higher concentration has lower drawability. This phenomenon can also be verified from the morphological structure of extracted UHMWPE fibers (see Fig. 5), low concentration fiber has loose network structure which will result in high drawability.

From Fig. 9, it can also be seen that the DR of gel fibers is higher than that of extracted fibers. During the quenching process of extruded filaments, a great deal polyethylene folded-chain crystals are formed in gel fibers. These crystals are much looser than that of extracted fibers and they begin to melt at the temperature of 117 °C (see Fig. 4), some irregular crystallized chains may be drawn out from the crystals when drawn at 100 °C, which results in higher DR of gel fibers. On the other hand, the solvent in gel fiber will act as the plasticizer to UHMWPE chains during drawing process, which will also contribute to higher DR of gel fibers. However, the DR of gel fibers decreases with the increasing of solvent content. This is because that much solvent cannot effectively transfer the drawing stress between UHMWPE chains, the chain slips quickly and the drawability becomes bad.

Actually, only the drawing of extracted fiber is effective which will contribute to the fibers' high strength. After drawn at certain temperature, high orientated and crystallized structure has been formed in UHMWPE fiber, only

Table 4 Tensile strength and measured sd of different concentration

Concentration (%)	8	10	12	14	16
Tensile strength of extracted fiber (cN/dtex)	0.68 ± 0.05	0.64 ± 0.04	0.64 ± 0.04	0.62 ± 0.04	0.62 ± 0.04
Tensile strength of ultradrawn fibers (cN/dtex)	35.27 ± 1.80	28.42 ± 1.50	27.93 ± 1.50	26.04 ± 1.30	25.26 ± 1.20

when drawn at higher temperature, the motion of PE chains in UHMWPE fibers becomes possible and the fiber's structure becomes more compact. In general, three-stage hot drawing process is used to prepare high strength and high modulus UHMWPE fibers [18]. In this study, UHMWPE extracted fibers were drawn with three-stage hot drawing process which was carried out at 80, 100, and 120 °C with the draw ratio of 15, 2, and 1.5, respectively. Table 4 shows the tensile strength of extracted UHMWPE fibers and ultradrawn fibers after three-stage hot drawing process. From Table 4, one can see that the tensile strength of UHMWPE fibers are remarkably enhanced after ultradrawn, and the tensile strength of ultradrawn fibers decrease with increasing of UHMWPE concentration, which is consistent with the DR results of extracted fibers.

Conclusions

High concentration solutions of 8–16 wt% UHMWPE in mineral oil are gel-spun to form gel fibers. After quenched into gel fibers, phase separation is happened and a great deal of solvent is separated out. The phase separation is severe in the first hour and reaches equilibrium state after about 48 h. During solvent extraction process, the solvent removing ratio of gel fibers increases with increasing of extraction bath ratio or extraction time and gradually reaches the equilibrium state. The critical extraction time of different gel fibers and the optimum bath ratios of extraction agent to gel fibers are 2 min and 10 mL/g, respectively. The melting point and the crystallinity of gel fibers and extracted fibers both increase with increasing of UHMWPE concentration. The melting temperature of extracted fibers are about 10 °C higher than that of gel fibers, and the crystallinity of fibers increases greatly after extracted because of the removing of solvent, and the crystal size decreases. The morphology structure of low concentration UHMWPE fiber is loose, while it becomes much denser when the UHMWPE concentration is higher. The maximum achieved DR of gel fibers were higher than that of extracted fibers. The drawing of extracted fibers can contribute to the fibers' tensile strength. The DR and tensile strength of extracted fibers decreased with increasing of UHMWPE concentration.

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