Investigation on the Thermal Behaviors and Mechanical Properties of Ultrahigh Molecular Weight Polyethylene (UHMW-PE) Fibers

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SYNOPSIS

Fibers of ultrahigh molecular weight polyethylene (UHMW-PE) were prepared with the gel fiber drawing method, and the solvent and extraction solvent used were a general kerosene and gasoline, respectively. The thermal behaviors and mechanical properties of the fiber were studied using thermal analysis, a wide-angle X-ray diffractiometer, density, the sound orientation factor, as well as mechanical property measurement. The results showed that the morphology of macromolecular chains was changed from the folded state to an extended-chain structure with increasing of the drawing ratio. In addition, the crystal form of the fiber also changed. These changes were more evident while the drawing ratio exceeded 20. The tensile strength, similar to the modulus of the fibers, increases with an increasing draw ratio in the range that we researched, whereas the sonic velocity orientation factor and the degree of crystallinity increase slowly when the draw ratio is over 30. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, research on various organic fibers with high performance has achieved considerable progress. There is a variety of routes for preparing high-modulus and high-strength polyethylene (PE) fiber, such as gel fiber drawing,[1-3] crystallization of fibrillar crystals under shear,[4] solid-state extrusion,[5,6] and zone drawing,[7] but only gel fiber drawing is used commercially. The gel spinning process is suitable for PE having a very high molecular weight ($> 1 \times 10^6$). The PE is first dissolved so that a dilute solution is obtained in which the macromolecules can disentangle. The solution is spun through a spinnerette and quenched. The gel fiber obtained is extracted, dried, and eventually drawn at elevated temperature in one or more steps to a very high draw ratio (> 30). During the draw process, a folded-chain conformation of PE is transformed into a nearly extended-chain one, i.e., molecules are fully extended and the degree of crystallization and orientation of fibers are considerably enhanced, which results in high-performance fibers.

The present work was concerned with the thermal behaviors and mechanical properties of ultrahigh molecular weight polyethylene (UHMW-PE) fiber that is obtained by the gel fiber drawing method, and the solvent and extraction solvent used were a general kerosene and gasoline, respectively. The results of the study showed that the morphology of macromolecular chains was changed from a folded state to an extended-chain structure with increasing of the drawing ratio. In addition, the crystal form of the fiber changed also during the drawing process. These changes were more evident while the drawing ratio exceeded 20. The mechanical properties of the fiber are enhanced with increasing of the drawing ratio, but the tenacity and modulus of the fiber are not linear relations with the crystallinity and sound orientation factor.

EXPERIMENTAL

The UHMW-PE fibers used in this study were obtained by dissolving 5% by weight of linear PE (by

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Beijing Auxilliaries Plant No. 2, China, with a weight-average molecular weight of 3×10^6) in kerosene (boiling point 160–180°C) to which 0.3% by weight of antioxidant was added. The gel fibers were spun through a self-made minispinning apparatus with 0.1 mm-diameter holes into water at approximately 5°C. The kerosene in the as-spun was first removed by phase separation occurring in the gel fibers when they were left for a certain time. Residual solvent in the gel fibers was then extracted with gasoline (boiling point 120°C). The gel fibers thus obtained were dried at room temperature. Dried gel fibers were drawn to a draw ratio from 0 to 50 with a hot oven at the range of 80 to 140°C.

Densities (ρ) of the fibers were measured using a density gradient column with heptane and carbon tetrachloride. The crystallinity of the fibers by the density method was calculated from eq. (1):

$$V_c = \rho_c(\rho - \rho_a)/\rho(\rho_c - \rho_a) \quad (1)$$

where ρ are measured densities, ρ_c is the density of the crystalline PE, assumed to be 1.00 g/cm^3, and ρ_a is the density of the amorphous phase PE, taken as 0.85 g/cm^3.

The orientation factor of sonic velocity was determined by measuring the transit time of a sound pulse between two tranducers coupled to the specimens. The measurements were made by using an SSY-I model fiber sonic velocity meter. From the measured sonic velocity C, the orientation factor of samples, f_s, was calculated from eq. (2):

$$f_s = 1 - (C_u/C)^2 \quad (2)$$

where C_u is the sonic velocity of the fully unoriented sample, taken as 1.65 km/s.

A wide-angle X-ray diffraction (WAXD) intensity profile of the fibers was measured with Ni-filtered CuKα radiation using a Rigaku D/MAX-YA model X-ray diffractometer.

The melting behavior of the fibers was investigated with a Perkin-Elmer DSC-2C differential scanning calorimeter (DSC) in a nitrogen atmosphere. An empty sample pan was taken as the reference sample. The samples were weighted accurately at 8 ± 0.5 mg and heated to 473 K. Two methods of sample preparation were used. For melting experiments of samples in an unstrained state, the fibers were cut into small pieces and the heating rate was 20 K/min. In the case of melting experiments on strained fibers, the fibers were tightly wound around a small aluminum frame and knotted onto the frame. Two heating rates of 5 and 20 K/min were used here. Another melting experiment on strained fibers having a draw ratio of 40 was made, in which the fibers were first heat-treated at temperatures of 390, 400, 410, and 426 K for 5 min on the DSC meter and cooled to room temperature at a rate of 320 K/min.

Mechanical properties were measured using an Uster tensorpid model tensile tester. Fibers were tested using a sample length of 500 mm and a constant crosshead speed of 50 mm/min.

RESULTS AND DISCUSSION

In Figure 1, the melting behavior of unstrained UHMW-PE fibers with various draw ratios is presented. By comparing the melting behavior of as-spun fiber with the fiber having a draw ratio of 10, several observations can be made. First, the melting peak temperature of the fiber with a draw ratio of 10 increases from 409.38 to 414.23 K (T_1). The shift of peak temperature to higher temperature can be attributed to that folded-chain crystals become more perfect. Second, although the peak width decreases and the peak area increases, only a single peak appeared on the DSC curve. This indicates increase of crystallinity with increase of the draw ratio. We concluded that drawing to this extent caused no crystalline morphology changes, but did increase crystallinity and the tendency of folded-chain crystals to become more perfect.

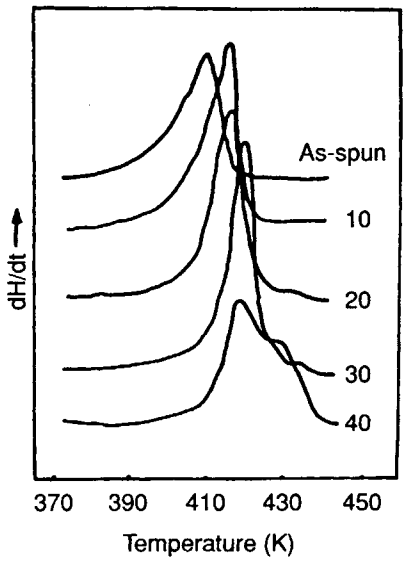

Figure 1 DSC thermgrams showing the melting behavior of unstrained UHMW-PE fibers with various draw ratios. The numbers on the right of the curves are draw ratios.

For the fibers drawn beyond 20, in addition to a shift of the peak melting temperature to higher temperatures and an increase in fusion heat, a small shoulder near the temperature of 426 K is observed at the high-temperature side of the main melting peak. The shoulder, which is characteristic for the melting of extended-chain crystals, becomes more remarkable at 427 K in the DSC curve of the fiber with a draw ratio of 40. So, the fraction of extended-chain crystals in the fibers drawn to a ratio 40 is much higher than in fibers drawn to a ratio 30. These results show that the folded-chain lamellar structure not only tends to be more perfect, but also gradually transforms into an extended one at higher draw ratios, and this transformation occurred most remarkably as the draw ratio increases from 30 to 40, which results in the fraction of extended-chain crystals also being increased.

In the DSC curves of fibers with a draw ratio > 20, a small peak (T_3) corresponding to the melting of monoclinic crystals appeared above 430 K, and with the increase of draw ratio, the fusion heat increases and the peak temperature shifts to higher temperatures. To determine whether the monoclinic crystals of PE exist in the fibers or are produced from the orthorhombic to monoclinic phase transition at elevated temperature during the measuring process of DSC, WAXD investigations on fibers with various draw ratios were made, as shown in Figure 2. On the WAXD curves of as-spun fiber and the fiber with a draw ratio of 10, there are only two diffraction peaks of $2\theta = 21.6°$ and 23.3°, which, respectively, correspond to (110) and (200) orthorhombic reflections of PE,[8,9] while on those of fibers with a draw ratio beyond 20, another peak of $2\theta = 19.2°$ appeared, presenting the characteristic of (001) reflection of the monoclinic PE phase,[10] which corresponds to the third peak (T_3) in the DSC curves. This indicates that the fiber with a higher draw ratio (> 20) contain the monoclinic phase.

Figure 3 represents the melting behavior as a function of the draw ratio by DSC experiments on strained fibers. There is a difference between the results from the two melting experiments, especially on the fibers with a draw ratio of 20. The melting behavior of strained fibers with a draw ratio of 20 is very complicated. A broad endotherm peak seems to be composed of three peaks, of which the first peak (lowest temperature) is the melting peak of folded-chain crystals, the third one (highest temperature) represents that of extended-chain crystals, and the one in the middle is possibly that of a crystalline morphology between folded- and extended-chain crystalline morphology. The small peak (near

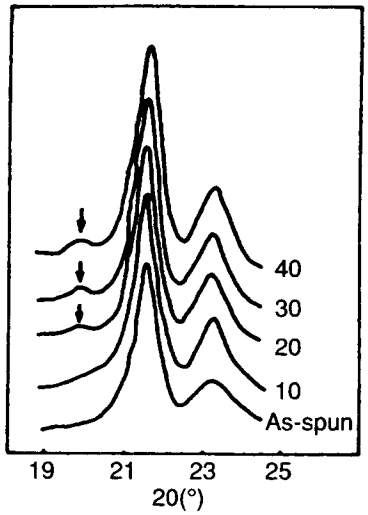

Figure 2 X-ray diffraction profile of UHMW-PE fibers.

430 K) characterized by the melting of the monoclinic phase is stronger than that in the DSC curves from the melting experiments on unstrained fibers with a draw ratio of 20, which indicates that in fibers under a strained state (constant-length state) the orthorhombic-to-monoclinic solid-state phase transitions increase.

This idea is also supported by the melting behavior of the fibers with a draw ratio beyond 30. On the DSC curves of strained fibers with a draw ratio > 30, the first peak (T_1, near 420 K) cannot been seen clearly, but, instead, a departure to the endotherm from the reference line, and the second peak (T_2) and the third one (T_3) are also been observed, respectively, near 428 and 432 K. All the above show that at a higher draw ratio (> 30) transformations of folded-to-extended-chain structure, the orthorhombic-to-monoclinic phase, occur in the fibers and the perfection of the folded-chain structure in the fibers is improved. In the measurements on strained fibers, these more perfect folded-chain structures possibly recrystallized into the extended-chain structure, even to the monoclinic phase. From these results, it is known that the state of the fiber samples, strained or not, affects DSC measurements deeply. In addition, comparing DSC curves obtained with different heating rates (Fig. 2), though the trends of these curves are largely analogous, the melting peaks of orthorhombic and monoclinic crystals in the curve with a lower heating rate appear more distinct, which shows that the heating rate also affects the results to a certain extent. Table I summarizes the characteristics of both melting curves on strained and unstrained fibers.

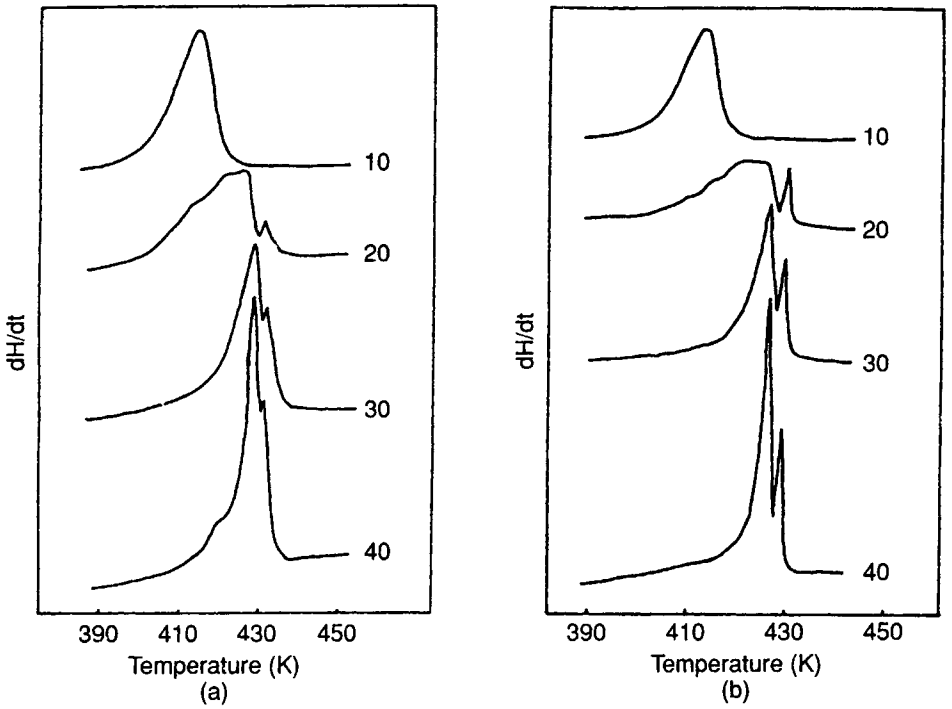

Figure 3 DSC thermograms showing the melting behavior of strained fibers: (a) 20°C/min; (b) 5°C/min.

The UHMW-PE gel fiber obtained through gel-spinning remains at a very low chain entanglement density and exhibits very high extensibility. During the drawing process, with increase of the draw ratio, polymer chains orient themselves and crystallize rapidly in the draw direction. The degree of orientation and crystallization are greatly enhanced, and at the same time, the characteristic folded-chain lamellar structure of flexible polymers convert into the fibrillar one. The higher the draw ratio, the higher the fractions of extended-chain structure and the monoclinic phase in the fiber obtained.

It is generally thought that the mechanical properties of the fibers depend mainly on the degree of orientation and crystallization of the fibers, when their molecular weights are constant.[11,12] For the UHMW-PE fibers of this system, when the draw ratio is over 30, the degree of orientation and crystallization increase slowly with increasing draw ratio, tending to a plateau value (Fig. 4), whereas the tensile strength and modulus obviously still increase (Fig. 5). From these results, it is known that simply using the structure parameters such as degree of orientation and crystallization can not comprehen-

Table I Characteristics of the DSC Curves of UHMW-PE Fibers

State	Draw Ratio	T_1 (K)	T_2 (K)	T_3 (K)	ΔH (J/g)
Unstrained	As-spun	409.38	—	—	175.42
	10	414.23	—	—	199.20
	20	415.16	—	430.87	209.38
	30	418.42	426.00	431.43	217.16
	40	418.63	427.98	432.43	218.17
Strained	10	414.52	—	—	189.78
	20	421.97	426.04	431.51	189.91
	30	—	428.96	431.98	199.79
	40	—	428.93	431.09	205.69

sively draw the relationship between the structure of the UHMW-PE fiber and the draw ratio, due to the transformations of folded-chain to extended-chain crystals and the orthorhombic-to-monoclinic phase occurring in the drawing process. It is these transformations that endow fibers with excellent tensile properties.

With increase of the content of the extended-chain structure, the number of molecules in the cross section of the fiber increases and the structure becomes more compact, which results in the fiber with excellent tensile properties. In terms of this research system, to obtain high-performance UHMW-PE fiber, the draw ratio should be above 30.

CONCLUSIONS

In the present work, the measurements of crystallinity, melting behavior, crystalline morphology, sonic velocity orientation factor, tensile strength, and modulus have been made on dry gel fibers as a function of the draw ratio. From the analysis of the data, the following results were obtained:

1. There are three crystalline morphologies, folded-chain crystals and extended-chain crystals of the orthorhombic system and the monoclinic system, existing in the fibers with a high draw ratio (>20).
2. With increase of the draw ratio, the fractions of extended-chain crystals and the monoclinic phase increase.

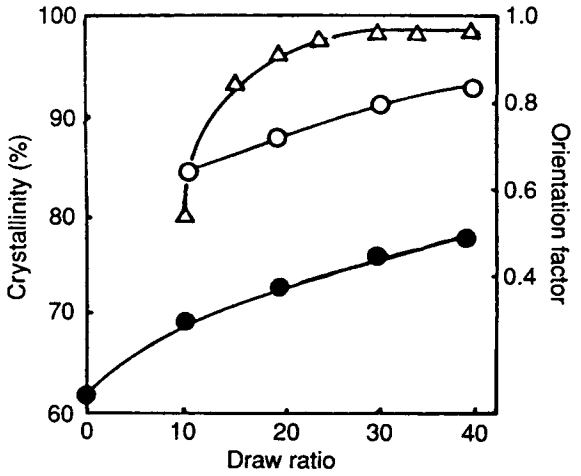

Figure 4 Crystallinity and sonic velocity orientation factor vs. draw ratio for UHMW-PE fibers: (●) crystallinity by DSC method; (○) crystallinity by density gradient column method; (△) sonic velocity orientation factor.

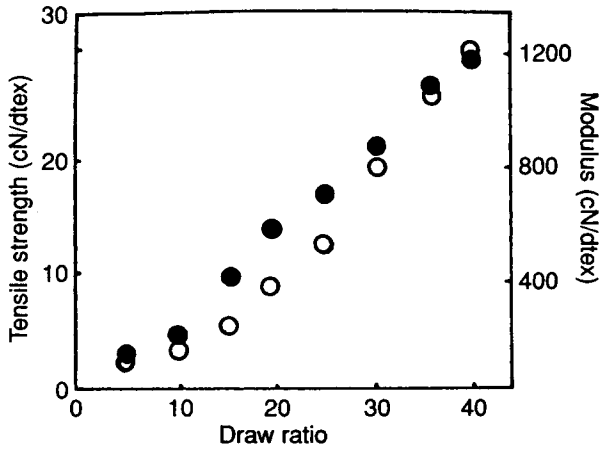

Figure 5 Tensile strength and modulus of UHMW-PE fibers as a function of draw ratio: (●) tesile strength; (○) modulus.

3. The tensile strength, similar to the modulus of the fibers, increases with increasing draw ratio in the range that we researched, whereas the sonic velocity orientation factor and the degree of crystallinity increase slowly when the draw ratio is over 30.

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