Study on Gel-Spinning Process of Ultra-High Molecular Weight Polyethylene

ZHANG YUFENG, XIAO CHANGFA, JIA GUANGXIA, AN SHULIN

Department of Material Science, Tianjin Institute of Textile Science and Technology,
Tianjin 300160, People's Republic of China

ABSTRACT: An ultra-high molecular weight polyethylene (UHMW-PE) fiber was prepared by gel spinning using general kerosene as the solvent and gasoline as the extraction solvent. The process of the phase separation of gel as-spun, spun under various spinning conditions, was investigated. Its extracting and drying process were also studied. The results reveal that the gel as-spun, spun under a lower spin draft and a lower spin quenching temperature, extracted in times and dried under free-shrinkage, exhibits a good afterdrawability that eventually endows the fiber with excellent mechanical behaviors. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 670–675, 1999

Key words: ultra-high molecular weight polyethylene; gel spinning; extraction; drying; drawing

INTRODUCTION

Fibers of rigid-rod polymer spun from liquid crystalline solution and melt exhibit high strength and modulus. High-performance fibers and films have also been obtained from flexible polymers by various methods such as zone drawing,[1–3] solid-state extrusion,[4–6] gel–fiber drawing,[7–10] and crystallization of fibrillar crystals under shear.[11] Among them, the gel–fiber drawing method has been commercially employed for producing high-performance ultra-high molecular weight polyethylene (UHMW-PE) fiber. In a previous article,[12] we reported that an UHMW-PE fiber was prepared by gel–fiber drawing using general kerosene and gasoline as the solvent and extraction solvent, respectively. The fiber exhibits excellent tensile strength and modulus. Investigations made in the article mainly focused on the changes of the thermal behaviors and the mechanical properties of the fiber during the drawing process.

The results showed that with the increase of draw ratio, the morphology of macromolecular chains was changed from a folded state to an extended chain structure and the crystal form was changed from orthorhombic to monoclinic phase, whereas the mechanical properties were thus enhanced linearly.

The present work was concerned with the process of gel spinning, extraction, and drying of the gel UHMW-PE fiber. Factors such as spin draft, quenching temperature, extraction and drying mode, etc. were taken into account as those affecting the afterdrawability of the gel as-spun, and the optimum conditions for preparing gel as-spun having good afterdrawability were obtained eventually.

EXPERIMENTAL

Preparation of UHMW-PE Gel As-Spun

The UHMW-PE gel as-spun samples used in this study were prepared by dissolving 5 wt % linear polyethylene (PE) (Beijing Auxiliaries, Plant No.

2, China; with a weight-average molecular weight of 3×10^6) in kerosene (boiling point, 160–180°C) into which 0.3 wt % antioxidant was added. The gel filaments were spun through a self-made minispinning apparatus with 0.1-mm diameter holes into a quenching water bath at a temperature range of 0–30°C and at various spinning drafts ranging from 1 to 10. The kerosene in the as-spun was first removed by a phase separation that occurred in the gel filaments, which began as soon as it got into quenching bath and continuing when it is left for a certain amount of time. Residual solvent in the gel filaments was then extracted with gasoline (boiling point, 120°C) in 1–4 times at a total bath ratio of 30. The gel filaments thus obtained were dried at room temperature under constant-length, controlled-shrinkage, and free-shrinkage mode, respectively. Dried gel as-spun was at last subjected to afterdrawing test.

Drawing Test of Gel As-Spun

The drawing of gel as-spun was carried out at a temperature of 80–100°C on a self-made drawing machine. The drawing rate ranges from 3 to 4 m/min.

Sonic Velocity Measurement

The orientation factor of sonic velocity was determined by measuring the transit time of a sound pulse between two transducers 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. (1),

$$f_s = 1 - (Cu/C)^2 \qquad (1)$$

where Cu is the sonic velocity of the fully unoriented sample, taken as 1.40 km/s.

Thermal Behavior Measurement

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 cut into small pieces, weighted accurately at 8 ± 0.5 mg, and heated to 473 K at a heating rate of 20 K/min.

RESULTS AND DISCUSSION

The Phase Separation of Gel As-Spun

Phase separation is one of the common characteristics of gel. It is known from thermodynamics whether a polymer can be dissolved into a solvent or remain as a homogeneous solution. It must be satisfied with eq. (2),

$$\Delta F_m = \Delta H_m - T\Delta S_m \qquad (2)$$

where ΔF_m is the free energy of dissolution; T is absolute temperature; ΔH_m is the heat of dissolution; and ΔS_m is the entropy of dissolution. For a process of a nonpolar polymer dissolving into a nonpolar solvent, $\Delta H_m \geqq 0$ and $\Delta S_m > 0$, it can only occur when T is high enough to meet $\Delta H_m < T\Delta S_m$. A homogeneous solution of a nonpolar polymer into a nonpolar solvent prepared at a high temperature may get unstable when the temperature decreases and the balance of the system is therefore upset and the polymer coagulates from the solution, which means phase separation occurs. The temperature at which phase separation begins is taken as the temperature of phase separation.

UHMW-PE is a typically nonpolar polymer with high molecular weight and chain regularity and is usually dissolved above 140°C. At this temperature, the process of dissolution can meet $\Delta H_m < T\Delta S_m$. When spun, the spinning stream is quenched to form a filament with a structure of low-chain entanglement at a quenching temperature of < 30°C, which is much lower than the temperature of the phase separation, and the phase separation occurs simultaneously. When the filament or the gel as-spun is placed at room temperature, the phase separation will continuously occur. Along with separating the solvent, the supermolecular structure of gel (a structure of molecular network with low entanglement) has to be gradually formed. There are a number of factors affecting the process of the phase separation such as the concentration of solution, characteristics of solvent, molecular weight, and its distribution of the polymer, conditions of spinning, conditions of placement, etc., whereas the formation of the structure of the gel as-spun relates closely to them during the phase-separation process.

The description of the phase separation of as-spun gel under various spinning draft and temperatures of quenching is shown in Figure 1. The ordinate indicates the weight-loss rate of the gel, R_w, described as

$$R_w = \frac{w_0 - w_t}{w_0} \times 100\% \qquad (3)$$

Figure 1 Changes of the weight-loss rate of gel as-spun with spinning conditions and time. (—○—) Spinning draft: 2; quenching temperature: 25°C. (—●—) Spinning draft: 2; quenching temperature: 5°C. (—□—) Spinning draft: 1; quenching temperature: 25°C. (—■—) Spinning draft: 1; quenching temperature: 5°C.

where w_0 is the original weight of as-spun, and w_t is the weight at time t. The abscissa is time.

From Figure 1 it can be seen that the rate of the phase separation of the gel is very fast and nearly 90% of the solvent separates from the gel at the initial 30 min. The rate of phase separation then tends to be slower. After about 4 h, the weight of as-spun is constant and the phase separation basically ends at this moment. It can also be found from Figure 1 that with the increase of spin draft or the elevation of quenching temperature and the amount of the solvent separated out increases but the rate of phase separation changes little. This result indicates that the gel as-spuns formed under different conditions contain differences in their structure. On the one hand, with the increase of spin draft, macromolecules tend to be extended and oriented and the macromolecular network tends to be compact in the draw direction of the gel as-spun. W. Hoogsteen, et al. have reported that the gel as-spun spun at a spinning draft of five is of a shish-kebab-type structure.[13] With the compaction of the structure of gel as-spun, more solvent in the gel is squeezed out during phase separation. On the other hand, a relatively temperate quenching condition enables the macromolecules to have enough relaxing time to arrange compactly, which also results in more solvent being squeezed out.

It should be noted that very little solvent separated in the quenching bath is neglected in Fig-ure 1, because the staying time of the gel getting through is extremely short. Whether this neglect could affect the result needs further investigation.

Extraction of Gel

The process of the extraction of gel is, in substance, a process during which the solvent 2 (extraction agent) diffuses and permeates with solvent 1 mutually contained in the gel and eventually replaces the solvent 1 in gel. Usually solvent 2 is called for as follows: (1) excellent compatibility with solvent 1; (2) low boiling point and high volatility; (3) constant state of macromolecules of gel during or after the extraction process; (4) high availability, low price, and feasibility in industrialization.

In the present work, by using general gasoline as the solvent 2, the extraction process of gel was investigated. Figure 2 shows changes of extraction rate with time. It can be observed that the extraction rate increases rapidly with time at the beginning and then tends to level off. The balance–extraction rate spin draft is nearly 90%. Further investigations revealed that the balance-extraction rate spin draft is relative to the bath ratio and the number of times of extraction, as shown in Figure 3. Figure 3(a) shows that the balance extraction rate increases to a plateau with the increase of bath ratio, and Figure 3(b) shows that the extraction times has more efficiency.

It should be pointed out that no matter how the balance extraction rate is enhanced, solvent 1 contained in the gel cannot be completely extracted. After drying, the gel still contains a cer-

Figure 2 Changes of extraction rate with time.

Figure 3 Relationship of the balanced extraction rate of gel as-spun with extraction bath ratio (a) and the number of times of extraction (b).

tain amount of solvent 1, which mainly consists of compositions with high boiling point and low volatility. These compositions are embraced in the inner of macromolecular network and result in a significant effect in the drawing process of gel as-spun.[14]

Drying of the Gel As-Spun

Gel as-spuns, spun under various conditions, were dried after equivalent extractions. Figure 4 shows the changes of shrinkage rate of the as-spuns with spin draft and quenching temperature. It can be seen that the shrinkage rate in drying decreases to a constant with the increase

Figure 4 Changes of the shrinkage rate in drying of gel as-spun with spinning conditions. Quenching temperature: (—●—) 5°C; (—■—) 10°C; (—□—) 25°C.

of spin draft to a ratio of >6 or so. In terms of this experiment, a higher quenching temperature results in a higher shrinkage rate in drying.

The shrinkage of gel in drying is mainly attributed to the formation of a large vacancy in the network, which results from volatilization of the solvent contained in the gel during the drying process.

As discussed above, the structure of the gel tends to be more compact as the spin draft increases or the temperature of quenching bath rises, the compaction in gel structure weakens the solvation, and therefore, results in the decrease of vacancy and of shrinkage in drying.

However, this kind of compaction in structure is very limited; in other words, the high-solvated macromolecular network system formed during the complete dissolution process is far from recovering the state previous to its dissolving to form a structure with high crystallinity and separated completely with the solvent. So the decrease of the shrinkage with the increase of spin draft in drying is limited too, that is, when spin draft is high enough, the shrinkage rate of dry gel tends to be constant and hardly decreases anymore.

Figure 5 shows the change of the sonic orientation factor, f_s, of the gel filaments obtained under various drying conditions. It can be seen that f_s decreases with the increase of shrinkage in drying, in constant-length and controlled-shrinkage drying. f_s also decreases with the increase in spin draft, but in this case is contrary to free-shrinkage drying, which is probably due to more vacancy formed in low spin-drafted samples than

Figure 5 Changes of sonic orientation factor of gel as-spun with spinning draft under various of drying conditions. (—■—) Constant-length drying; (—●—) 10% shrinkage drying; (—▲—) 20% shrinkage drying; (—▼—) Free-shrinkage drying.

in high spin-drafted samples during drying. There thus exists greater shrink tension in low stretched samples that enforces macromolecules to orient to a certain extent in constant-length and controlled-shrinkage drying but which results in a higher shrinkage in free-shrinkage drying. These results further prove that differences exist among gel samples with various spin drafts.

Drawing of Gel As-Spun

The mechanical properties of UHMW-PE gel fiber increases with the increase of afterdrawing ratio,[12,13] so it is important to improve the afterdrawability of the gel fiber. Figure 6 shows the maximum draw ratios, λ_{max}, of various samples. It can be seen that λ_{max} increases with a decreasing spin draft or a decreasing quenching temperature. In addition, the maximum draw ratio of samples under free-shrinkage drying is significantly higher than under constant-length drying. Through DSC measurements, it is known that the DSC curves are considerably different between the two drawn samples in that the main peak for free-shrinkage is narrower and has a larger area. This indicates that the structure of the drawn fibers from the free-shrinkage drying samples are perfect.

It thus can be concluded that the sufficient shrink of gel as-spun in drying improves its afterdrawability and behaviors after its drawing.

Figure 6 Relationships between the maximum draw ratio of gel filaments with spinning draft and quenching temperature after drying under various conditions. (—■—) Quenching temperature 25°C, constant-length drying; (—●—) quenching temperature 25°C, free-shrinkage drying; (—▲—) quenching temperature 5°C, constant-length drying; (—▼—) quenching temperature 5°C, free-shrinkage drying.

CONCLUSIONS

UHMW-PE gel as-spun prepared under a low spin draft (≤2) and a low quenching temperature

Figure 7 DSC curves of the two drawn filaments. (1) Dried under free-shrink condition; (2) dried under constant-length condition.

(≤5°C) by proper extraction and drying conditions (extracting times and a free-shrinkage drying, respectively) can result in good afterdrawability and eventually a better structure and excellent behavior.

REFERENCES

1. Savitskij, A. V.; Levin, B. Ya.; Demicheva, V. P. Vysokomol Soedin, Ser A 1973, 15, 1286.
2. Kamezawa, M.; Yamada, K.; Takayanagi, M. J Appl Polym Sci 1979, 24, 1227.
3. Nakagawa, K.; Yamamoto, F.; Takeuchi, Y.; Yamakawa, S. J Polym Sci, Polym Phys Ed 1985, 23, 1193.
4. Perkins, W. M.; Capitati, N. J.; Porter, R. S. Polym Eng Sci 1976, 16, 200.
5. Kanamoto, T.; Zacharides, A. E.; Porter, R. S. J Polym Sci, Polym Phys Ed 1981, 18, 575.
6. Smith, P.; Lemstra, P. J. Makromol Chem 1979, 189, 2983.
7. Smith, P.; Lemstra, P. J. J Mater Sci 1980, 15, 505.
8. Smith, P.; Lemstra, P. J. Polymer 1980, 21, 1341.
9. Smith, P.; Lemstra, P. J.; Pijpers, J. P. L.; Kiel, A. M. Colloid Polym Sci 1981, 259, 1070.
10. Torfs, J. C. M.; Pennings, A. J. J Appl Polym Sci 1981, 26, 303.
11. Xiao, C. F.; Zhang, Y. F.; An, S. L.; Jia, G. X. J Appl Polym Sci 1996, 159, 931–935.
12. Hoogsteen, W.; ten Brinke, G.; Pinnings, A. J. Colloid Polym Sci 1988, 266, 1003.
13. Zhang, Y. F.; An, S. L.; Jia, G. X.; Xiao, C. F.; Tianjin, J. Inst Text Sci Technol 1996, 15(2), 18.