Structure of PAN Precursor in Thermal-Induced Gel Spinning

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ABSTRACT: The thermal-induced gel spinning of polyacrylonitrile/dimethyl sulfoxide/water solutions were performed. The structure and performance of the PAN precursor fibers were characterized by mechanical properties testing, swelling capacity testing, scanning electron microscopy, and X-ray diffraction. The effects of the water content, polymer concentration, coagulation bath temperature, and draw ratio on the cross-sectional morphology, structure, and tensile properties are reported. The results show that 2% water content is optimal due to dispersed small pores found in the fibers' cross section. With the coagulating bath temperature decreased, the large pores in fibers also decreased. Large pores almost disappeared up to −9°C. The mechanical properties of the PAN fibers increased with the enhancement of PAN concentration, while the decrease of the coagulating bath temperature or water content would induce the improvement of the fibers' mechanical properties. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1176–1181, 2011

Key words: PAN precursor; gel spinning; gels; fibers; morphology

INTRODUCTION

PAN-based precursor fibers are widely known for producing high performance carbon fibers.[1–5] Conventional spinning processes for PAN precursor fiber, such as wet spinning and dry-wet spinning,[6,7] have inherent disadvantages of uneven skin and core structure due to the phase-separation process in the coagulation bath, hence greatly weakening the performance of the carbon fiber. To avoid this skin and core disparity, gel spinning is introduced by doping nonsolvent into the PAN spinning solution and/or using a low-processing temperature.[8,9] Because of the spinning dope changed from solution state to gel state before the filament entering into coagulation bath, the "skin-core" structure resulted from mass transfer can be greatly inhibited because of the fixation of the configuration of PAN chain. Thus, perfect precursors are supposed to be achieved and greatly improved the performance of the final carbon fibers.[10] PAN gel spinning with ultrahigh molecular weight PAN and low concentration has been researched.[11] However, PAN with ultrahigh molecular weight is difficult to dissolve and further obtain a homogeneous solution. On the other hand, the low PAN concentration is adverse to increase mechanical property of the fibers. Our group has studied the rheology behavior of PAN solutions with conventional PAN molecular weight and comparative high PAN concentration.[12–14]

In this article, solutions with regular molecular weight and comparatively high concentration PAN were used. The effects of the nonsolvent (H_2O), polymer concentration, coagulation bath temperature, and draw ratio on the cross-sectional morphology, structure, and tensile properties are reported.

EXPERIMENTAL

Materials

PAN copolymers (acrylonitrile: itaconic acid = 98 : 2 by weight) were provided by Shanghai Institute of Synthetic Fiber with a viscosity-average molecular weight about 7.8×10^4 g·mol^{-1}. All the other reagents are analytical grade, if not otherwise stated. Dimethyl sulfoxide (DMSO) was obtained from Boer chemical (Shanghai). Deionization water was used without further treatment.

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TABLE I
Content of PAN, DMSO, and H_2O in the Each Spinning Solution (wt %)

No.	PAN	DMSO	H_2O
1	20	78	2
2	20	76	4
3	23	73	4

TABLE II
Swelling Capacity of PAN Precursors at Different Processing Conditions

Samples	Temperature in first coagulation bath (°C)	Swelling capacity (%)
1	0	200
1	−3	178
1	−9	152
2	−9	165
3	−9	145

Preparation of PAN/DMSO/H_2O spinning solutions

All the experimental equipments and PAN materials were dried at 70°C for 3 h in advance to insure desiccation. The solvent used for the experiments were mixtures of DMSO and nonsolvent, H_2O. A given amount of PAN was swelled statically in the mixed solvent at 55°C for 4 h first, and then stirred at 70°C for another 4 h to ensure PAN dissolved evenly. The solutions were deaerated in a vacuum drying oven at 70 °C for the removal of air bubbles before spinning. The weight percent (wt %) of each component was listed in Table I. The viscosities of spinning solutions can refer to Ref. 15.

Fiber spinning

A homemade piston-type spinning machine was used to fabricate PAN precursor fibers. The spinning temperature was 70 ± 0.2°C, and the air gap length was 30 mm. The length-diameter ratio and diameter of the single-hole spinneret are 10 and 0.8 mm, respectively. The velocity of freely extruded solution was 3.3 $m \cdot min^{-1}$. The spinning solutions was gel spun in a 70-wt % DMSO coagulation bath first, the temperature of which was controlled by a thermostat, as seen in Table II. Then, the filaments were introduced to the second coagulating bath containing 40-wt % DMSO at room temperature. The obtained fibers were drawn at various stages: first in water at 25°C drawn to a draw ratio 1.4, then predrawn 1.5-fold in water at 85°C. Finally, the fiber was stretched 2.0-fold in boiling water and 1.5-fold in dry air at 145°C. The schematic diagram of gel spinning process is shown in Figure 1.

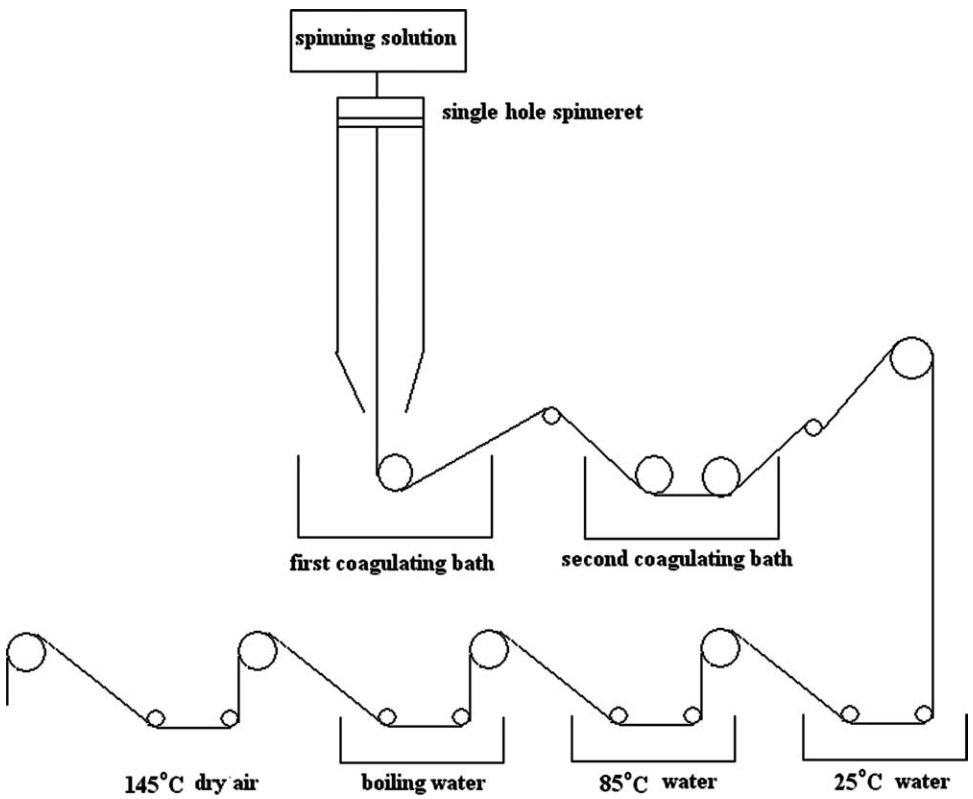

Figure 1 Schematic diagram of gel spinning process.

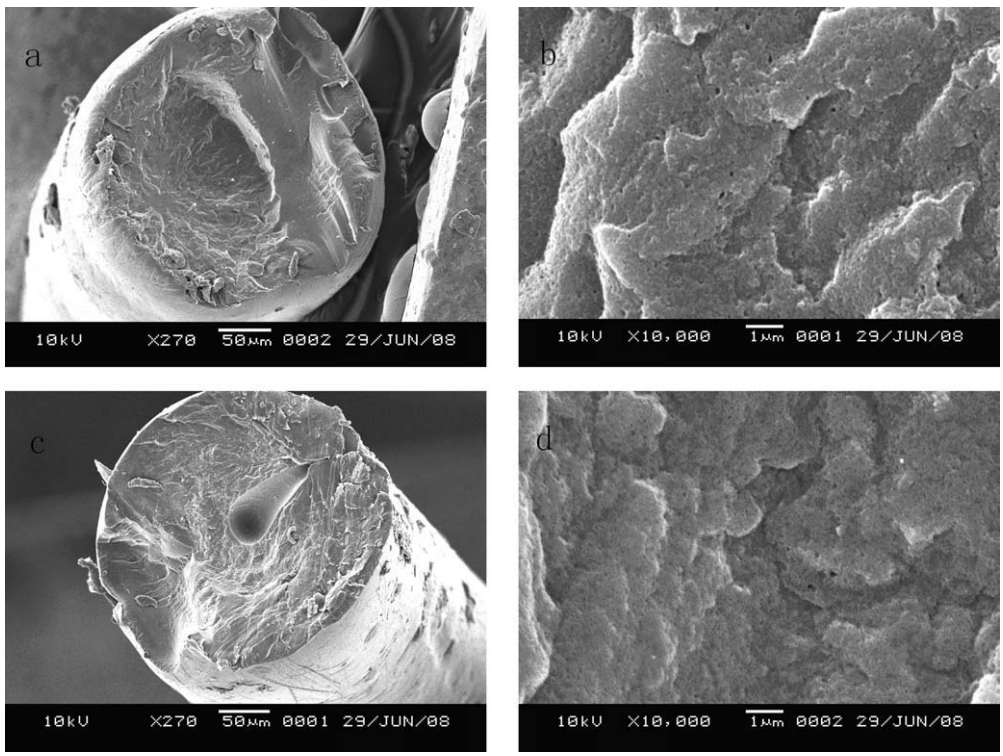

Figure 2 SEM photographs of PAN fibers spun with different H_2O content. (a and b) H_2O = 2% and (c and d) H_2O = 4%. PAN = 20%. The magnifications for a,c and b,d is 270 and 10,000, respectively.

Measurement

The mechanical properties of PAN precursors were measured by a XQ-1 tensile testing machine(Donghua University, China) at a crosshead speed of 10 mm min^{-1} with a testing length of 10 mm and load cell of 10 g. In each case, at least 30 sample filaments were tested, and the average of 30 filaments was taken for each experiment.

A given fiber sample was immersed in the mixture of water and ice for 24 h, then dehydrated in a centrifuge (TGL-16C, Anting, shanghai)(ω = 4000 r min^{-1}) for 5 min. The weight of the fiber was set as W_1. Then the fibers were dried in oven at 100°C for 1 h to a constant weight, W_0. The swelling capacity (P) was calculated as eq. (1):

$$P = \{(W_1 - W_0)/W_0\} \times 100\% \quad (1)$$

Scanning electron microscopic (SEM) observations of sample surfaces were made on a JSM-5600LV scanning electron microscope (JEOL, Japan). SEM photographs were taken at magnifications of 270–10,000×.

A D/max-2550 PC X-ray diffractometer(Rigaku, Japan) with Ni-filtered Cu Ka radiation (the wavelength λ = 0.1541 nm) was used to determine the structure of fibers with an accelerated voltage of 40 kV and a current of 60 mA, a scanning rate of 3° min^{-1} and a scanning step of 0.02°. The crystallinity (χ_c), and the crystallite size Lc of the fibers can be calculated by eq. (2) and Scherrer formula [eq. (3)][16] as follows:

$$\chi_c = \frac{A_c}{A_a + A_c} \times 100\% \quad (2)$$

$$L_c = \frac{K\lambda}{B\cos\theta} \quad (3)$$

where A_c and A_a are the areas under the crystalline and amorphous curves, respectively. λ = 0.1541 nm is the wavelength of Cu Ka radiation, B is the full width at half the maximum intensity (FWHM) of the (002) peak around 2θ = 25.5°, K is a constant, assigned as 0.89. For orientation measurements, the fiber samples were cut into 3 cm. The 2θ angle of 16.9° was used to determine the fiber orientation. With 2θ set at 16.9°, an azimuthal scan was taken.

RESULTS AND DISCUSSION

Effect of H_2O content

The SEM photographs of PAN precursor fibers after the first coagulating bath at −9°C spun with different H_2O content are given in Figure 2. It can be seen that the cross-sectional shape of both fibers is almost rotundity, which would improve the mechanical characteristic of the final carbon fiber compared with the PAN precursor with a kidney shape produced through dry-wet spinning. No fibers exhibited the

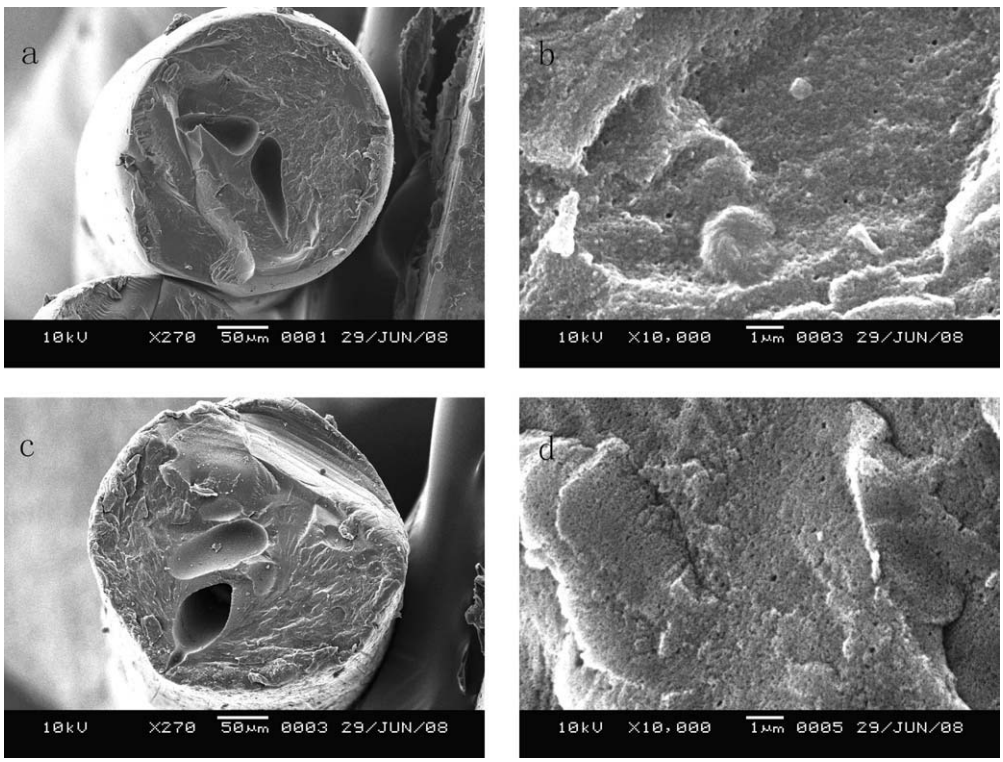

Figure 3 SEM photographs of PAN fibers spun at different first coagulation bath temperatures. (a) (b) −3°C, and (c and d) 0°C. PAN = 20%, H_2O = 2%. The magnifications for a and c and b and d is 270 and 10,000, respectively.

obvious large voids. Comparatively, the sample with 2% H_2O show uniform dispersed small voids.

Effect of the coagulation bath temperature

The SEM photographs of Sample 1 (H_2O 2%, PAN = 20%) at various first coagulation bath temperature are given in Figures 3. It can be seen that the cross-sectional shape of both fibers is rotundity too in spite of the coagulation bath temperature. Compared with Figure 2(a,b), when the coagulation bath temperature was decreased to −9°C, the fiber exhibited the minimum number of large voids. From our early study, 0°C is lower than the gel point of Sample 1, whose gel point is only 26.3°C.[17] But, the gel point is only the temperature that the spinning solution begin to gel, not having been a gel. So, the degree of gelation depended on not only the temperature but also the time. The filaments stay at the first coagulation bath only a few seconds, so increase the difference in temperature between spinning solution, and the coagulation bath is an effective method to ensure gelation as much as possible.

The swelling capacity

The swelling capacity can character the voids volume of the PAN precursors. A high value of swelling capacity means a big void volume in the precursor fiber. Table II shows us the swelling capacity of PAN precursors at different processing conditions. As can be seen, the swelling capacity decreases along the temperature in first coagulation bath reducing, which also expresses fewer voids can be found in lower coagulation bath temperature. Compared the samples with different H_2O content, the sample with 2% H_2O show lower swelling capacity, which is consistent with what we get in Figure 2. In addition, higher PAN concentration induced lower swelling capacity.

Mechanical properties

Tensile strength and breaking elongation ratio are the main characteristics of the mechanical properties of the fibers. Table III shows the mechanical properties of the PAN precursors produced at different coagulation bath temperatures. The tensile strength

TABLE III
Mechanical Properties of PAN Gel Fibers After Different First Coagulation Bath

Samples	Temperature in first coagulation bath (°C)	Tensile strength (CN/dtex)	Elongation at break (%)
1	0	5.09 ± 0.43	14.41 ± 1.35
1	−3	5.47 ± 0.43	12.16 ± 1.07
1	−9	5.82 ± 0.50	14.63 ± 1.15
2	−9	5.64 ± 0.44	10.01 ± 0.92
3	−9	6.01 ± 0.53	12.61 ± 1.31

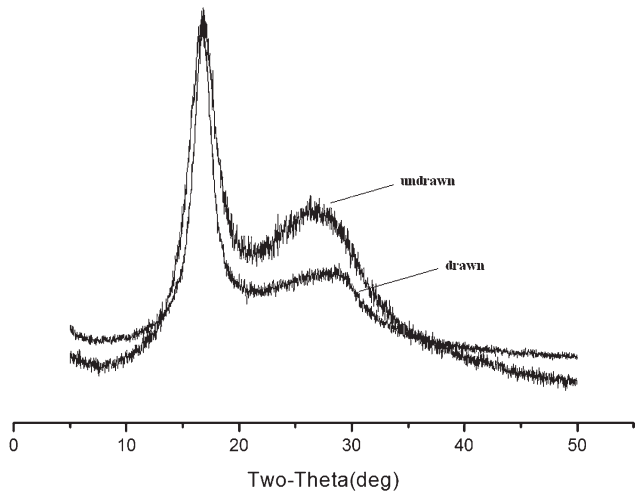

Figure 4 XRD patterns of drawn and undrawn PAN fibers. PAN = 20%, H_2O = 4%.

and elongation at break of the gel fibers obtained from first coagulation bath decrease with an increasing coagulation bath temperature. The tensile strength of the gel fiber produced at 0°C coagulation bath temperature is 5.09 CN·dtex^{-1}, and that at −9°C is 5.82 CN·dtex^{-1}. The percentage elongation at break of the gel fiber also decreases from 14.63 to 12.16% with an increase in temperature. The strength and elongation at break of the gel fibers depend largely on the number and size of voids present. The number and size of the voids of the gel fibers at 0°C are greater (Fig. 3) than those obtained at −9°C, so the strength and elongation at break of the fiber at 0°C will be lower than −9°C, as the voids acted as weak linkages or sites for breakage.

On the other hand, the tensile strength rises when the H_2O content decreases or PAN concentration increases, due to small and little voids of the gel fibers. In addition, the gel point increases when PAN concentration rises. So, at the same coagulation bath temperature, the filament with more PAN occur gelation more easily, which prohibits the diffusion of the solvent and nonsolvent to some extent and improves the mechanical properties of the fibers.

Crystallinity and orientation

High-performance carbon fibers must possess high tensile strength and breaking elongation ratio, which lies on the crystallinity and orientation of the PAN precursor fibers. The X-ray diffraction patterns of Sample 2 are given in Figure 4. The tendency of the drawn and undrawn pattern of Sample 1 is similar. The crystallinity degree, orientation, and crystalline size of PAN precursors with different H_2O content are listed in Table IV. It can be seen that the crystallinity degree and crystalline size drop when the H_2O content increases for the drawn gel fibers. While, for the undrawn gel fibers, the trend is opposite. This can be explained that the arrangement of PAN macromolecule chains is more difficult under stretch when more H_2O molecules exist in the system. On the other hand, when the fibers are stretched, the molecules become oriented toward the fiber axis and contribute toward the total strength. The sample with 2% H_2O shows an increase of crystallinity degree, orientation, and crystalline size after stretch compared with the sample with 4% H_2O. The increase of the orientation, crystallinity index, and crystalline size led to an increase in tensile strength and crystallinity for PAN precursors, which would determine the crystalline parameters and mechanical properties of final carbon fibers.[18] For the drawn fibers, the cross section is also rotundity. The sample with 2% H_2O has a relative high mechanical property after drawn, as seen in Table IV. This means H_2O content is a very important factor in the PAN gel spinning, and proper H_2O content is beneficial to improve the mechanical properties of final carbon fibers. In this system, 2% H_2O content is optimal.

CONCLUSIONS

The structure development during thermal-induced gel spinning of polyacrylonitrile/DMSO/water system was studied. The cross-sectional shape of the obtained fibers is almost rotundity and exhibits few obvious large voids, which would improve the mechanical characteristic of the final carbon fiber compared with the PAN precursor produced through dry-wet spinning. When the coagulation bath temperature is decreased from 0 to −9°C, the fiber exhibits the minimum number of large voids. Increasing the difference in temperature between spinning solution and the coagulation bath is an effective method to ensure gelation. The swelling capacity decreases when the temperature in first

TABLE IV
Crystallinity Degree, Orientation, Crystalline Size, and Tensile Strength of PAN Precursors with Different H_2O Content and Draw Ratio

Samples	Crystalline size (Å)		Crystallinity (%)		Orientation (%)	Tensile strength (GPa)
	Undrawn	Drawn	Undrawn	Drawn	Drawn	Drawn
1	27	38	41.13	54.37	77.8	0.93
2	39	28	59.17	47.56	74.2	0.87

coagulation bath decreases. For different H_2O content, the sample with 2% H_2O shows lower swelling capacity. The tensile strength and elongation at break of the gel fibers obtained from first coagulation bath decrease with an increasing coagulation bath temperature. The tensile strength rises when the H_2O content decreases or PAN concentration increases, due to small and little voids of the gel fibers. The sample with 2% H_2O shows an increase of crystallinity degree, orientation, and crystalline size after stretch, which means 2% H_2O content is better for the gel spinning of PAN/DMSO system.

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