Investigating the Jet Stretch in the Wet Spinning of PAN Fiber

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ABSTRACT: The jet stretch of wet-spun PAN fiber and its effects on the cross-section shape and properties of fibers were investigated for the PAN-DMSO-H_2O system. Evidently, the spinning parameters, such as dope temperature, bath concentration, and bath temperature, influenced the jet stretch. Also, under uniform conditions, the postdrawing ratio changed as well as that of jet stretch. When coagulation temperature was 35°C simultaneously with bath concentration of 70%, jet stretch impacted obviously the cross-section shapes of PAN fiber, but had little effect when the temperature was below 10°C or above 70°C. As the jet stretch ratio increased, the crystallinity, crystal size, sonic orientation, and mechanical properties of the as-spun fiber changed rapidly to a major value for jet stretch ratio of 0.9 where the cross section of as-spun fiber was circular. With further increasing of jet stretch ratio, the properties changed slightly but the fiber shape was not circular. The results indicated that appropriate jet stretch, under milder formation conditions in wet-spinning, could result in the higher postdrawing ratio and circular profile of PAN fiber, which were helpful to produce round PAN precursor with minor titer and perfect properties for carbon fiber. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2267–2273, 2007

Key words: carbon fiber; PAN fiber; wet spinning; jet stretch; drawing process; cross-section shape

INTRODUCTION

Carbon fiber made from polyacrylonitrile (PAN) precursors has several beneficial features that make it attractive for those industries such as the aerospace, aviation, atomic, ship building industries, and production of high quality sporting goods.[1] A significant prerequisite for fabricating carbon fiber with high performance is first to spin PAN fibers with circular cross-section shape and excellent properties, such as a high orientation, high crystallinity, and minor titer. Generally, such PAN fiber is wet spun using organic solvent solution as coagulation bath, for example, DMSO. This is a concentration process so that manufacturing such fiber is theoretically, very difficult. Some researchers[2,3] have been made PAN fiber with circular cross-section shape with high bath temperature or using water as the coagulation bath. Like any wet-spun process, the fiber structure is controlled by the rate of counterdiffusion of solvent (DMSO) and nonsolvent (H_2O) and phase separation of the PAN copolymers. It impacts the fiber physical properties and the type of aftertreatments of the final product. However, under these coagulation conditions the rate of diffusion and phase separation was too high to obtain perfect structure and properties even the cross-section shape of the obtained PAN fiber is circular.

Stretching of wet-spun process includes two types of drawing: stretching in bath (jet stretch) and postdrawing. The postdrawing process is very important in altering fiber structure and enhancing fiber properties. In this stretching process the orientation of the fibrillar network (formed in the coagulation bath) increases, thereby improving the fiber strength and decreasing its titer. Attempts have been made to describe its influence on PAN fiber's structure and properties.[4–6] As for stretching in bath, some literatures of early days[7,8] demonstrated the influence of jet stretch on the spinning process and properties of polyester, polyvinyl alcohol, viscose fiber, etc. But opinion as regards the influence of the jet stretch on the fiber properties was not unanimous. To date, however, a good description of stretch in bath in a wet-spinning of PAN fiber has not materialized.

The jet stretch is generally accepted as a comprehensive index of the rheology and hydrodynamic process of wet spinning. It influences the shear rate

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at the capillary wall and degree of dope swell at the exit of the capillary and thus alters the rates of diffusion. Increasing jet stretch ratio decreases the rate diffusion, and then affects the profile and structure of fiber. High-jet-stretch conditions produce small void structures. Also, small void structures dry, collapse, and relax under milder conditions than larger void structures (low jet stretch). These structures ultimately determine the process equipment and conditions for producing wet-spun fiber.

However, stretching in bath is too complex with multiple variables to consider and control. When calculating the true jet stretch account must be taken of the jet swell and, in certain cases, of the shrinkage of the as-spun fiber. Therefore, the simpler parameter, the apparent jet stretch, is used to describe the stretching process.

The apparent jet stretch (ϕ_a) is simply defined as the ratio of the first roller take-up velocity to the dope extrusion velocity. It is commonly calculated from the expression

$$\Phi_a = V_1/V_0 \quad (1)$$

where V_0 is the extrusion velocity of the spinning dope through the spinneret hole and V_1 is the taking-up speed.

In this study, to obtain circular PAN fiber with high orientation, high crystallinity and minor titer, the apparent jet-stretch of wet spinning and its effects on the postdrawing ratios, including drawing in wash water and boiling water, and on the properties of PAN fibers were investigated. It is noted that a publication of particular experiment on the jet stretch in PAN fiber wet-spinning for the PAN-DMSO-H_2O system is no existence.

EXPERIMENTAL

Materials

PAN copolymers (acrylonitrile: methylacrylate: itaconic acid = 96 : 2.5 : 1.5), purchased from Shanghai Petrochemical Ltd and with a viscometric average molecular weight of 1.5×10^5 g mol^{-1}, were dissolved in the mixture of DMSO with the weight percent of 3% water to get a homogenous dope. The polymer weight percent concentration was 20.9%. A mixture of H_2O/DMSO was used as the coagulation bath. The water used for the PAN dope, the washing bath and the coagulation bath was deionized water.

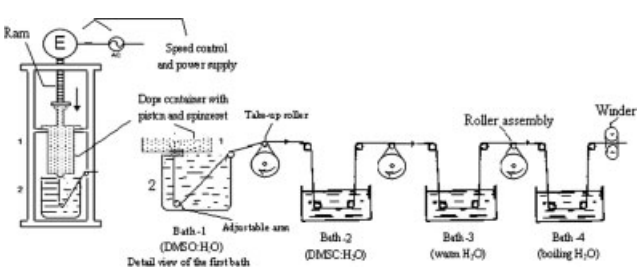

Figure 1 Sketch of laboratory spinning apparatus.

TABLE I
Process Parameters and Spinning Conditions

Process parameters/spinning conditions	Constant	Variation limits
Spinning solution temperature (°C)	75	65–95
Extrusion velocities (m min^{-1})	9.67	–
Apparent jet-stretch (%)	–	−1.00–3.00
Temperature of coagulation bath (°C)	35	10–70
Concentration of coagulation bath (%)	70	0–70

Wet spinning and sampling

A sketch of the self-built experimental spinning apparatus is shown in Figure 1. The dope was passed through a spinneret of six holes (diameter of 0.1 mm) directly into the coagulation bath. The as-spun fibers were collected out from the first coagulation bath with different apparent jet-stretch for cross-section shape and property investigation and then passed over a roller into the second bath, which contained DMSO and H_2O.

The as-spun fibers were stretched up to different drawing ratio at this stage. The fibers were then washed in a bath containing water at 60°C. The fibers were subsequently washed in water at boil and further drawn up.

To study the effect of jet-stretch on the properties of the as-spun fiber, the gel fiber samples were taken from the coagulation bath, washed thoroughly with cold distilled water, and preserved at low temperature before studying their characteristics. The resulting fibers from the boiling water were also washed thoroughly with distilled water to remove residual DMSO. After rinsing and drying in air for 2 days at 25°C, the fibers were put in an oven of 115°C with vacuum for 15–20 min for determining their properties. Table I summarized the detailed process parameters and spinning conditions.

Cross-section shape of gel fibers

The ultrathin cross sections of the gel fibers, collected at different coagulation conditions, were made on Y172 Fiber microtome (Hardy's thin cross-section sampling device), and then were studied under an optical microscope using 400× magnification.

Mechanical properties

The mechanical properties of PAN fibers were measured on a tensile-testing machine (Taicang Textile Machinery, China) under standard conditions (i.e., relative humidity = 65 ± 2%, temperature = 27 ± 2°C) with a crosshead speed of 10 mm/min and a testing length of 20 mm. In each case, at least 30 samples were tested, and the average value was obtained.

Sonic orientation

The sonic orientation of the as-spun fibers was measured on a pulse propagation meter so that we could get an idea about the overall orientation. A single filament was mounted between two transducers containing a piezoelectric ceramic crystal with a natural frequency of 5 kHz.

Wide-angle X-ray diffraction (WAXD)

To calculate the crystallinity and crystal size of the as-spun fiber, X-ray diffraction of the powdered specimens was obtained on a Rigaku D/max-2500PC X-ray diffractometer with nickel-filtered Cu Kα radiation at a 1° scan rate. The size of the ordered domains was estimated by the Scherrer equation:

$$L_c = \frac{K\lambda}{\beta \cos \theta} \tag{2}$$

where L_c is the average lateral size (crystal size); β is the width at half maximum intensity at $2\theta = 17^\circ$; K is the Scherrer constant (0.89); and λ is the wavelength of the X-ray used (1.54 Å).

RESULTS AND DISCUSSION

Effect of process parameters and spinning conditions on maximum jet stretch

In this spinning process, the ram speed (V_r) was kept at 0.2899 cm/min. The volumetric throughput rate (Q) was adjusted at

TABLE II
Effect of Spinning Dope Temperature on Maximum Jet-stretch and Postdrawing Ratio at Bath Temperature 35°C, at Bath Concentration 70%

Sample	Dope temperature (°C)	Maximum jet-stretch ratio	Maximum postdrawing ratio
1	65	2.27	8.39
2	75	2.35	11.18
3	85	2.44	12.13
4	95	2.37	9.28

TABLE III
Effect of Bath Concentration on Maximum Jet-stretch and Postdrawing Ratio at Dope Temperature 75°C, at Bath Temperture 70°C

Sample	Bath concentration (%)	Maximum jet stretch	Maximum postdrawing ratio
1	0	2. 02	8.36
2	10	1.99	7.71
3	30	1.95	6.96
4	55	2.13	10.77
5	70	2.35	11.18

$$Q = V_r \pi R^2 = 1.83 \text{ mL/min} \tag{3}$$

where R was the radius (cm) of the dope container.

Now, the average jet velocity was calculated as

$$V_0 = Q/\pi n r^2 \tag{4}$$

where r and n are the radius (mm) and the number of the spinneret hole, respectively.

$$V_0 = \frac{1.8283}{6 \times 3.14 \times (0.01/2)^2} = 3.88 \times 10^3 \text{ cm/min} \tag{5}$$

Therefore, according to eq. (1), the jet stretch ratios can be easily fixed by changing the speed (V_1) of the taking-up roller.

It is clear that for a given throughput rate, the take-up velocity cannot be increased infinitely. The maximum jet stretch is the highest ratio that is attainable without filament breakage in the coagulation bath.

Table II shows the plots of the temperature of spinning dope versus maximum jet stretch ($(V_1/V_0)m$) and maximum postdrawing ratio. It is seen that the maximum jet-stretch increases firstly then goes down as the dope temperature increases. The maximum postdrawing ratio changes similarly. Evidently, controlling dope temperature (75–85°C) results in the higher maximum jet-stretch and postdrawing.

Table III shows the coagulation bath concentration versus maximum jet stretch and maximum postdrawing ratio. It is found that below bath concentration of 30%, the maximum jet stretch decreases with an increase of the bath concentration, but increases as bath concentration increases up to 70%. A similar result is reported in paper.[9–11] Capone G. J.[12] believed a concept of maximum coagulation bath stretch is a function of solvent concentration. When ratio of water to solvent is a value, for instance 30% bath concentration, where the dope viscosity goes through a maximum, the jet-stretch is minimum.

TABLE IV
Effect of Bath Temperature on Maximum Jet-stretch and Postdrawing Ratio at Dope Temperature 75°C, at Bath Concentration 70%

Sample	Bath temperature (°C)	Maximum jet stretch	Maximum postdrawing ratio
1	10	2.63	12.07
2	35	2. 35	11.18
3	55	2.10	11.03
4	70	1.98	9.28

Below the ratio, there is an excess of water in the system, coagulation occurs rapidly, and a porous structure, i.e. the outer skin, is formed. This porous structure can be drawn and supports high stretch tensions. As bath concentration is approached the coagulation slows, the associated solvent/nonsolvent pair behaves as a coagulant, and the fiber structural differences from the coagulated outer radius to the fluid center of filament cannot support the higher stress. As the solvent level is increased further, there is excess solvent relative to the water, less driving force for phase separation, the radial structure differences within the fiber are less with a thinner skin, and therefore the maximum jet stretch ratio increases dramatically, so does the maximum postdrawing ratio.

As would be expected, increasing the bath temperature decreases the maximum jet stretch and postdrawing ratio (as shown in Table IV). The mechanism is again the acceleration in the rates of diffusion and phase separation.

Table V shows the coagulation bath time versus maximum jet stretch and maximum postdrawing ratio. From the Table, maximum jet stretch increases as the coagulation time increases. As in most processes of wet spinning, a long duration of the stay of fiber in coagulation bath cause the longitudinal precipitation of as-spun fiber that results in the decrease of gel proportion in the fiber. So does the maximum postdrawing ratio. Both of these results are in agreement with general expectations.

TABLE V
Effect of Coagulant Time on Maximum Jet-stretch and Postdrawing Ratio at Dope Temperature 75°C, at Bath Concentration 70% and Temperature 35°C

Sample	Coagulant time (min)	Maximum jet stretch	Maximum postdrawing ratio
1	<5	2.04	9.06
2	25	2.13	12.35
3	50	2.15	13.07
4	100	2.42	15.09

Effect of jet-stretch on maximum postdrawing ratio

Stretching of as-spun fiber in bath has great effect on its subsequent stretchability. An analysis of this carried out by changing taking-up speed are plotted in Figure 2. It shows that a sudden decrease in maximum postdrawing under the range of jet stretch ratio (from 0.9 to 2.0). Generally, under some coagulating conditions, due to the decreasing in the degree of dope swell, the ability to draw the fiber also decreases and limits the jet stretch. If the ratios of the jet stretch go beyond the limit, the weak gel network is easily broken, thereby decreasing evidently the postdrawing ratio.

However, when the ratio of jet stretch is from 0.6 to 1.0, the maximum postdrawing is higher enough to obtain circular cross-section shape and excellent properties of as-spun fiber for PAN precursor (Shown in Figure 3 and Table VI).

Effect of jet stretch on the cross-section of PAN as-spun fiber

When the bath coagulating concentration was 70%, the cross-section shapes of as-spun fiber with different jet stretch ratio were determined under the bath temperature 0, 10, 15, 25, 35, 45, and 70°C, respectively. It was experimentally found that all cross-section shapes of different jet stretch ratio were kidney shape as the bath temperature was 0°C. Within the temperature of 15–25°C, as the jet stretch ratio increased, they didn't change significantly, just from a kidney shape to a flat shape. At the temperature of 35°C, they change clearly from a circular shape to a bean shape. With the temperature 45°C, they altered similarly to that of bath

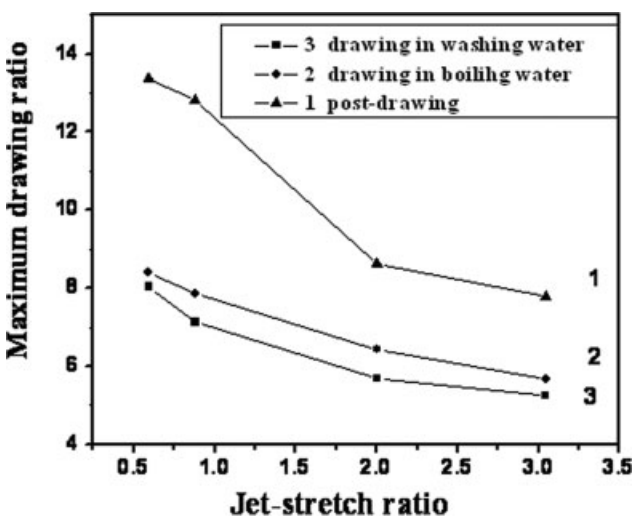

Figure 2 Effects of jet-stretch on maximum postdrawing ratio.

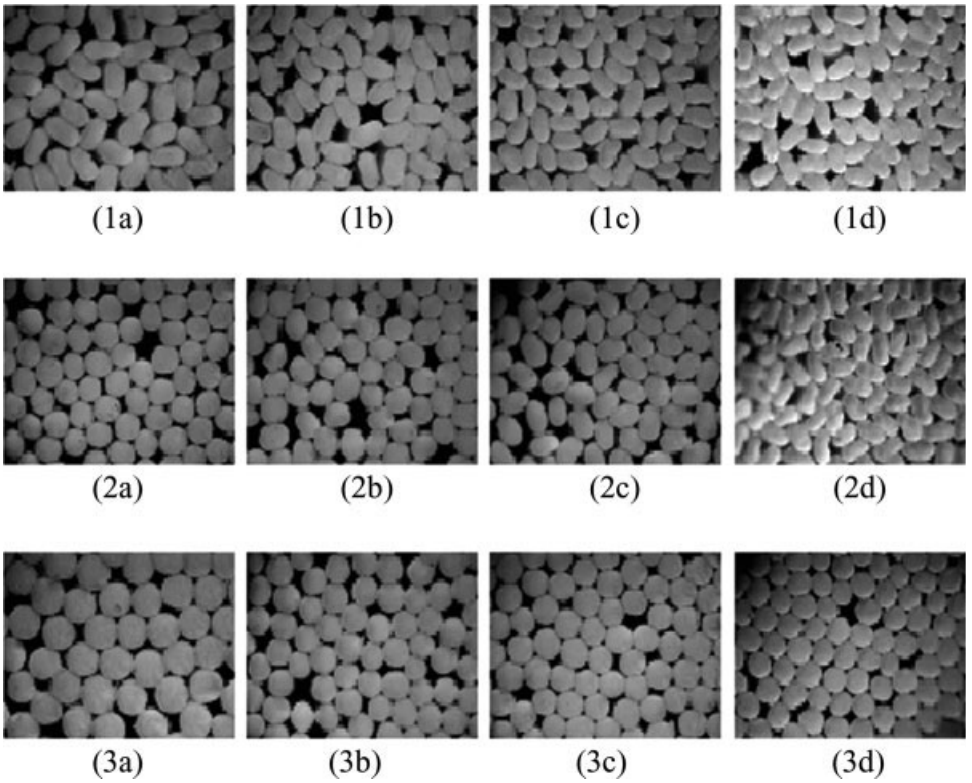

Figure 3 OM photographs of PAN as-spun fibers with different formation conditions: *jet-stretch: 0.00, 1.06, 1.94, 2.72; Bath temperature: 1a–1d: 10°C; 2a–2d: 35°C; 3a–3d: 70°C.

temperature 35°C, but started to change, just a little variation from round shape into to an approximate circular shape as the jet stretch ratio increase up to 1.94. To illustrate these phenomena, the cross sections of three typical kinds corresponding to various coagulating temperature observed under an optical microscope are shown in Figure 3. From Figure 3, when the temperature is below 10°C or above 70°C, the cross-section shapes remain almost unchanged with an increasing jet stretch. Furthermore, the similar results were found for the other bath concentration. For example, as the bath concentration was 55%, the cross-section shapes did not change significantly from a round shape to a bean shape with jet stretch ratio until the bath temperature was up to 45°C.

Generally, round fiber by wet-spinning process can be produced by two methods: (1) increasing the coagulation rate by using high bath temperature [shown in Fig. 3: 3(a–d)] or using pure water as coagulation bath, as in the preceding case, and building a thick outer structure that remains round as diffusion process; (2) decreasing the coagulation rate and producing a thin outer structure that uniformly coagulates with the interior of the fiber, like Figure 3: 2(a–d). Thus, under mild formation conditions that excellent structure and properties of PAN can be obtained with DMSO solvent, the PAN fiber with circular cross-section can be manufactured by controlling the appropriate jet stretch, i.e. jet stretch ratio below 1.0.

Effect of jet-stretch on properties of PAN fibers

The change in the properties of the as-spun, maximum postdrawing and postdrawing ratio of 9.0 fiber with a variation of the jet stretch ratio are shown in Table VI.

When the jet stretch ratio increase by increasing the taking-up speed, the crystallinity, crystal size, sonic orientation and tenacity of the as-spun fiber begin to increase slightly, but increase suddenly with the creasing of jet stretch ratio up to 0.9, evidently owing to the increased orientation resulting from the increased jet stretch, the hydrodynamic resistance of the bath liquor to the fiber movement is reinforced, which results in mild coagulation and slow diffusion interchange.[13] When the jet stretch ratio increases furtherly, they increase again, but gradually. With an overly increasing in the spinning speed, the duration of the stay of the fiber in the bath decreases so that the orientation effect is

TABLE VI
Mechanical Properties of Fibers Collected before and after Postdrawing at Bath Concentration 70% and Temperature 35°C

	Properties of as-spun fiber					Properties of postdrawing					
						Maximum postdrawing			Postdrawing ratio of 9.0		
Apparent jet stretch	Sonic orientation (%)	Crystallinity (%)	Crystal size (nm)	Titer (dtex)	Tenacity cN/dtex (cv%)	Crystal size (nm)	Titer (dtex)	Tenacity cN/dtex (cv%)	Breaking elongation % (cv%)	Tenacity cN/dtex (cv%)	Breaking elongation % (cv%)
0.30	65	35.6	1.006	40.76	0.62 (15.1)	3.867	16.32	3.84 (20.3)	21.54 (11.3)	3.51 (16.0)	23.61 (6.8)
0.59	67	37.5	1.052	38.63	0.73 (14.3)	3.958	14.38	4.06 (16.9)	20.11 (14.6)	3.96 (14.1)	21.19 (9.5)
0.88	75	44.7	1.398	34.76	0.95 (10.0)	4.231	8.37	4.89 (18.0)	18.65 (12.0)	4.54 (11.5)	20.23 (7.5)
1.20	78	44.9	1.423	30.62	1.02 (13.2)	4.232	9.59	4.48 (22.3)	18.32 (17.0)	4.21 (15.2)	19.38 (10.2)
2.05	79	44.8	1.425	29.41	1.03 (17.4)	4.234	12.73	3.95 (33.9)	17.67 (18.2)	3.91 (18.6)	18.67 (13.7)

reduced. The titers of as-spun fiber drop from 40.76 to 29.41 dtex with an increase in the jet stretch ratios.

From Table VI, it can also be seen that the firmness of postdrawing fiber begins to increase sharply and reaches up to a maximum also with jet stretch ratio of 0.9, then decreases gradually when the jet stretch ratio increases. This is because that an improving of as-spun fiber properties by increasing jet-stretch cause the tenacity of the postdrawing fiber increases. Similar behavior is observed for the crystal size of the postdrawing fiber and as-spun fiber. This result shows that the crystalline state of PAN, which can be described as two-phase with distinct pseudocrystalline (ordered) and amorphous (disordered) phases, was mainly controlled by drawing in coagulation bath. The postdrawing plays an important role on the crystalline perfection. Comparing the titers of the as-spun fiber, the variation of postdrawing fiber's titers differs from that of as-spun fiber. They firstly decrease from 16.32 to 8.37 dtex when the jet stretch ratio increases from 0.3 to 0.88, then go up to 12.73 dtex. Evidently, a too great increasing of the jet stretch decreases the titers of as-spun fiber, also decreasing postdrawing ratio. Hence, the total drawing ratios goes up firstly then drops in spinning process, which causes the variation of the post drawing fiber's titer. These results are in agreement with those showed in Figures 2 and 3, and also indicate it is possible to achieve the fiber with circular cross-section shape and properties of high orientation and crystallinity, minor titer by controlling appropriate jet stretch ratio.

CONCLUSIONS

The results showed that a correlation existed between the jet stretch and the coagulation conditions, subsequent stretchability of the as-spun fiber and cross-section shape and properties of PAN fiber. The spinning parameters had a uniform influence, which indicated that it was possible to obtain simultaneously higher ratio of jet stretch and postdrawing, resulting in minor fiber titer. It was also noted that, under some mild coagulation conditions of wet spinning with DMSO solvent, controlling the jet stretch ratio closing to 1.00 leaded to the PAN fiber of circular cross section, minor titer and high orientation and crystallinity. These results of our experiments would hopefully be useful for preparing PAN precursor with perfect properties for carbon fiber.

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