Investigation the Jet Stretch in PAN Fiber Dry-Jet Wet Spinning for PAN-DMSO-H_2O System

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ABSTRACT: The jet stretch of dry-jet wet spun PAN fiber and its effects on the cross-section shape of fibers were investigated for a PAN-DMSO-H_2O system. Clearly, the spinning parameters, such as dope temperature, bath concentration, bath temperature, and air gap, all influenced the jet stretch. Also, under uniform conditions, the postdrawing ratio as well as that of jet stretch changed. Under given conditions, as the bath temperature was below 30°C or above 45°C, jet stretch had little effect on the cross-sectional shapes of PAN fiber. Within the temperature of 30–45°C, fiber's cross-section shapes change obviously from round over an approximate circular shape into to an elliptical or a flat shape. The scope of jet stretch produced PAN fiber with circular cross-section was bigger than that in wet spinning. These results indicated that appropriate air gap height, under milder formation conditions in dry-jet wet spinning, could result in higher jet stretch and higher postdrawing ratio. The appropriate jet stretch and postdrawing ratio could result in circular profile of PAN fiber, which were helpful to produce round PAN precursor with finer size and better properties for carbon fiber. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3621–3625, 2009

Key words: carbon fiber; pan fiber; dry-jet wet spinning; jet stretch; shape factor; cross-section shape

INTRODUCTION

Carbon fibers not only combine high tensile strength and modulus with low weigh, but also exhibit exceptional thermophysical properties and excellent damping characteristics.[1–4] Polyacrylonitrile (PAN) fibers are the most widely used precursors for producing carbon fibers, owing to a variety of reasons.[5–9]

Generally, optimum PAN precursors have many features, such as homogeneous structure, fine denier, high crystallinity, high orientation, and so on. Such fibers are either wet spun or dry-jet wet spun using dimethyl sulfoxide (DMSO)-water solution as a coagulation bath. To obtain them, attempts have been made by increasing drawing ratio, usually by increasing the postdrawing ratio during stretching process of both spinning methods. But in both spinning processes the postdrawing ratio is not very high and is influenced by jet stretch.[10]

Like postdrawing process, the jet stretch step is very important in altering fiber structure and enhancing fiber properties. In wet spinning, the extruded dope is brought into coagulation bath such that the exchange between the solvent and nonsolvent takes place until the polymer precipitates. Hence, the jet stretch occurs inside the coagulation bath, and is affected by the properties of the extrusion dope and the coagulation conditions. Some literatures[11,12] demonstrated such influence on the spinning process of wet spinning and hence the resulting properties of polyester, polyvinyl alcohol, and viscose fibers in general. A few reports focused on the jet stretch in PAN fibers wet spinning.[13,14] Dry-jet wet spinning is a modification of the wet spinning, whereby the freshly extruded dope passes through an air gap before entering a coagulation bath. In the air gap region, heat transfer and solvent transpiration from the surface of the extruded fluid to environment occur. Once inside the coagulation bath, similar to the wet spinning case, diffusions of

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solvent and nonsolvent between the solidified skin and the fluid core, as well as between the filament and the coagulation bath take place.[15–17] Thus, the jet stretch in dry-jet wet spinning is influenced not only by the properties of the spinning dope and the coagulation conditions, but also by the air gap. Compared to wet spinning, jet stretch in dry-jet wet spinning is more complicated.

Like in wet spinning, the apparent jet stretch (Φ_a) is simply defined as the ratio of the first roller take-up velocity (V_1) to the dope extrusion velocity (V_0) as defined in eq. (1).

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

That is, different jet stretches can be attained by changing either V_1 or V_0. Keeping V_0 constant, the maximum jet stretch is determined by the maximum take-up velocity, which characterizes the spinnability of the spinning dope.

In our previous study,[10] we investigated experimental process and results of jet stretch in wet spinning. It was found that jet stretch ratio had key effect on postdrawing process, and a too great increasing of the jet stretch decreased the properties of as-spun fiber and PAN fiber, also decreasing postdrawing ratio. Clearly, it is very important to control appropriate jet stretch for PAN precursor with finer size and perfect properties. However, in case of dry-jet wet spinning, no such a comprehensive study has been reported publicly upto now. In this article, we presented the results from our recent experimental investigation on the apparent jet stretch in PAN fiber dry-jet wet spinning process for the PAN-DMSO-H_2O system.

EXPERIMENTAL

Material and spinning

PAN copolymers (the weight percent of acrylonitrile : methylacrylate : itaconic acid = 96 : 2.5 : 1.5), purchased from Shanghai Petrochemical, with a viscometric average molecular weight of 1.5×10^5 g mol^{-1}, were dissolved in a mixture of DMSO and water (3 wt %) to form a homogenous dope (20.9 wt %). A coagulation bath of H_2O/DMSO was used. The water used for the PAN dope, the washing bath and the coagulation bath was all deionized. The spinning dope was passed through a spinneret of six holes (diameter of 0.1 mm), over an air gap with a varying height (0–15 mm), then into the coagulation bath in the dry-jet wet spinning process, the sketch of laboratory spinning apparatus was shown in Figure 1. The as-spun fibers at different apparent jet stretches by adjusting the drawing ratio were collected from the first coagulation bath for cross-section shape examination.

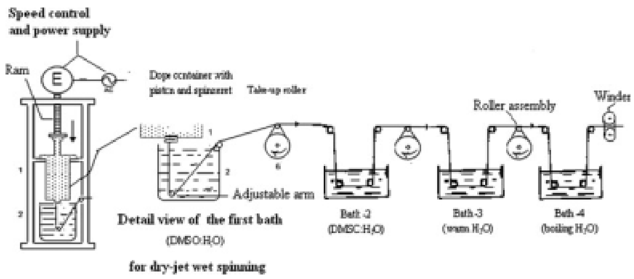

Figure 1 Sketch of laboratory spinning apparatus.

In this spinning process, the extrusion velocity through the spinneret hole (V_0) was calculated as

$$V_0 = Q/\pi n r_s^2 \qquad (2)$$

Where Q, r_s, and n were the volumetric throughput rate (mL/min), the radius (mm), and the number of the spinneret hole, respectively. In this study, the dope extrusion velocity constant (V_0) was kept constant, the jet stretch was controlled by changing the speed of the first roller take-up velocity (V_1).

The postdrawing processes included warm water bath drawing and boiling water bath drawing, their ratio were calculated as

$$p = p_1 \times (\ldots) \times p_n \qquad (3)$$

$$p_n = V_n/V_{n-1} \qquad (4)$$

where p, p_n, n, and V_n were the total drawing ratio, drawing ratio in bath-n, the number of bath, and the velocity of roller-n, respectively.

Cross-section shape of gel fibers

Generally, the shape factor (De), the extent of deviation from the circular shape, is used to characterize the fiber cross-section shape. The ultra thin cross-sections of the gel fibers, collected under different coagulation conditions, were made using an Y172FiberMicrotome (Hardy's thin cross-section sampling device), and examined under an optical microscope at 400× magnification. According to Chinese National Standards FZ/T 50,002-91,[18] after measuring the circum-radius (R) and inter circle radius (r) of the cross-sections from the fiber samples, their shape factors were calculated with eq. (5). In practice, when $De < 5\%$, the cross-section shape is considered a round shape; $5\% < De < 10\%$, an approximately circular shape; $10\% < De < 17\%$, an elliptical shape; $17\% < De < 30\%$, a flat shape; and $De > 30\%$, a kidney shape. In each case, at least 30 samples were tested, and the average value was obtained.

$$De\ (\%) = \frac{R - r}{R} \times 100\% \qquad (5)$$

RESULTS AND DISCUSSION

Effect of process parameters and spinning conditions on maximum jet stretch

Table I summarizes the maximum jet stretch ratio and the maximum postdrawing ratio versus spinning dope temperature. It is seen that the jet stretch and postdrawing ratio decrease as the dope temperature increases. Evidently, controlling low dope temperature, like 70°C, in dry-jet wet spinning would result in the higher jet stretch and postdrawing ratio. However, in dry-jet wet spinning, the effect of dope temperature is not remarkable and is associated with temperature-dependent viscoelastic characteristics of the extruded dope in air gap.

The results presented in Table II show a simultaneous increase of the maximum jet stretch and maximum postdrawing ratio with an increase of the bath concentration. These differ from the results in wet spinning process of our previous work.[10] In wet spinning, below bath concentration of 30 wt %, the maximum jet stretch and postdrawing ratio decrease with increasing bath concentration, but increase as bath concentration increases upto 70 wt %. Furthermore, the influence of bath concentration in wet spinning is more conspicuous. This indicates that, in wet spinning, counterdiffusion controlled phase transitions plays a determining role. In dry-jet wet spinning, however, due to evaporation of solvent from the surface of the fluid in the air gap, accompanied by the heat transfer, the air gap would obviously affect on jet stretch and postdrawing ratio. Thus, as will be shown in the following results, the jet stretch is directly related to coagulation conditions and air gap height in dry-jet wet spinning.

Table III presents the relationship between the bath temperatures, the maximum jet stretch, and postdrawing ratio. According to Table III, it can be seen that increasing the bath temperature decreases the maximum jet stretch and postdrawing ratio. Like the mechanism in wet spinning, increasing the bath temperature causes the acceleration in the rates of counterdiffusion and phase separation, thereby decreasing the jet stretch and postdrawing ratio.

TABLE II
Effect of Bath Concentration on Maximum jet stretch and Postdrawing Ratio at Dope Temperature 75°C, at Bath Temperature 35°C, with Air Gap 8 mm in Dry-Jet Wet Spinning

Sample	Bath concentration (wt %)	Maximum jet stretch ratio	Maximum postdrawing ratio
1#	0	5.6	11.16
2#	10	6.3	11.80
3#	30	6.58	12.18
4#	55	6.84	13.86
5#	70	7.22	14.83

Both of these results are in agreement with general expectations.

Figure 2 shows the plots of maximum jet stretch and postdrawing ratio versus air gap height at the same coagulation conditions. The maximum jet stretch increases as air gap height increases upto 10 mm. So does the maximum postdrawing ratio. Above air gap height of 10 mm, the jet stretch increases again, just a little variation. But the maximum postdrawing ratio decreases obviously. Thus, in the dry-jet wet spinning of PAN fiber, appropriate air gap height would result in high jet stretch and postdrawing ratio. In this work, the maximum jet stretch and postdrawing ratio were obtained at the air gap of 10 mm. It is to be noted, however, that the jet stretch increases sharply from 2.35 to 6.90 and the postdrawing ratio also increases sharply from 11.18 to 13.31 when the air gap height changes from 0 mm (wet spinning) to 5.0 mm (dry-jet wet spinning), while variation is slight as air gap height is above 5.0 mm. That is to say, under the same spinning conditions from Figure 2, jet stretch and postdrawing ratio in dry-jet wet spinning exceeds greatly in wet spinning. Generally, an appropriate increasing of drawing ratio would result in PAN fibers with excellent properties, such as high orientation, high crystallinity, and fine denier. This is just one of the advantages of dry-jet wet spinning.

In dry-jet wet spinning, there are two formation mechanisms taking place in the air gap region and in coagulation bath, respectively. In air gap region,

TABLE I
Effect of Spinning Dope Temperature on Maximum jet stretch and Postdrawing Ratio at Bath Temperature 35°C, at Bath Concentration 70 wt %, with Air Gap 8 mm in Dry-Jet Wet Spinning

Sample	Dope temperature (°C)	Maximum jetstretch ratio	Maximum postdrawing ratio
1#	65	7.28	14.95
2#	75	7.22	14.83
3#	85	6.93	13.56
4#	95	6.89	12.68

TABLE III
Effect of Bath Temperature on Maximum jet stretch and Postdrawing Ratio at Dope Temperature 75°C, at Bath Concentration 70 wt %, with Air Gap 8 mm in Dry-Jet Wet Spinning

Sample	Bath temperature (°C)	Maximum jet stretch ratio	Maximum postdrawing ratio
1#	10	8.05	16.43
2#	35	7.22	14.83
3#	55	7.10	12.53
4#	70	6.49	12.11

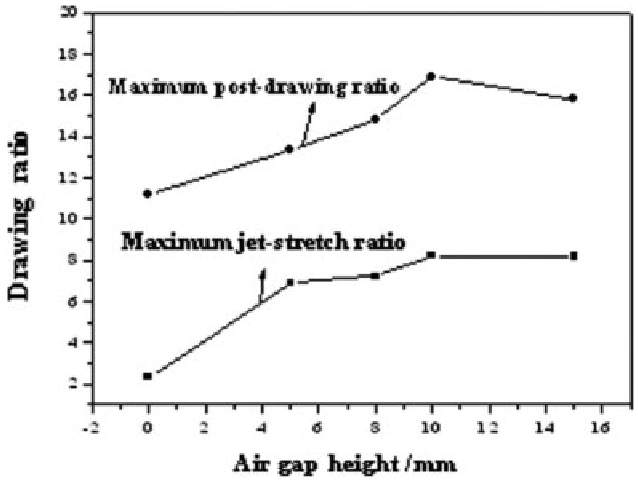

Figure 2 Effect of air gap on maximum jet stretch and postdrawing ratio at dope temperature 75°C, at bath concentration 70 wt % and bath temperature 35°C.

due to a volatilization of solvent and gravity, and the absorption of water,[19] there occur orientation and phase separation. Then a thin membrane appears on the surface of the filament. Compared with the rapid precipitation process that occurred in a fiber wet spinning process, phase separation in air gap region seems to be much slower. The skin may be more homogeneous and denser in dry-jet wet spinning. The skin is not only helpful to increase jet stretch in air gap, but also to give much resistance to counterdiffusion when the dope is immersed inside coagulation bath, thereby increasing the jet stretch in dry-jet wet spinning, even improving the properties of PAN fiber. Namely, although with short air gap, the jet stretch of dry-jet wet spinning is too much than that of wet spinning. However, air gap introduces an elongation stress on filaments because of gravity. A too long air gap results in high elongation stress, which may pull molecular chains or phase-separated domains apart in the early stage of phase separation and create porous weak skin. This would lead to filament breakage decreasing the jet stretch or bring rupture of the skin, which would increase diffusion rate in coagulation bath and result in the decreasing of postdrawing ratio. In addition, because of a too long air gap, the axial elastic strain relaxation in air gap would play a more important role than axial orientation in jet stretch and fiber properties.[20] In given conditions above, the air gap height should be controlled at 10 mm.

Comprehensively analyzing those results in Table I, II, and III, the effect of dope temperature on the jet stretch is rather small in dry-jet wet spinning for PAN-DMSO-H_2O system. The influences of the coagulation conditions, like bath temperature and concentration is more important. The influence of air gap is most remarkable. These results further interpret that jet stretch concur in the air gap and the coagulation bath during dry-jet wet spinning, while mostly in air gap. The region where jet stretch occurs is longer than that in wet spinning. Thus, jet stretch in dry-jet wet spinning is distinctly bigger than that of wet spinning.

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

When the bath concentration was 70 wt %, the cross-section shapes of as-spun fiber with different jet stretch ratio were determined at the bath temperature 0°C, 10°C, 15°C, 25°C, 35°C, 45°C, 55°C, and 70°C, respectively. It was experimentally found that the influence of jet stretch on the cross-section shape of PAN as-spun fiber was different with different coagulation conditions. All cross-section shapes of different jet stretch ratio were kidney shaped as the bath temperature was 0°C. Within the temperature of 15–25°C, with an increase of jet stretch ratio, they change slightly from kidney shape to flat shape. Temperature above 55°C, the cross-sections remained almost circular. To illustrate these phenomena, the cross-sections of four typical kinds corresponding to various coagulating temperature were observed under an optical microscope. Their corresponding shape factors are shown in Figure 3.

From Figure 3, as the bath temperature is 10°C, the cross-sectional shapes of different jet stretch ratios were kidney shaped. Their shape factors remain almost unchanged. At temperature 30°C, as the jet stretch ratio increases, fibers' shape factors firstly decrease then increase. Their cross-section shape change accordingly from round shape over an approximate circular shape into to an elliptical or a flat shape. With the temperature 45°C, they alter similarly to that of bath temperature 30°C but start

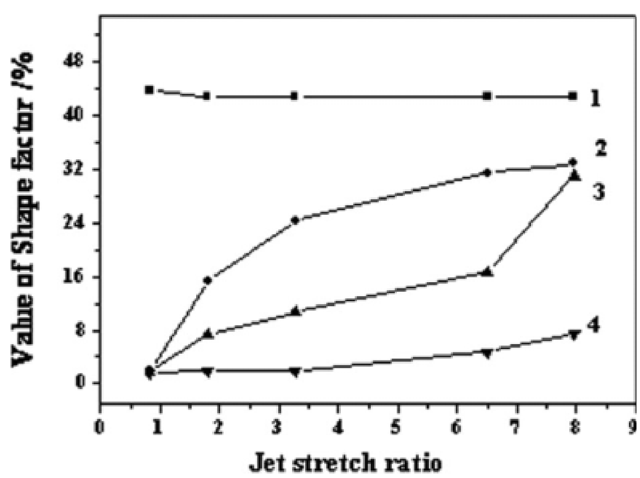

Figure 3 Effect of jet stretch on the cross-section of pan as-spun fiber: dope temperature: 75°C; bath concentration: 70 wt %; bath temperature: 1–4: 10°C, 30°C, 35°C, and 45°C.

Figure 4 OM photographs of PAN as-spun fibers with jet stretch of 9. 27, bath temperature of 30°C, dope temperature of 75°C, and bath concentration of 70 wt %.

to change, just a little variation from round shape into to an approximate circular shape as the jet stretch ratio increases upto 3.2.

Under milder formation conditions of high bath concentration 70 wt % and temperature above 30°C, the rate of diffusion and phase separation in dry-jet wet spinning is very slow. Heightening reasonably jet stretch will produce a soft and thin outer structure that uniformly coagulates with the interior of the fiber, together with the circular shape. But too great increase in jet stretch will deform the soft outer skin and lead to irregularly shaped PAN fiber (As shown in Fig. 4).

From Figure 3, in conclusions, at bath concentration 70 wt % and temperature above 30°C, PAN fibers with circular cross-section, excellent structure and properties can be manufactured by controlling the appropriate jet stretch, i.e. jet stretch below 1.35 in dry-jet wet spinning. Its jet stretch scope with this type of PAN fiber is bigger than that in wet spinning.

CONCLUSIONS

In this article, we reported a correlation existed between the jet stretch and the spinning conditions, subsequent stretchability of the as-spun fiber and cross-section shape of PAN fiber. Like in wet spinning, the spinning parameters in dry-jet wet spinning had a uniform influence on jet stretch and postdrawing ratio, which indicated that it was possible to obtain simultaneously higher ratio of jet stretch and postdrawing, resulting in fine denier fiber. Among the spinning parameters, the influence of air gap on jet stretch and postdrawing ratio is most remarkable. And also, under the same spinning parameters, the jet stretch and postdrawing ratio in dry-jet wet spinning exceed greatly those in wet spinning.

It was also noted that, the jet stretch in dry-jet wet spinning has important effect on the cross-sectional shape of PAN as-spun fiber. The scope of jet stretch produced PAN fiber with circular cross-section is bigger than that in wet spinning.

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