

Effect of Jet Stretch on Polyacrylonitrile As-Spun Fiber Formation

Bao-Hua Ji, Cheng-Guo Wang, Yan-Xiang Wang

Carbon Fiber Research Center, College of Material Science and Engineering, Shandong University, Jinan 250061

Received 7 November 2005; accepted 11 September 2006

DOI 10.1002/app.25490

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this article, the effect of jet stretch ratio on the extrudate die-swell effect of polyacrylonitrile spinning solution and the structure and properties of as-spun fibers was systematically analyzed by means of X-ray diffraction (XRD), electron microprobe analysis, and the measurement of die-swell ratio, boiling-water shrinkage, porosity, mechanical properties analysis, etc. It revealed the formation mechanism of the die-swell effect and spin orientation and its influences on the structure and properties of as-spun fibers. It showed that with the increase of the jet stretch ra-

tio the die-swell ratio became smaller, both the degree of spin orientation and the crystallinity increased, the microstructure of as-spun fibers became compact and homogeneous, and the cross section tended to be circular. As a result, the breaking tenacity of as-spun fibers and resultant precursors all increased. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3348–3352, 2007

Key words: jet stretch; die-swell effect; spin orientation; as-spun fibers

INTRODUCTION

It is well known that the subsequent textile properties of the fiber depends on its structure, particularly on the die-swell effect being extruded from the spinneret end, the spin orientation formed during coagulation process, the regularity of the cross-sectional shape, the integrity of the external skin, and the number and size of voids. Only if the counter-diffusion and phase equilibrium condition is met in the meantime can the coagulation of polymer solution occur favorably. Otherwise the internal and/or external defects will occur. As the primary congregation structure of the as-spun fiber and its defects will further evolve and be inherited into the resultant PAN precursors and carbon fibers, the study on the formation mechanism of the as-spun fibers is of great importance. Many scholars have been making some investigations on this aspect for many years.^{1–7} But the study focusing on the die-swell effect and the spin orientation was seldom and very inadequate. So it is urgent to carry out systematical investigation on these aspects to release its formation mechanism and corresponding evolution regularity. In this article, the effect of the jet stretch ratio on the die-swell effect, the spin orientation, and crystallinity of the as-spun fibers was discussed by applying many technical designs to the wet spinning system; then the morphology and inner defects of the as-spun fibers at various jet stretch ratios were studied to correlate the coagulation variables with the structure and properties of the as-spun fibers.

EXPERIMENTAL

Fiber formation process

DMSO solution polymerization was used to synthesize AN polymer solution. The obtained dope was deaerated, filtered, and then pumped through a spinneret (1000 holes, 0.06 mm/hole, $L/D = 1.5$) to a coagulation bath. The as-spun fibers were obtained by adjusting the jet stretch on the wet-spinning system.

Characterization

The die-swell ratio was measured as follows.⁸ Under certain extruding condition (DMSO/H₂O mixture is used as the coagulation bath, DMSO content is 65%, coagulation bath temperature 60°C, extruding temperature is about 70°C), a freely extruded as-spun fibers of certain length was chosen, the weight M was weighed after washing and drying (about 70°C). The diameter of the samples D was calculated according to formula (1). Then the die-swell ratio was calculated according to formula (2).

$$D = \sqrt{\frac{4M}{n\pi\rho CL}} \quad (1)$$

$$B = \frac{D}{D_0} \quad (2)$$

where n is the amount of the filaments, ρ is the density of the polymer solution (g/cm³), C is the mass fraction (%); L is the length of the filament (cm); M is the dried weigh of the as-spun fibers (g); D is the diameter of the as-spun fibers (cm); and D_0 is the diameter of the capillary (cm).

Correspondence to: C.-G. Wang (Wangchg@sdu.edu.cn).

The boiling-water shrinkage was measured according to GB/T 6505-1986. Samples of certain length were chosen, put into boiling water (100°C), and cooked for 30 min. The samples were taken out and their length was remeasured. Then the orientation extent of the noncrystal region was calculated by $R_a = [(L_0 - L)/L_0] \times 100\%$.⁹

X-ray data was collected with an X-ray diffractometer (Japan Rigaku D/max-Rc type, using Ni-filtered, CuK α radiation. A 2θ was made from 4° to 40°). The crystallinity of the as-spun fibers was measured by $C = (S_c/S_t) \times 100\% = [S_c/(S_a + S_t)] \times 100\%$, where S_t is the total peak area, S_a is the amorphous peak area, S_c and is the crystalline peak area.

The crystal size was directly calculated by $L = K\lambda/\beta \cos\theta$, where $\lambda = 1.541 \text{ \AA}$, K signifies the Scherrer constant (0.89 was used), and $\beta(\text{arc})$ represents the half-width at mid height around $2\theta = 17^\circ$. The degree of orientation of as-spun fibers was calculated by $\pi = [(180^\circ - \beta^\circ)/180^\circ] \times 100\%$.

The porosity of samples was measured as follows. The sample was washed and frozen in the liquid nitrogen to fix its structure. Accurately, 0.2 g of the sample was weighed and put into the dilatometer. Then, mercury-injection device was used to vacuum the vessel and mercury was injected into it. The amount of mercury that penetrates inside the sample was measured with a dilatometer, which is also the volume of voids. The porosity was calculated by formula: $\text{Porosity} = V_1/(V_1 + V_2)$ where V_1 is the volume of voids, V_2 is the volume of the sample.

The cross-sectional shapes of the as-spun fibers were observed by electron microprobe analysis (Japan JXA-8800R type).

The breaking tenacity of as-spun fibers and precursors was measured by XD-1 fineness instrument and XQ-1 tenacity-elongation instrument.

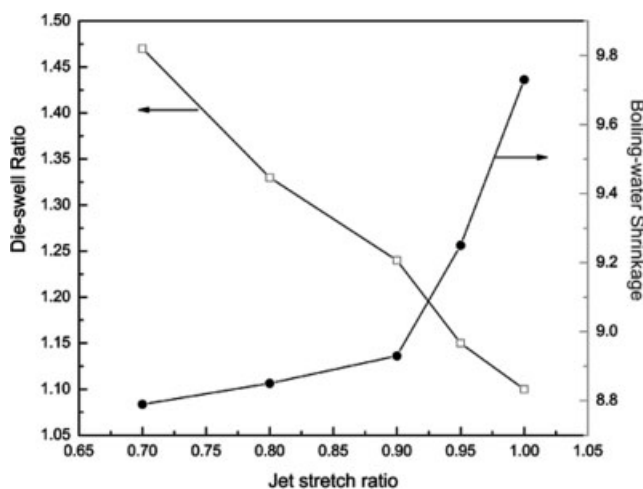


Figure 1 Effect of jet stretch ratio on the die-swell ratio and boiling-water shrinkage of as-spun fibers.

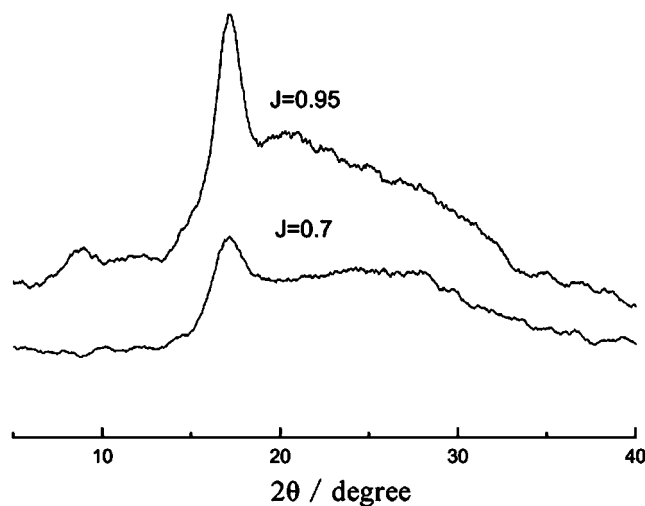


Figure 2 XRD patterns of the as-spun fibers with different jet stretch ratio.

RESULTS AND DISCUSSION

Effect of jet stretch ratio on the die-swell effect

The elastic memory of the spinning dope, stress caused by the shear field, velocity gradient on leaving the capillary, and the interaction with the coagulation bath constitutes the die-swell effect, i.e., the Barus effect. It caused a series of sequence such as: (1) The free extrusion velocity decreased largely, $V_f < V_0$ (where V_f represents the freely extruded velocity under no external stress and V_0 is the pumping velocity), and so the original jet stretch V_1/V_0 changed into V_1/V_f . The latter was much larger than the former and the amplitude even up to hundredfold. The as-spun fiber was so weak that it could hardly bear this big tensile stress and the failure in the filaments occurred; (2) The elongational viscosity increased and the counter-diffusion was hard to occur; (3) The rheological force enhanced and the as-spun fibers were easy to be injured.

As shown in Figure 1, with the increase of the jet stretch ratio, the die-swell ratio became small and the Barus effect reduced. The die-swell effect is a common characteristic of viscous-elastic polymers, which includes the entrance elastic response generated by the velocity gradient at the entrance and the elastic response generated by the shear velocity gradient in the capillary. Keeping other coagulation variables unchangeable, with the increase of the jet stretch ratio, the tensile stress along the fiber axis enhances accordingly; thus the parallel velocity gradient outside the capillary increases. According to the energy conservation principle, this increment of kinetic energy is originated from the elastic potential energy that will otherwise release along the radial direction. Thus the die-swell effect is weakened. In the meantime, the resident time in the coagulation bath becomes shorter, the interaction with the coagulation bath is reduced correspondingly, and

TABLE I
Effect of the Jet Stretch Ratio on the Structure and Properties of Fibers

Jet stretch ratio	Crystallinity of as-spun fibers (%)	Crystal size of as-spun fibers (nm)	Orientation of as-spun fibers (%)	Tenacity of as-spun fiber (cN dtex ⁻¹)	Tenacity of precursors (cN dtex ⁻¹)
1.0	39.8	1.454	19.20	0.71	7.25
0.95	37.9	1.283	17.37	0.68	7.12
0.9	35.8	1.106	15.09	0.64	6.94
0.8	33.7	1.011	13.95	0.61	6.86
0.7	32.6	0.986	12.23	0.58	6.73

so the swollen action of the as-spun fibers reduces and it favors to weaken the Barus effect.

Effect of jet stretch ratio on the spin orientation of as-spun fibers

Here the boiling-water shrinkage is used to characterize the orientation index of the noncrystal region of the as-spun fibers. As shown in Figure 1, along with the increase of the jet stretch ratio, the boiling-water shrinkage increased gradually. Because the temperature of coagulation bath does not exceed the glass-transition temperatures of the as-spun fibers, their molecular chains are basically in twist and relaxation state and the spin orientation acquired is very low. With the hoist of the jet stretch ratio, the tensile stress increases gradually. Under the action of the tensile stress the segments located in the noncrystal region can preferentially orient along the axis partly. In the meantime, because of the action of water molecules within the fibers, the interaction between the molecules becomes weakened largely and makes it easy to be oriented by drawing. Further, with the hoist of jet stretch ratio the die-swell effect is weakened and the as-spun fibers become fine, as a result of which the amount of inner microvoids contained is small, the arrangement of the molecular chains is also orderly and it favors to apply tensile stress, and thus the spin orientation is enhanced.

The mechanism of spin orientation of the as-spun fibers is as follows. The freshly coagulated as-spun fibers are divided into fluid and solid regions. In the fluid region the polymer chains are oriented by the shear velocity gradient in the capillary and the axial velocity gradient in the fluid outside the capillary; in the solid region, the spinning tension due to the elastic and viscous tensions generated within the fluid filament draws the solidified filament and thus orients the polymer chains.¹⁰

Effect of jet stretch ratio on the crystallinity and orientation of as-spun fibers

Figure 2 is the X-ray diffraction (XRD) patterns of the as-spun fibers with different jet stretch ratio. It can be seen that the as-spun fibers have strong diffraction peak around $2\theta = 17^\circ$ and 29° , which is consistent

basically with the characteristic peak of the AN/IA copolymers reported by documents.¹¹⁻¹³ Effect of the jet stretch ratio on the crystallinity and orientation of as-spun fibers is shown in Table I. While applying certain tensile stress during the coagulation process of the PAN dope, because of the action of the applied tension towards the PAN macromolecules, they are easy to orient and precipitate during coagulation process and favorable to obtain higher crystallinity and orientation degree. Under certain spinning speed the low jet stretch ratio implies a longer resident time in the coagulation bath, while the augment of the coagulation time is propitious to the hoist of the crystallinity. With the increase of the jet stretch ratio, although the shortened coagulation time renders the crystallinity of the as-spun fibers have a downward trend, the drawing action of the applied tension towards the macromolecules makes the degree of orderly arrangement of the molecular chains increase, leading to a larger crystallinity and orientation degree.

Effect of jet stretch ratio on the porosity of the as-spun fibers

The higher the jet stretch ratio is, the weaker the die-swell effect becomes and the thinner the fineness of the as-spun fibers is, and thus the smaller the probability

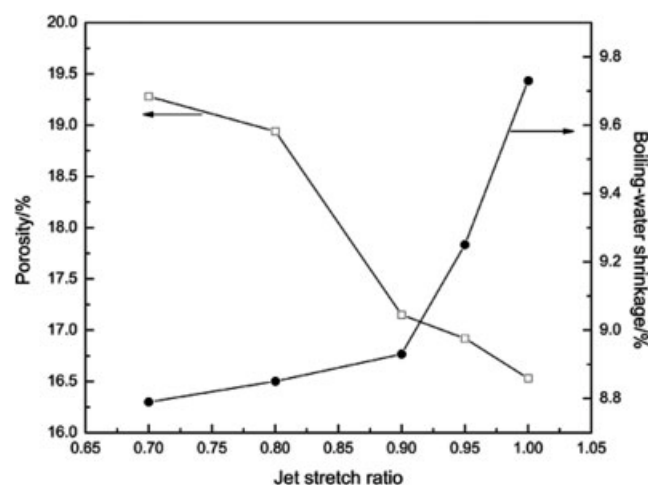


Figure 3 Effect of jet stretch ratio on the porosity and boiling-water shrinkage of as-spun fibers.

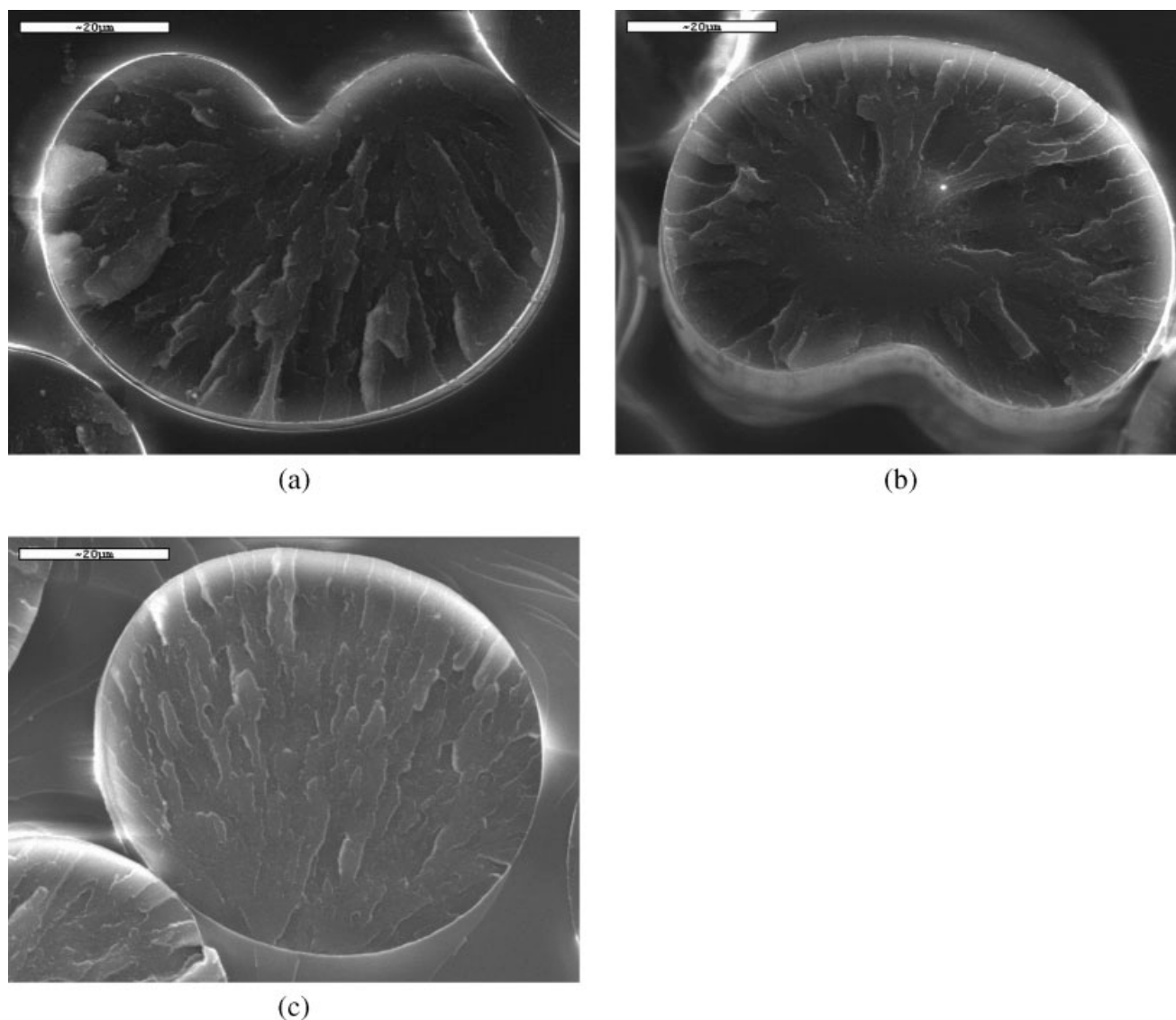


Figure 4 Effect of jet stretch ratio on the cross-sectional morphology of as-spun fiber. (a) 0.45; (b) 0.5; and (c) 0.6.

of the occurrence of defects is. The tension along the fiber axis enhances, the inner voids becomes longer and thinner along the axis, and some vanish. As the increase of jet stretch ratio means a larger tension, which restricts the mobility of the polymer segment, the diffusion of species is impeded.¹⁴ It causes a lower diffusion rate and favors the formation of an even and compact microstructure of the as-spun fibers. As a result the porosity of the as-spun fibers decreases.

As shown in Figure 3, the larger the porosity is, the smaller the boiling-water shrinkage and the lower the spin orientation is. It can be explained as follows. The as-spun fibers usually possess a porous, fibrillar meshwork structure, and their orientation includes fibril orientation with respect to the fiber axis and molecular orientation within fibrils. The more the amount of inner microvoids is, the more random and disorderly the arrangement of molecular chains is,

which is unfit to apply the tensile stress, and thus the spin orientation is lower.

Effect of jet stretch ratio on the cross-sectional shapes of as-spun fibers

Figure 4 shows the effect of jet stretch ratio on the cross-sectional shapes of as-spun fibers. With the increase of jet stretch ratio the tension applied to the as-spun fibers during coagulation process becomes large, the orientation degree of the outer layer enhances, and the inner structure becomes more regular, as a result of which the ability of the outer layer to shrink and deform inwards becomes weaker. On the other hand, the resident time becomes shorter, the coagulation extent of the inner core reduces, and the trend of the cross section to shrink and deform falls. The two factors make the cross section tend to be circular.

Effect of jet stretch ratio on the breaking tenacity of as-spun fibers

As shown in Table I, with the increase of jet stretch ratio the breaking tenacity of the as-spun fibers and corresponding precursors increase gradually.

The higher the jet stretch ratio is, the weaker the die-swell effect and the lower the rheological force applied to the as-spun fibers is, and thus the smaller the harm to the fibers. Secondly, the thinner the fineness of the as-spun fibers the smaller the probability including the defects. The inner voids become longer and thinner along the axis by the action of tension, and some vanish. Thirdly, the elongational viscosity decreases and makes the counter-diffusion easy to occur. In addition, the increase of the tensile stress promotes the gelation and is favorable to the formation of the primary structure of the as-spun fibers. At last, the drawing action of the applied tension towards the macromolecules makes the orderly arrangement of the molecular chains increase, leading to a larger crystallinity and orientation extent, and thus the breaking tenacity of the as-spun fibers increased.

The jet stretch ratio can not be too high; otherwise the failure in the filaments will occur. And it can not be too low, because when exceeding the critical value, the orientation extent of the polymer chains will descend, causing a downward breaking tenacity.

CONCLUSIONS

With the increase of the jet stretch ratio the die-swell ratio becomes small and the Barus effect reduces. The spin orientation of the as-spun fibers is improved and their crystallinity and crystal size both have more or less increment. As the increase of jet stretch ratio means a larger tension, it causes a lower diffusion rate and favors the formation of an even and compact congregation structure of the as-spun fibers. So the breaking tenacity of the as-spun fibers and corresponding precursors enhances, respectively.

References

1. Doppert, H. L.; Harmsen, G. J. *J Appl Polym Sci* 1973, 17, 893.
2. Liu, C.-K.; Cuculo, J. A.; Smith, B. *J Polym Sci Part B: Polym Phys* 1989, 27, 2493.
3. Tarafdar, N.; Chatterijee, S. M. *Text Trend* 1988, 31, 35.
4. Rende, A. *J Appl Polym Sci* 1972, 16, 585.
5. Oh, S. C.; Wang, Y. S.; Yeo, Y.-K. *Ind Eng Chem Res* 1996, 35, 4796.
6. Hou, Z.; Chen, L.; Wang, Q. *J China Text Univ* 1996, 22, 68.
7. Paul, D. R. *J Appl Polym Sci* 1968, 12, 383.
8. Zeng, X.; Zhang, Y.; Zhao, J. *Synth Technol Appl* 2004, 19, 9.
9. Tang, C.-H.; Zhang, W.; Cao, X.-Y.; Liu, J.; Wu, G. *China Plast Ind* 2004, 32, 55.
10. Paul, D. R. *J Appl Polym Sci* 1969, 13, 825.
11. Liu, X. D.; Ruland, W. *Macromolecules* 1993, 26, 3030.
12. Hobson, R. J.; Windle, A. H. *Macromolecules* 1993, 26, 6903.
13. Xu, L.-H.; Zhang, W.; Tong, Y.-J. *New Carbon Mater* 1997, 12, 31.
14. Doppert, H. L.; Harmsen, G. J. *J Appl Polym Sci* 1973, 17, 903.