Fibers and Polymers 2012, Vol.13, No.7, 846-849 DOI 10.1007/s12221-012-0846-9

Spinnability in Pre-gelled Gel Spinning of Polyacrylonitrile Precursor Fibers

Shuiping Liu, Huiyu Jiang[1], Weiping Du[1]*, and Ding Pan[1]

College of Textile & Clothing, Jiangnan University, Wuxi 214122, China
[1]*State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China*

(Received August 13, 2011; Revised January 20, 2012; Accepted February 11, 2012)

Abstract: The spinnability in pre-gelled gel spinning of polyacrylonitrile (PAN) precursor fibers was investigated. The spinning solutions were aged at 25 °C for different times prior to fiber spinning. The pre-gelled spinning solution aged for 2.5 h was much more strain hardening than the ungelled one, which can increase the spinnability of the solution. The maximum take-up velocity of the first winding roller V_{1m}, which reflects the spinnability of the spinning solutions, was found to be largest when the aging time was 1.5 h. The spinnability increased with the increase of the air gap length and the length-diameter ratio *L/D* of the spinnerette. Once the *L/D* increased beyond 15, the spinnability hardly changed. The fibers spun from the spinning solution aged for 1.5 h had the best mechanical properties and favorable structure, showing that good spinnability favors the performance increase of resultant PAN precursor fibers.

Keywords: Polyacrylonitrile precursor fiber, Pre-gelled gel spinning, Spinnability, First winding roller, Maximum take-up velocity

Introduction

Polyacrylonitrile (PAN) is a main precursor material used for manufacturing high-performance carbon fibers [1-5]. PAN precursor fibers are usually fabricated by wet spinning or dry-jet wet spinning [6,7], using solvents such as sodium thiocyanate, dimethyl sulphoxide (DMSO), dimethyl formamide (DMF), etc. The main chemical characteristic of PAN is the presence of a permanent dipole in the monomer unit caused by the bulky CN group with strong polarity, which makes the gelation of PAN solutions possible if proper solvents are used. Recently, pre-gelled gel spinning has been developed as a new spinning method for PAN precursor fibers [8,9]. A PAN spinning solution is aged at a temperature lower than its gelation temperature before the spinning process. The spinning solution gels but still keeps flowability [9], which can be used for spinning.

Generally speaking, spinnability refers to the ability or the ease of making fibers from a given set of raw materials. It was reported that [10] the allowable maximum take-up velocity of the first winding roller V_{1m} can be used to characterize the spinnability, which was defined as the critical take-up velocity of the first winding roller beyond which the as-spun fibers will break in fiber spinning [11]. Theoretically, spinnability was influenced by many spinning variables, including the rheological properties of the liquid to be spun, spinning temperature, the coagulation conditions, jet stretch, the spinneret hole size and shape, etc. [12].

Although the spinnability in wet spinning and dry-jet wet spinning of PAN fibers have been studied by some researchers, the spinnability in the new pre-gelled gel spinning has not been studied so far. In this article, the spinnability in pre-gelled gel spinning of PAN precursor fiber was investigated. The influences of aging time, air gap length and length-diameter ratio (*L/D*) of the spinnerette on the spinnability were examined and the pre-gelled gel spun PAN fibers were also characterized.

*Corresponding author: 110611276@qq.com

Experimental

Materials

PAN copolymers (acrylonitrile:itaconic acid=98:2) were purchased from Shanghai Institute of Synthetic Fiber with a viscosity–average molecular weight W_η=7.8×104 g·mol^{-1}. DMSO (analytically pure) was purchased from Shanghai Wulian Chemical Industry, and deionized water was used as the nonsolvent.

Preparation of Pre-gelled Spinning Solution

Certain amounts of PAN copolymers were dissolved in the mixture of DMSO/water (5/95, w/w) to produce viscous spinning solutions with the PAN concentration of 23 wt %. The solutions were deaerated for 3 h at 70 °C in a vacuum oven. Several such fresh spinning solutions were kept at 25 °C for a different periods of time to undergo thermal-induced gelation prior to spinning.

Extensional Rheology

The break-up extensional rheological tests were conducted on a HAAKE CaBER1 Extensional Rheometer (Thermo Fisher Scientific, US) with two plates of diameter 6 mm at 25 °C. Plate separation was changed from L_i=2 mm to L_f= 12 mm within 50 ms. The extension rate 35.84 s^{-1}, was determined according to the relation $L=L_0\exp(\dot{\varepsilon}t)$. The

choice of these parameters ensured that the initial solution filament diameter at the beginning of the filament thinning process was controlled between 1 and 1.5 mm.

Measurements of Spinnability

A coagulation bath with a concentration of 60 wt% DMSO and a temperature of 10 °C was used. The spinneret fills with individual holes of diameter 0.8 mm and length-diameter ratios (*L/D*) 2, 5, 10, 15 and 20, respectively. Seven different aging times were chosen for the gelation of spinning solutions. The rotational speed of the first winding roller was measured and V_{1m} determined as $V_{1m}=\pi D\omega_m$, where D is the diameter of the roller and ω_m is its maximum rotational speed. The velocity of freely extruded solutions was 3.6 m/min. The as-spun fibers were collected out of the coagulation bath with a jet stretch ratio of 10, washed thoroughly with cold deionized water to remove residual DMSO. After rinsing and drying in air for 6 h at 50 °C, the fibers were preserved at 25 °C before characterization.

Fiber Characterization

The fineness of as-spun PAN precursor fibers was measured on an XD-1 fiber fineness machine. The mechanical properties of the fibers were examined using a XQ-1 tensile-testing machine (Donghua University, Shanghai, China) under standard conditions (i.e., relative humidity=65±2 %, temperature=27±2 °C) with a crosshead speed 10 mm/min, at gauge length 20 mm, and an applied tension 0.15 cN. In each case, at least 10 samples were tested, and the average value was used.

The cross sections of the as-spun fibers extruded after aging for different times were made on a Hardy's thin cross-section sampling device and observed using an ALPHAPHOT-2 YS2 optical microscope (Nikon, Japan).

Surface morphology of the as-spun fibers was observed using a JSM-5600LV scanning electron microscope (JEOL, Japan). The samples were gold coated prior to observation.

Results and Discussion

Extensional Rheological Behavior

Figure 1 shows the curves of extensional viscosity η_e versus Hencky strain (true strain) for the ungelled and pre-gelled spinning solutions. The η_e of the ungelled solution initially increased with the increase of Hencky strain, and then leveled off as the strain exceeded 6. In contrast, the η_e of the pre-gelled solution increased more significantly as the strain increased. More specifically, η_e increased by 1 order of magnitude at the strain below 5, exhibiting strong strain hardening behavior. It is evident that thermal-induced gelation can enhance the strain hardening of a PAN spinning solution, most likely due to the formation of a more elastic network caused by increased interaction between molecular chains. Such pre-gelled spinning solutions are expected to have better drawability and be able to withstand higher draw ratios. Therefore, the pre-gelled spinning solutions may exhibit better spinnability.

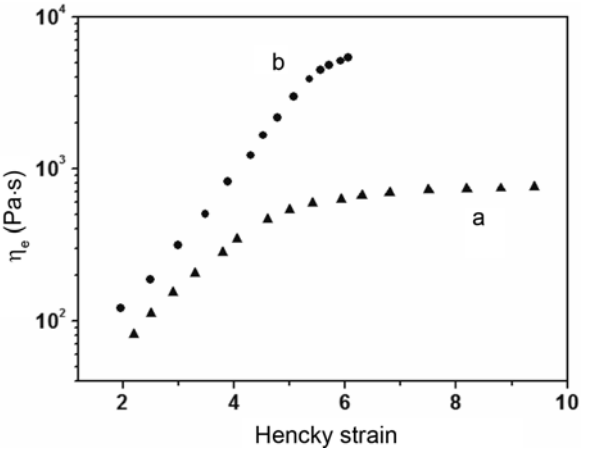

Figure 1. Extensional viscosity as a function of Hencky strain for (a) ungelled PAN spinning solution and (b) pre-gelled PAN spinning solution aged for 1.5 h.

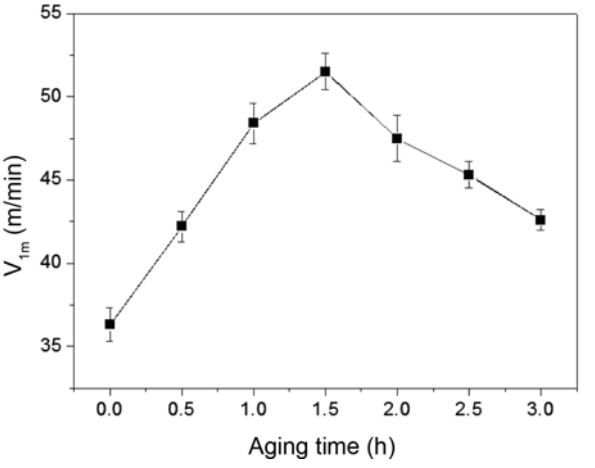

Figure 2. Relationship between V_{1m} and aging time. The air gap length was 30 mm and the *L/D* of the spinnerette was 15.

Influence of Aging Time on Spinnability

Figure 2 shows that the spinnability improved with the increase of aging time, reflected by a larger V_{1m} when the aging time was longer. Though V_{1m} began decreasing once the aging time exceeded 1.5 h, it was still large compared with the case of no aging.

The breakage of the viscoelastic fluid jets is the type of cohesive failure resulted from excessive storage of elastic energy [7]. This will occur once a critical stress level, expressed by equation (1), is reached [13]:

$$\sigma_c = \sqrt{2KE} \quad (1)$$

where σ_c is the critical stress applied to the fluid jets, K and

E are the cohesive energy density and the tensile modulus of the fluid flow, respectively. The existence of air gap helps to improve spinnability in that an air gap in appropriate length favors the stress relaxation of the fluid flow as well as the orientation of the PAN molecules. In pre-gelled gel spinning, the spinning streams will not break easily even at large deformation rate not only because of the existence of air gap, but also due to the aging process of the spinning solution before entering the coagulation bath. Aging will cause the occurrence of gelation [14]. A three dimensional network gradually forms and hence the viscosity and elasticity of the spinning solution increase. When the aging time was below 1.5 h, the spinning solution was in sol state though the molecular chains tended to interconnect and form network structure. A certain degree of gelation was achieved, which favored the stress relaxation of the fluid flow. However, as the aging time increased beyond 1.5 h, the high degree of gelation made the spinning solution an elastic gel and the viscosity of the spinning stream grew dramatically with the increase of aging time. The spinning streams gradually lost flowability, leading to more difficult extrusion and lower spinning stability. Therefore, the spinnability represented by V_{1m} was significantly reduced when aging time was over 1.5 h.

Influence of Air Gap Length on Spinnability

The relationship between the V_{1m} and the air gap length is shown in Figure 3. For given spinning solutions, V_{1m} increased with the increase of air gap length and showed no maximum in the data range. Ziabicki [10] studied the mechanism of capillarity, and the disturbance propagated by the capillarity can be represented by the amplitude of capillary waves:

$$\delta = \delta_0 \exp(\mu t)\cos(2x/\lambda) \quad (2)$$

where δ_0 is the initial amplitude of capillary waves, μ the growth factor of capillary waves, t the time, x the distance from the spinneret, and λ the wavelength. If the amplitude δ increases to equal the radius of the unperturbed fluid jets, the jets will break down. Increasing air gap length will prolong the amplitude of the capillary waves. The increase of V_{1m} is attributed to the air gap, which facilitates the stress relaxation and makes the cohesive failure more difficult to occur. Nevertheless, in the case of dry-jet wet spinning [4], once the air gap length exceeds 3 cm, the effect from the capillarity, causing the surface tension-induced breakage of fluid streams, becomes the dominant fracture mechanism. In Figure 3, V_{1m} kept increasing when the air gap length exceeded 3 cm, demonstrating that the influence of surface tension-induced breakage of fluid streams on V_{1m}, caused by increasing air gap length, is much smaller in gel spinning than in dry-jet wet spinning. As the air gap length was beyond 6 cm, the growth of V_{1m} significantly slowed. These phenomena can be explained as follows: a certain gelation degree of the spinning solution facilitated the stress relaxation and made the cohesive failure more difficult to occur. Also, the surface tension-induced breakage was reduced by the gelation of the spinning solution. When the air gap length increased to a high value, the spinning stream became less stable as it stayed in the air for longer time. Although a larger air gap leads to better spinnability, it should be controlled below 10 cm in consideration of spinning stability.

Influence of Length-diameter Ratio on Spinnability

It can be seen in Figure 4 that the V_{1m} increased with the increase of *L/D* when the *L/D* was below 15. The die swell of spinning solutions will decrease if the length of spinnerette increases, since there is more time for macromolecular chains to relax in a longer spinnerette. As the *L/D* of the spinnerette increased, the pre-gelled spinning solution had more time to relax, leading to reduced die swell and thus enhanced spinnability. It is noted that the V_{1m} kept almost constant when the *L/D* further increased to 20, suggesting

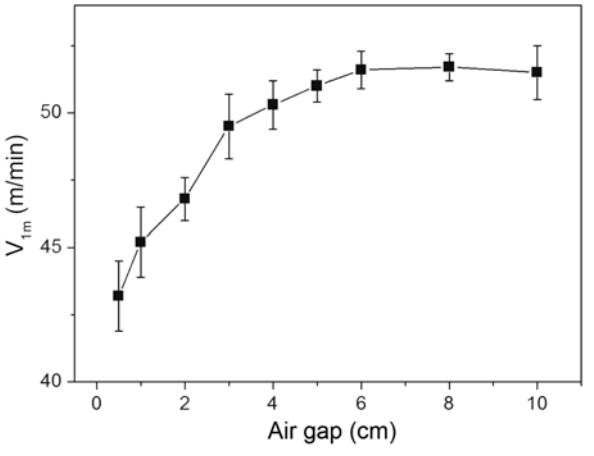

Figure 3. Relationship between V_{1m} and air gap length. The aging time was 1.5 h and the *L/D* of the spinnerette was 15.

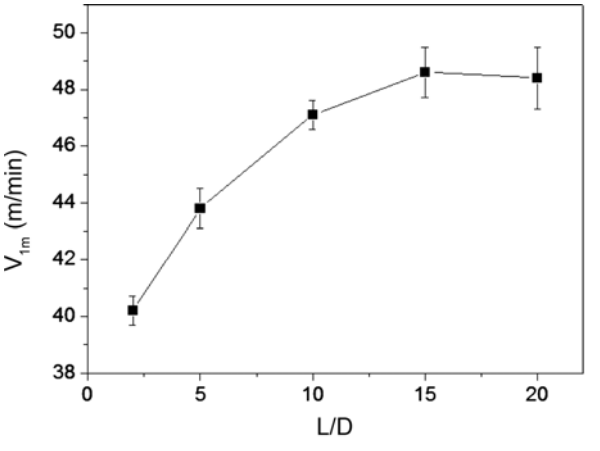

Figure 4. Relationship between V_{1m} and *L/D* of the spinnerette. The aging time was 1.5 h and the air gap length was 30 mm.

that an *L/D* of 15 was enough for the spinning solution to relax.

Properties of As-spun PAN Precursor Fibers

To determine the correlation between the spinnability and the properties of the resultant PAN fibers, the mechanical properties and the surface morphology of the fibers were examined. As summarized in Table 1, the tenacity of the fibers changed slightly with the increase of aging time. However, the breaking elongation and Young's modulus of the fibers increased with increasing aging time until 1.5 h. Once the aging time exceeded 1.5 h, the mechanical propertie breaking elongation and Young's modulus began to decrease, in good agreement with the variation of spinnability with the aging time. This phenomenon indicates that the spinnability exerts influences on the mechanical properties of resultant fibers.

Figure 5 shows the surface morphology of different as-spun PAN fibers. The cross section of the fibers became more circular as the aging time increased, since the aged solution is more elastic and is thus less likely to deform during the spinning process. The fibers spun from the spinning solution aged for 1.5 h had smoother surface with fewer defects compared with the ones spun from the ungelled spinning solution (i.e., dry-jet wet spinning), as can be seen from the SEM micrographs. Three-dimensional network structure had formed in pre-gelled spinning solution, and when the solution entered the coagulation bath, the double diffusion that causes the coagulation of fibers in dry-jet wet spinning contributed much less to the solidification of the fibers in pre-gelled gel spinning. The low temperature in the coagulation bath made the pre-gelled solution further solidified and the resultant as-spun fibers had more homogeneous structure with fewer surface defects.

Table 1. Mechanical properties of as-spun PAN precursor fibers from pre-gelled spinning solution aged for different times at 25 °C. The air gap length was 30 mm and the *L/D* of the spinnerette was 15

Aging time (h)	Tenacity (cN/dtex)	Breaking elongation (%)	Young's modulus (cN/dtex)
0	1.03±0.05	24.6±1.3	8.46±0.42
1	1.08±0.05	28.6±1.0	9.03±0.49
1.5	1.10±0.04	30.7±1.5	9.69±0.52
2	1.09±0.07	29.9±1.8	9.66±0.37
3	1.05±0.08	25.7±1.2	8.87±0.58

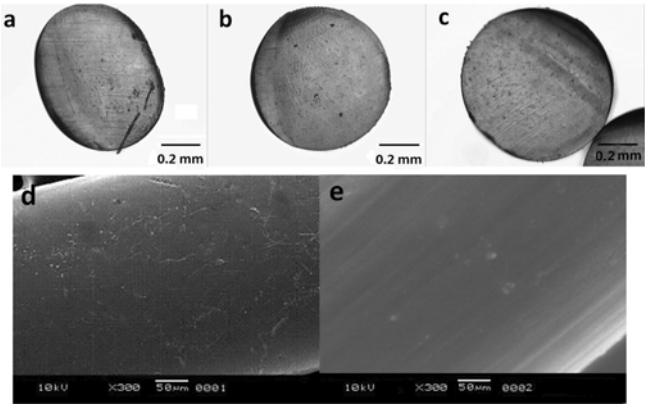

Figure 5. Cross-section morphology of as-spun PAN precursor fibers from pre-gelled spinning solution aged for (a) 0 h, (b) 1 h, (c) 1.5 h; SEM micrographs of as-spun PAN precursor fibers from pre-gelled spinning solution aged for (d) 0 h and (e) 1.5 h.

Conclusion

The pre-gelled PAN spinning solutions showed more significant strain-hardening behavior than ungelled ones, which increased their spinnability. The aging time, air gap length and length-diameter ratio of the spinnerette were found to influence the spinnability in pre-gelled gel spinning in different ways. When the length-diameter ratio and the air gap length were fixed, the spinning solution aged for 1.5 h exhibited best spinnability. The fibers spun from the spinning solution aged for 1.5 h possessed better mechanical properties, more circular cross section and fewer surface defects compared with those spun from the solutions aged for other different times. Good spinnability favors the performance increase of resultant PAN precursor fibers.

References

1. L. Tan, H. Chen, D. Pan, and N. Pan, *Eur. Polym. J.*, **45**, 1617 (2009).
2. L. Tan, S. Liu, and D. Pan, *Colloid. Surf. A.*, **340**, 168 (2009).
3. S. Y. Gu, J. Ren, and G. J. Vancso, *Eur. Polym. J.*, **41**, 2559 (2005).
4. A. Shindo, "Comprehensive Composite Materials", Elsevier Science, Hyogo, pp.1-30, 2000.
5. L. Tan and A. Wan. *Mater. Lett.*, **65**, 3109 (2011).
6. X. Zeng, J. Hu, J. Zhao, Y. Zhang, and D. Pan, *J. Appl. Polym. Sci.,* **106**, 2267 (2007).
7. L. Tan, H. Chen, D. Pan, and N. Pan, *J. Appl. Polym. Sci.,* **110**, 1997 (2008).
8. L. Tan, A. Wan, and D. Pan, *Mater. Lett.*, **65**, 887 (2011).
9. L. Tan, S. Liu, K. Song, H. Chen, and D. Pan, *Polym. Eng. Sci.*, **50**, 1290 (2010).
10. D. R. Paul, *J. Appl. Polym. Sci.,* **12**, 2273 (1968).
11. Y. Ide and J. L. White, *J. Appl. Polym. Sci.,* **20**, 2511 (1976).
12. C. D. Han, *Rheol. Acta.*, **9**, 355 (1970).
13. A. Ziabicki, Wiley-Interscience Publication, New York, 182 (1976).
14. S. Liu, L. Tan, D. Pan, and H. Chen, *Polym. Int.,* **60**, 453 (2010).