Investigating the Spinnability in the Dry-Jet Wet Spinning of PAN Precursor Fiber

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ABSTRACT: The spinnability of a spinning solution using DMSO as the solvent was investigated for dry-jet wet spinning of PAN precursor fiber. Among many variables responsible for spinnability, the coagulating conditions, the air gap length, the nonsolvent content in spinning solution, and the spinning temperature have been viewed as the key factors, and they were investigated in this study. It was found however, unlike in the wet spinning, the spinnability in dry-jet wet spinning process was barely influenced by the coagulating conditions, likely attributable to the existence of the air gap. However, the spinnability worsened when the air gap was longer than 30 mm. The quality of the spinning solution deteriorated with the increasing water content in it. The spinnability improved when the spinning temperature was maintained between 60 and 72°C and turned down once the temperature was over 72°C. The experimental results indicated that all the factors should be comprehensively considered to ensure good spinnability in dry-jet wet spinning process. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1997–2000, 2008

Key words: PAN precursor fiber; dry-jet wet spinning; spinnability; take-up velocity

INTRODUCTION

PAN-based carbon fiber is widely used in many industries such as aviation, aerospace, sporting goods, and construction. Properties of PAN precursor fiber are critical for yielding high-quality PAN-based carbon fiber.[1] In preparing PAN solutions for manufacturing PAN precursor fibers, the first issue is the solution spinnability. In general, spinnability refers to the ability or the ease of making fibers from a given set of raw materials.[2] Ide and White[3] denoted spinnability as the ability to form threads from polymer solutions and melts. Jizheng et al.[4] defined spinnability as the deformability of a spinning solution under stable stretching force. According to the literature,[2,4] the allowable maximum take-up velocity of the first winding roller V_{1m} can be used to characterize the spinnability; for wet spinning, V_{1m} was the critical take-up velocity below which the spinning will remain stable. Spinning above this velocity is impossible, for no continuous filament can be obtained. In the case of dry-jet wet spinning, we define V_{1m} as the critical take-up velocity of the first winding roller beyond which the as-spun fiber in the air gap (before entering the coagulating bath) will break.

Theoretically, spinnability depends on many spinning variables, including the rheological properties of the liquid to be spun, spinning temperature, jet stretch, the spinneret hole size and shape, the rate of mass, and heat transfer between the extruded liquid flow, and the coagulation medium and coagulation conditions.[5,6] Studies on the influences of these factors on the spinnability of various solutions have been reported by many researchers, most of which however were aimed at wet spinning and/or melt spinning.[2,3,5] In this article, the spinnability of PAN-DMSO solution in dry-jet wet spinning process and the important factors involved were investigated.

EXPERIMENTAL

Materials and equipment

PAN copolymers (acrylonitrile : itaconic acid = 98 : 2) were purchased from Shanghai Institute of Synthetic Fiber with a viscosity–average molecular weight

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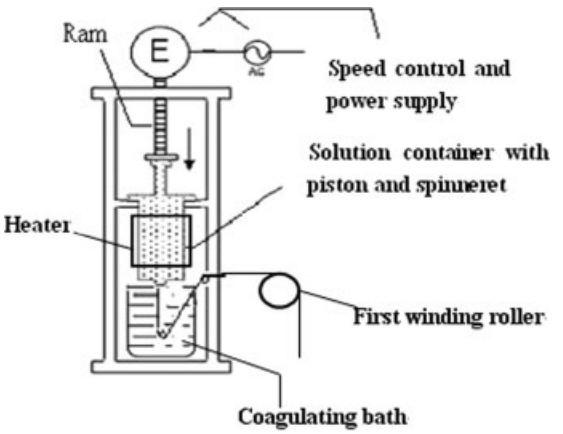

Figure 1 Sketch of the experimental spinning machine.

$\overline{W_V} = 7.8 \times 10^4$ g mol^{-1}. DMSO (analytically pure) was purchased from Shanghai Wulian Chemical Industry, and deionized water was used as the nonsolvent.

A sketch of a piston-type spinning machine custom made to fabricate PAN precursor fibers is shown in Figure 1. A precisely controlled heater was attached to the solution container to adjust the spinning temperature accurately. The coagulating bath temperature was also controlled by a thermostat. The two small rollers in and near the coagulating bath were both passive and made of polished stainless steel. They are guide rollers to assure a smooth movement of the spun thread. Whereas the first winding roller in the figure was active whose rotational speed was adjustable via a motor. It was made of nylon 6 with the surface appropriately roughened to avoid slippage of the spun thread. In addition, the as-spun fiber was still sticky enough that the slippage during winding is negligible. It is thus clear that the maximum take-up velocity of the first winding roller V_{1m} is equivalent to the linear velocity of the filament.

Experimental conditions

Spinning solutions of different PAN concentrations by weight (17, 20, and 23%) were prepared with DMSO as the solvent. The ones with 20 wt % PAN were then added to different amount of water (0, 2, 3, 4, and 5 wt %). The coagulating baths with concentrations of 0, 25, 50, and 75% DMSO by weight were prepared, of which the one with 50 wt % DMSO was used as the control in this work. The spinneret fills with individual holes of the length-diameter ratio 10 and diameter 0.8 mm. The velocity of freely extruded solution was 3.3 m/min.

Measurement

The rotational speed of the first winding roller was measured and V_{1m} determined as $V_{1m} = \pi D \cdot \omega_m$,

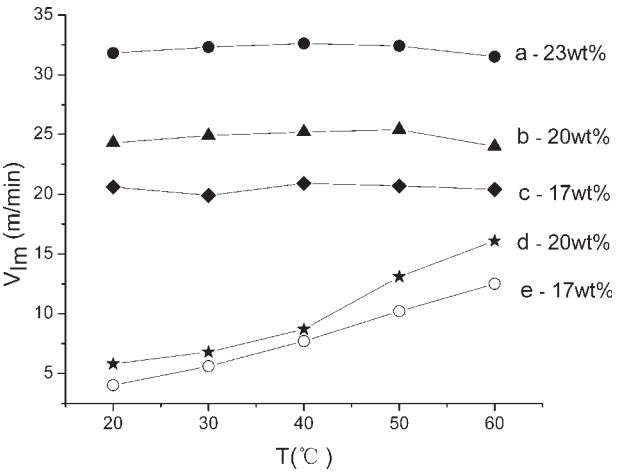

Figure 2 Relations between the coagulating bath temperature T and V_{1m}. The spinning temperature was 70°C and the coagulating bath concentration was 50 wt %, air gap length 30 mm (for dry-jet wet spinning).

where D is the diameter of the roller and ω_m is its maximum rotational speed.

RESULTS AND DISCUSSION

Influence of the coagulation conditions on spinnability

Figures 2 and 3 show that both the temperature and concentration of the coagulating bath exert little influence on spinnability (V_{1m}) in the case of dry-jet wet spinning (curves a, b, and c), unlike in wet spinning where V_{1m} is greatly affected by these two conditions (curves d and e).

For wet spinning, the fluid flow coagulates upon it emerges from the spinneret hole. The viscoelastic fluid streams will break if the deformation rate

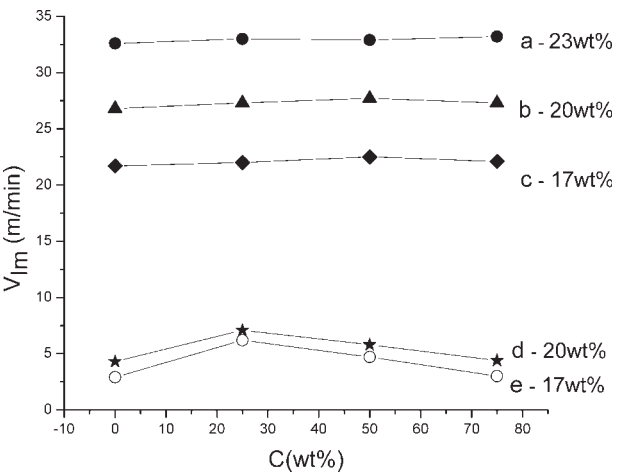

Figure 3 Relations between the coagulating bath concentration C and V_{1m}. The spinning temperature was 70°C, the coagulating bath temperature 20°C, air gap length 30 mm (for dry-jet wet spinning).

exceeds a critical value, thus V_{1m} is defined and restricted. We can see from Figure 2(d,e) that V_{1m} increases with the coagulating bath temperature, for higher temperature accelerates the mutual diffusion between the fluid flow and the coagulating bath, resulting in quicker solidification. Also in Figure 3(d,e), V_{1m} increases with the coagulating bath concentration when the concentration is below 25 wt %. When the concentration is higher, however, V_{1m} begins to decrease. This can also be explained by the mutual diffusion mechanism.

For dry-jet wet spinning, the fluid streams will not break as easily even at large deformation rate because of the existence of the dry air gap before entering the coagulating bath. 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 eq. (1), is reached:[3,8]

$$\sigma_c = \sqrt{2KE} \tag{1}$$

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. V_{1m} in dry-jet wet spinning is hence much larger than that in wet spinning, indicating a much better spinnability. Because breakage of the fluid jets always occurs in the air gap, the spinnability (V_{1m}) is not affected by the coagulation conditions, as illustrated clearly in Figures 2 and 3.

Another intriguing phenomenon demonstrated by Figures 2 and 3 is that the influence of the concentration of the spinning solution on V_{1m} is greater in dry-jet wet spinning than in wet spinning. The likely mechanisms are as follows. For wet spinning, the die swell and the quickly formed skin-core structure of the fluid flow when it enters the coagulating bath are the main factors affecting the spinnability. In the data range of this article, the effect of concentration is minor compared with that of the two factors above. For the dry-jet wet spinning, however, the effects of both die swell and the skin-core structure are greatly reduced due to the existence of the air gap. Also, the increased concentration enhances the interaction between PAN molecules and thus promotes the aggregation. Therefore, the spinnability represented by V_{1m} is significantly improved in the dry-jet wet spinning process.

Influence of the air gap length on spinnability

The relations between the spinnability V_{1m} and the air gap length d in dry-jet wet spinning were also examined in this study as shown in Figure 4. For given spinning solutions, V_{1m} goes up with the increase of d from 10 to 30 mm but decreases when d is further raised to 40 mm. The initial increase of V_{1m} is ascribed to the air gap, which facilitates the stress relaxation and makes the cohesive failure more difficult to occur, as mentioned earlier. Nevertheless, once the air gap length exceeds 30 mm, the effect from the capillarity, causing the surface tension-induced breakage of fluid streams, becomes the dominant fracture mechanism. Ziabicki[8] studied the mechanism of capillarity, and the disturbance propagated by the capillarity can be represented by the amplitude of capillary waves:

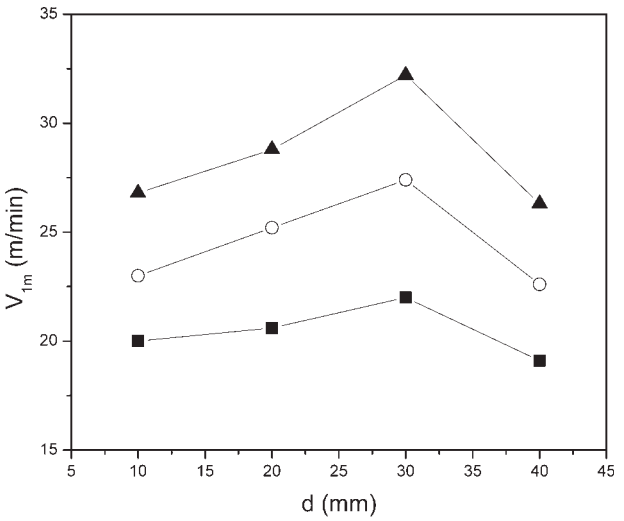

Figure 4 Relations between V_{1m} and the air gap length d. The concentration of spinning solution: ■—17 wt %, ○—20 wt %, and ▲—23 wt %. The coagulating bath concentration and temperature were 50 wt % and 20°C, respectively. The spinning temperature was 70°C.

$$\delta = \delta_0 \exp(\mu t) \cos(2x/\lambda) \tag{2}$$

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 the same value as the radius of the unperturbed fluid jets, the fluid jets will break down. Increased air gap length will prolong the amplitude of the capillary waves. Therefore, too long an air gap length will render the fluid jets vulnerable as well.

Influence of the nonsolvent content in spinning solution on spinnability

We can see from our data in Figure 5 that the influence of the water content on V_{1m} is nonmonotonic. Addition of water into the PAN-DMSO solution weakens the interaction between PAN and the sol-

vent DMSO whilst strengthens the attraction force between PAN molecular chains, both causing the PAN molecular chains to aggregate and form physical crosslinkings, leading to gelation of the solution. The viscosity of the gelled solution is too large for fiber spinning.

Influence of the spinning temperature on spinnability

In Figure 6, V_{1m} rises with the spinning temperature in the range of 65–72°C while falls in the range of 72–80°C, despite the amount of water added in the spinning solution. If we consider the relationship between temperature → solution viscosity → solution spinnability, the explanation is obvious: the optimal temperature → optimal viscosity → optimal spinnability, all because of changes in the mobility of molecular chains. Besides, the growing surface tension at too high a temperature tends to break the liquid jets into drops as mentioned earlier. It can be expected that the spinnability would further deteriorate if the spinning temperature exceeds beyond 80°C.

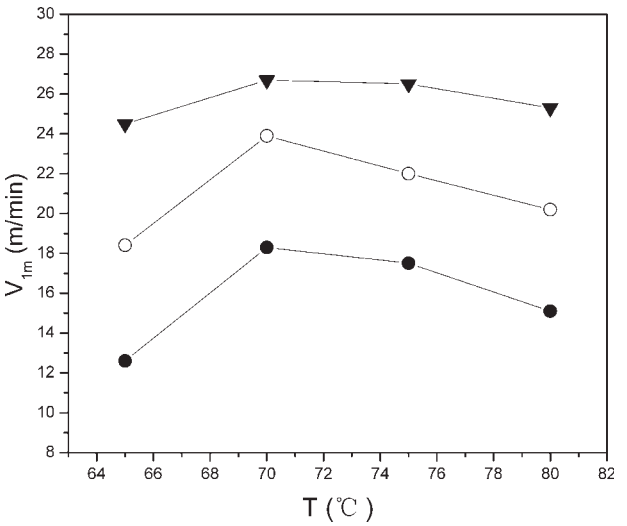

Figure 6 Relations between V_{1m} and spinning temperature T. The water content in spinning solution: ▼—0 wt %, ○—2 wt %, and ●—4 wt %. The concentration of spinning solution was 20 wt %. The coagulating bath concentration and temperature were 50 wt % and 20°C, respectively. The air gap length was 30 mm.

CONCLUSIONS

Both the temperature and concentration of the coagulating bath exert little influence on spinnability (V_{1m}) in the case of dry-jet wet spinning, unlike in wet spinning where V_{1m} is greatly affected by these conditions. Also, V_{1m} in dry-jet wet spinning is much greater than that in wet spinning, because of the existence of an air gap with appropriate length, which facilitates the spinning process. According to our experimental result, the best air gap length is 30 mm under the given conditions.

The addition of nonsolvent into the spinning solution, in general, worsens the spinnability, for it adversely alters the rheological properties of the solution. Hence, water should be avoided during the preparation of spinning solution. Spinnability improves with the spinning temperature in the range of 65–72°C, in which the solution viscosity is most favorable for fiber spinning due to the reduced entanglement of PAN molecular chains and the increased stress relaxation rate in the fluid jets. At higher temperature, the reduced viscosity as well as the rapidly growing surface tension results in breakage of the fluid streams.

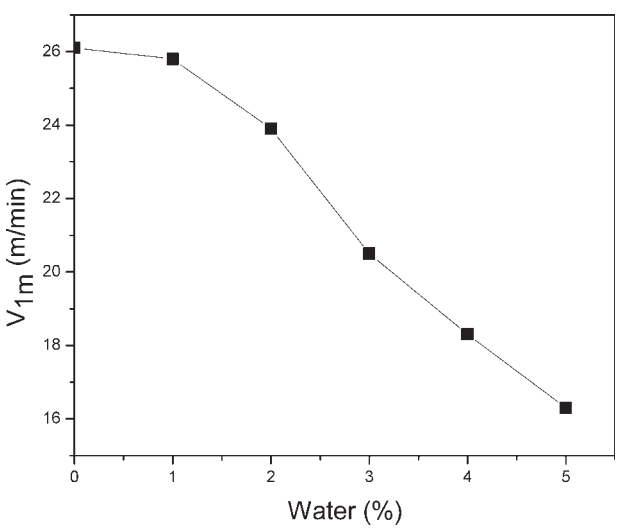

Figure 5 Relation between V_{1m} and the water content in spinning solution. The coagulating bath concentration and temperature were 50 wt % and 20°C, respectively. The concentration of spinning solution was 20 wt %, and the spinning temperature was 70°C. The air gap length was 30 mm.

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