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Diffusion Mechanism of As-spun Polyacrylonitrile Fiber in a Dimethyl Sulfoxide-Water Coagulation Bath

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In this paper, the diffusion mechanism of as-spun PAN fiber was investigated in dimethyl sulfoxide-water by determining the dynamic compositions of the fibers and the diffusion coefficients of solvent and nonsolvent during coagulation. The diffusion process could be divided into two stages. Results showed that the first stage of the diffusion process was the most important during the whole process, which was fundamental to further study on the formation mechanism. Also, compared with wet spinning, the dry-jet wet spinning method had the advantage of mild coagulating at a high jet-stretch. At high concentrations, the diffusion coefficients increased and the ratio of solvent diffusion coefficient to nonsolvent diffusion coefficient decreased; an increasing temperature resulted in the increase of both diffusion coefficients with a decrease in their ratios. To some extent, for the PAN-DMSO-water system, the more the ratios D_s^*/D_n^* tended to 1, the more the cross-section shapes of as-spun PAN fiber tended to be circular.

Keywords polyacrylonitrile fiber, PAN-DMSO-H_2O system, diffusion process, diffusion coefficients, formation mechanism, carbon fiber

Introduction

Polyacrylonitrile (PAN) fiber is the best precursor for carbon fiber due to its excellent properties such as high carbon yield, high strength and modulus of PAN fiber, especially when it is made by dry-jet wet spinning using dimethyl sulfoxide (DMSO) as the solvent. Generally, circular cross-sections of fibers are used as a precursor of reinforcement carbon fibers in fiber-reinforced composites since the physical and mechanical properties of the carbon fibers depend largely on the shape and structure of the fiber. Thus, the shape is of great importance for further treatment into the carbon fiber and possible applications. However, it is difficult to obtain PAN precursors with circular cross-sections and homogeneous dense structure due to processing problems. In qualitative terms, it is the magnitude of the overall material transfer between fiber and bath during the formation

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process that plays an important role in the structures and properties obtained by this process.

Formation features of PAN fibers by wet spinning have been discussed in the literatures (1–7), but the formation mechanism has not been fully understood up to now. Furthermore, no papers exist on the diffusion process of DMSO/water for PAN systems for either dry-jet wet spinning or wet-spinning techniques. To clarify the mechanism, the method of determination of diffusion coefficients was optimized. Also, the determination of diffusion coefficients of DMSO and water through the surface of the coagulating fiber was accomplished permitting discussion of the relationship between fiber shape and the diffusion coefficients.

Experimental

Materials

PAN polymer (acrylonitrile: methylacrylate: itaconic acid = 96 : 2.5 : 1.5) was used as the polymer precursor for carbon fibers with DMSO as the solvent. Both materials were purchased from Shanghai Petrochemical Ltd. The weight percent concentrations of each component in the PAN dope were 20.9% of PAN, 73.6% of DMSO, and 5.5% of H_2O. The coagulation baths were prepared by dissolving different amounts of pure DMSO in distilled water.

Processing

A sketch of the self-built experimental spinning machine is shown in Figure 1. The PAN spinning solution was extruded through two filter gauzes and a single-hole spinneret (diameter 0.5 mm) immersed in a coagulation bath (wet spinning) or not (dry-jet wet

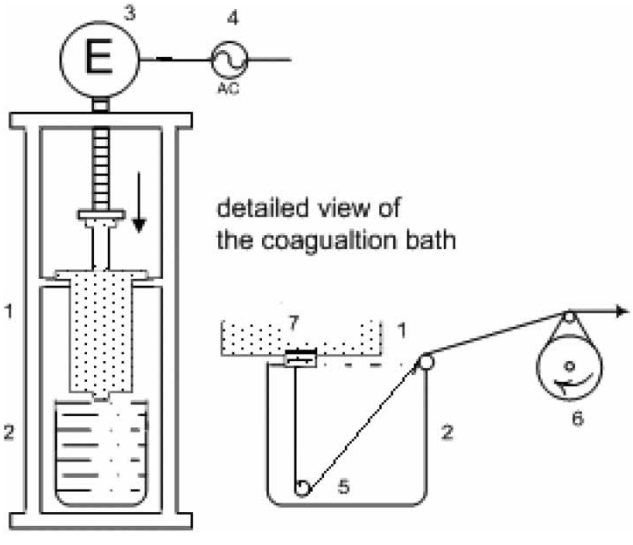

Figure 1. Sketch of experimental spinning apparatus: (1) spinning drum with piston and spinneret, (2) coagulation bath, (3) engine, (4) speed control and power supply, (5) adjustable arm, (6) take-up roller (7) filter.

Table 1
Relationship between the DMSO concentration in the extraction solution and extraction time

Extraction Time/Hour	8	10	12	14	16	18	20
C/ $\times 10^{-7}$mol/mL	3.687	4.2803	4.830	5.179	5.247	5.248	5.248

spinning). In order to stop the exchange action of solvent and nonsolvent abruptly at the instant of sampling, a sample must be taken at definite distance from the spinning jet, and also the adhered bath liquid on the fiber must be removed instantaneously once the coagulating fiber is wound spirally onto the guide roller with filter papers. The accuracy of this sampling was high (precision $<3\%$). DMSO contents inside fibers were determined by ultraviolet spectrophotometry via 16 h extraction using water (for the reason shown in Table 1). This analysis has many advantages such as simple operation, short time, high repeatability and high sensitivity (see Figure 2 and Table 2). The spinning conditions are shown in Table 3.

The solvent diffusion equations (1,6) can be written as follows:

$$\frac{M_t^s}{M_\infty^s} = 1 + 4\left(\frac{C_0}{C_\infty} - 1\right)\sum_{n=1}^{\infty}\frac{1}{\lambda_n^2}e^{-\lambda_n^2 D_s^* t/r^2} (C_\infty > 0) \tag{1}$$

$$\frac{M_t^s}{M_\infty^s} = 4\sum_{n=1}^{\infty}\frac{1}{\lambda_n^2}e^{-\lambda_n^2 D_s^* t/r^2} \quad (C_\infty) = 0 \tag{2}$$

The nonsolvent diffusion equation (8) is as follows:

$$\frac{M_t^n}{M_\infty^n} = 1 - 4\sum_{n=1}^{\infty}\frac{1}{\lambda_n^2}e^{-\lambda_n^2 D_n^* t/r^2} \tag{3}$$

Here M_t is the relative mass of a component in the fiber at time t; M_∞ is the equilibrium amount of the component; C_0, C_∞ are the initial and equilibrium concentrations; R is the

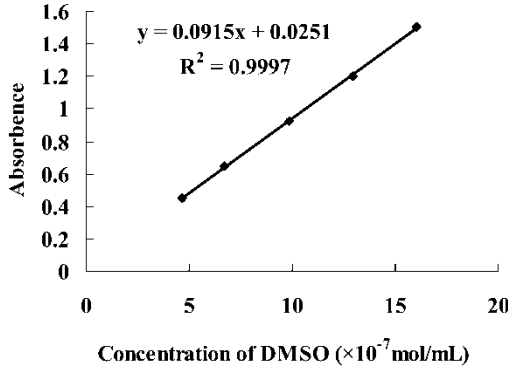

Figure 2. UV absorption calibration curve of DMSO standard solutions.

Table 2
Measurements of DMSO inside the PAN fiber samples

Sample	Found/%	Average/%	C.V./% (n = 7)
1#	64.18 64.25 64.15 64.02 64.26 64.32 64.06	64.17	0.17
2#	53.90 53.91 53.98 53.95 53.89 53.90 53.87	53.91	0.07
3#	46.68 46.56 46.43 46.65 46.38 46.79 46.20	46.53	0.44

radius of fiber; the symbol D^* is the diffusion coefficient; the superscripts s and n mean solvents and nonsolvents; λ_n is the positive root satisfying the zero order Bessel function.

Results and Discussion

Process Coagulation of the As-spun PAN Fibers

From Figure 3, the diffusion process can be divided into two stages according to the diffusion coefficients of solvent and nonsolvent and their contents inside the fiber. During the first stage (from 0 to 50 sec), the diffusion coefficients of the nonsolvent and solvent change quickly, as well as their amount, with increasing coagulation time. The diffusion coefficients are higher by almost several times compared to those in the second stage where diffusion coefficients change slowly and then tend to a constant. In the second stage, from 50s to 60s, then to 120s, although their contents also change quickly, the values of diffusion coefficient are very small. These results indicate that the first stage (From 0s to 50s) undoubtedly play a decisive role in the structure and properties of PAN fiber. In fact, this was found experimentally. Thus, the first stage is the most important during the whole diffusion process and is fundamental to further study on the formation mechanism of PAN fiber. In this study, according to the results above, to obtain optimal fiber samples, we should collect the fiber samples with coagulation times of 5, 15, 40, and 600 sec.

It should be noted that in the first stage the change of the two contents do not always remain in the same direction. For example, the content of solvent decreases during the

Table 3
Spinning conditions used in the experiments

Concentration of coagulation bath (C_{DMSO} in water)/%	30, 57, 70
Extrusion velocities (V_0)/cm s^{-1}	10.46, 16.77, 23.71
Apparent jet-stretch (φ)/%	−51.2, −69.5, −78.4
Coagulation time of fibers (t)/s	5, 15, 40, 600
Gas gap height (h)/mm	0, 3, 6, 10
Temperature of coagulation bath (T)/°C	10, 25, 50

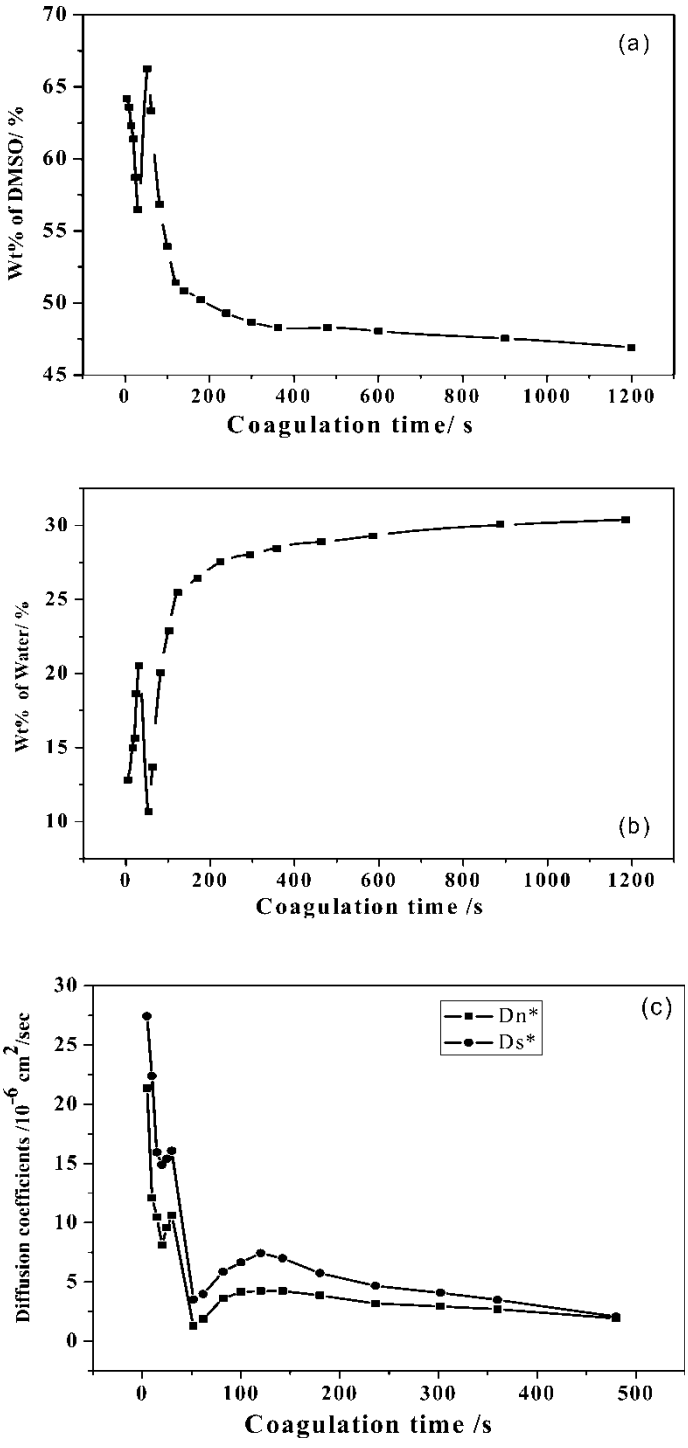

Figure 3. (a) Relationship between the amount of DMSO inside PAN fibers and coagulation time, (b) Relationship between the amount of water inside the PAN fibers and coagulation time, (c) Relationship between diffusion coefficients and coagulation time.

coagulation time from 0s to 50s, rises and then drop again till to 100s. The diffusion coefficients change similarly. Up to now, there is no reasonable explanation for this, but it has large effect on the sampling.

Results of Diffusion Coefficients Measurement

The value of the ratio D_s^*/D_n^* means the degree of mildness of coagulation while its reciprocal reflects the coagulating power.

Figure 4 shows the effects of extrusion velocities on the diffusion coefficients for both dry-jet wet and wet spinning processes. It can be seen that the diffusion coefficients increase with increasing V_0, while D_s^*/D_n^* decreases. At the low extrusion velocities (offering higher apparent jet-stretch with the same spinning speed), D_s^*/D_n^* of dry-jet wet spinning is smaller than the corresponding one of wet spinning, but bigger than that

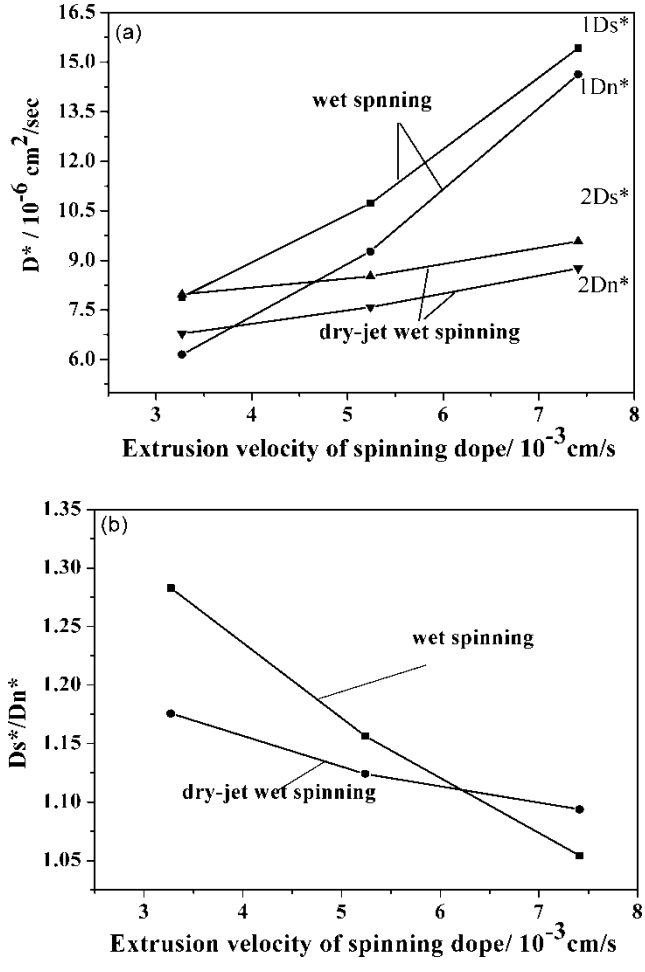

Figure 4. (a) Relationship between diffusion coefficients and extrusion velocities of the spinning dope, (b) Relationship between D_s^*/D_n^* and extrusion velocities of the spinning dope: The temperature of the coagulation bath was 25°C and the concentration of the coagulation bath was 57%.

at the high extrusion velocities. This result indicates that the advantages of dry-jet wet spinning, such as mild coagulation and slow diffusion interchange, can only be found at a high jet-stretch.

At different extrusion velocity the gas gap results in a different effect on the diffusion coefficients (Figure 5). At high extrusion velocity, the diffusion coefficients decrease quickly, especially with the increasing gap from 0mm to 6 mm (Figure 5(a)). Above this value, the diffusion coefficients remain almost constant. The reason for this behavior is the "skin" of coagulated polymer formed in the gap is denser and offered more resistance. Moreover, with a bigger gap the time for the skin formation is longer. This results in a higher density and better orientation. Further, these results account for the advantage of dry-jet wet spinning, like mild coagulation, slow diffusion interchange and higher jet-stretch. They are similar to those obtained by Baojun (1).

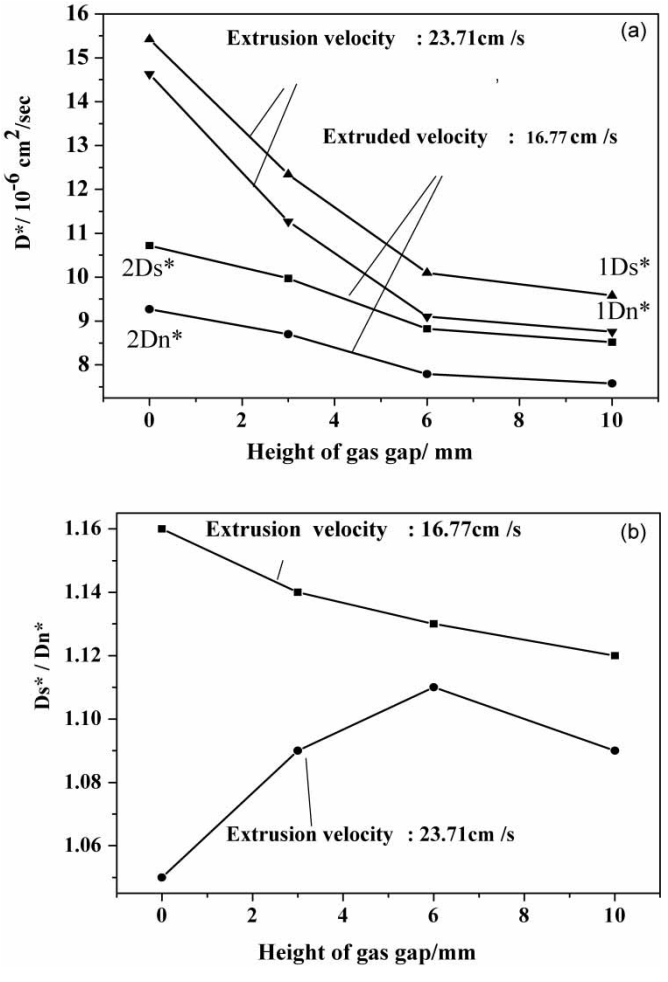

Figure 5. (a) Relationship between diffusion coefficients and height of gas gap, (b) Relationship between D_s^*/D_n^* and height of gas gap: The temperature of the coagulation bath was 25°C and the concentration of the coagulation bath was 57%.

In Figure 6, we can see that the diffusion coefficients increased with increasing temperature. But D_s^*/D_n^* decreases and its value gradually tends to 1. Also, the corresponding ratios of dry-jet wet spinning are always lower than those of wet spinning. As in most diffusion processes, a higher temperature (coagulation bath temperature) results in an increase of the diffusion coefficients, which make the apparent coagulation rate higher and a thick outer skin form on contacting with the bath. This resists further diffusion and the fiber forms slowly. However, due to the weaker gel structure and rupture of the skin the penetration of nonsolvent occurs rapidly.

From Figure 7, it is evident that the diffusion coefficients increase with increasing the concentration of DMSO in the coagulation bath (C_{DMSO}), but D_s^*/D_n^* drops. This must be due to the coagulation ability of nonsolvent (water). When C_{DMSO} is low, the amount of

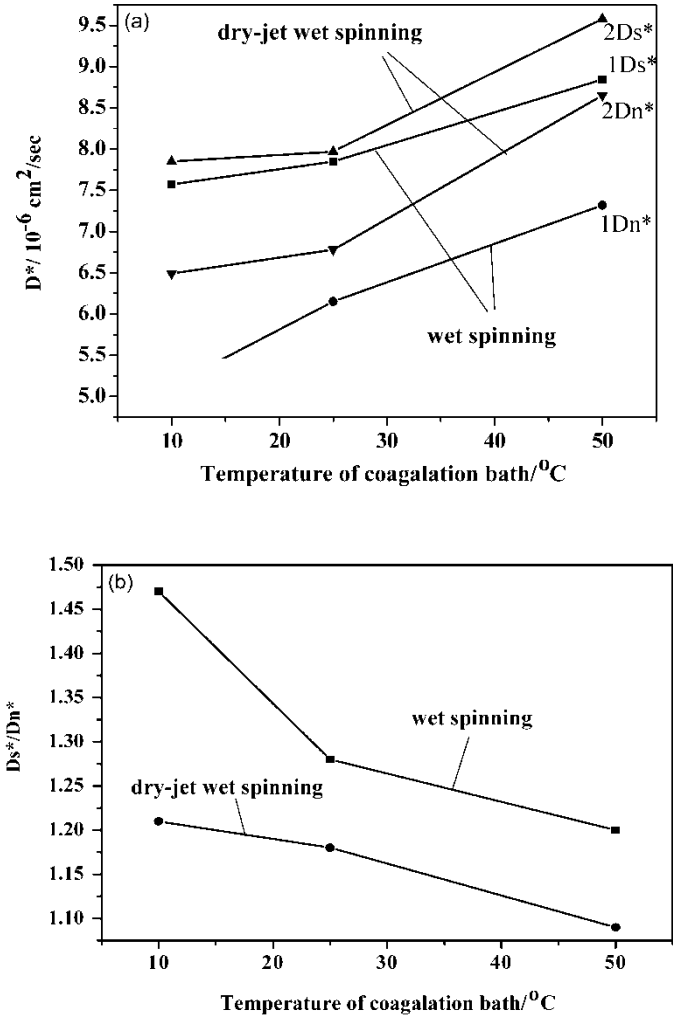

Figure 6. (a) Relationship between diffusion coefficients and temperature of the coagulation bath, (b) Relationship between D_s^*/D_n^* and temperature of the coagulation bath: The concentration of the coagulation bath was 57%; the extrusion velocity was 16.77cm $\cdot$ s^{-1}.

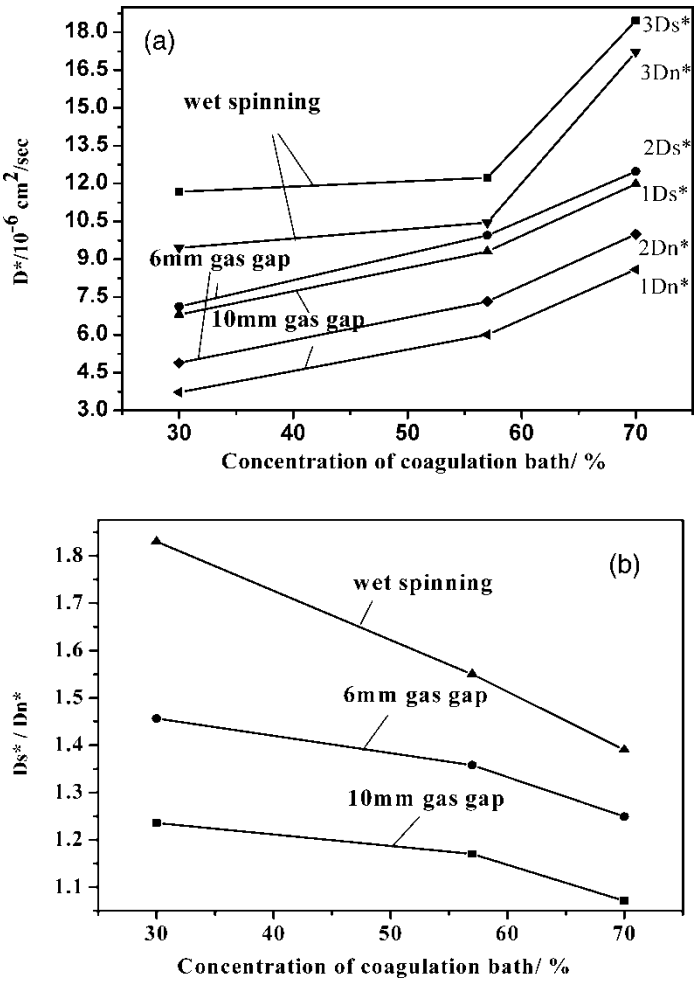

Figure 7. (a) Relationship between diffusion coefficients and concentration of the coagulation bath, (b) Relationship between D_s^*/D_n^* and concentration of the coagulation bath: The temperature of the coagulation bath was 25°C; the extrusion velocity was 16.77cm · s^{-1}.

water is higher, which causes stronger agglomeration of PAN and a denser skin. With high C_{DMSO}, the skin of the fiber forms slowly and the structure of the skin is loose, soft, deformable, and with more micro voids, which make diffusion easier and the ratios of D_s^*/D_n^* are small. That's to say, higher bath concentration causes the low ratios of D_s^*/D_n^*.

Takahashi et al. (9) have reported that the PAN as-spun fiber's cross section changed from a kidney shape to a circular shape as the temperature or concentration of the coagulation bath increased. From Figures 6 and 7, it is evident that the ratio of D_s^*/D_n^* is close to 1 under the conditions of high temperature or concentration of coagulation bath, which means the velocity of nonsolvent going into fiber is nearly equal to that of solvent out of fiber. This leads to the lower ratios D_s^*/D_n^* and a fiber with micro voids and a circular cross-section shape, but without apparent core-skin structure. Furthermore, the higher the temperature or concentration of the coagulation bath, the more the value of D_s^*/D_n^* approaches 1. Correspondingly, the cross-section shapes of the fibers tend to

circular. Thus, temperature and concentration of the coagulation bath is a key variable controlling the diffusion of solvent and nonsolvent. These mean it is possible to obtain different fiber profiles, as desired, by controlling the value of D_s^*/D_n^*.

Conclusions

The discussion is intended as a clarification that the influence of coagulation conditions on the diffusion processes, compared with wet spinning, is smaller in the case of dry-jet wet spinning and the formation process is more stable due to the different fiber structure resulting from the two formation processes. This is the advantage of dry-jet wet spinning, especially at a high jet-stretch.

As pointed out previously, the PAN as-spun fiber's cross section changes from a kidney shape to a circular shape as the temperature or concentration of coagulation bath increase, in agreement with the increase of the diffusion coefficients and the decrease of the ratios D_s^*/D_n^*. These indicate the relationship between the cross-section shape of as-spun PAN fiber and the diffusion coefficients: the smaller the ratios D_s^*/D_n^* are, the more mild the process of coagulating and then the cross-section shapes of as-spun PAN fiber tend to a circular shape.

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