

Effect of DMSO/H₂O Coagulation Bath on the Structure and Property of Polyacrylonitrile Fibers During Wet-Spinning

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Received 25 April 2006; accepted 17 October 2006

DOI 10.1002/app.25665

Published online 13 April 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effect of coagulation bath condition on the structure and property of the nascent fibers and polyacrylonitrile fibers during wet-spinning is studied. The best coagulation condition to produce polyacrylonitrile fibers has been found by examination of EA, XRD, SEM, and so on. The results indicated that when the coagulation bath was DMSO/H₂O system, the temperature was 60°C, the concentration was 65%, the minus stretch ratio was -10%,

fine crystallites and high degree of crystallization in the nascent fibers and polyacrylonitrile fibers could be achieved, and less solvents remained in the nascent fibers with circular cross section morphology. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1221–1227, 2007

Key words: coagulation bath; wet-spinning; nascent fiber; PAN fibers

INTRODUCTION

Carbon fibers have a series of excellent properties including high intensity, high modulus, antiradiation, and so on, which have been widely used in high-tech fields like spacelight and general fields like advanced physical training things. Many professors think that the properties of carbon fibers mainly depend on the quality of precursor fibers used to produce carbon fibers. Since polyacrylonitrile (PAN) fiber has higher molecular orientation, higher melting point, and higher efficiency of carbon fibers, compared with those of others like asphaltum, it has been considered as the most important and most promising fiber. At the same time, the properties of nascent fiber formed in coagulation bath have an important effect on the PAN fiber,^{1–5} so it is necessary to study the first step of wet-spinning.

During the formation of nascent fiber, the conditions of coagulation bath, such as temperature, concentration, minus stretch ratio, strongly affect the degree of crystallization, the residual solvent, and morphology of the nascent fibers and PAN fibers. Many people have studied the diffusion in DMF/H₂O system and the microstructure of nascent fibers,^{6–14} but most of them did not refer to the relationship of structure and property between the nascent fibers and PAN fibers.

In this study, we chose the DMSO/H₂O system as coagulation bath. At the same time, we designed different conditions of coagulation bath, especially the minus stretch ratio, from which we received the best coagulation process to produce excellent nascent fibers and PAN fibers with higher degree of crystallization and low residual solvent content during wet-spinning.

EXPERIMENTAL

Materials

The nascent fibers and PAN fibers was produced by wet-spinning, in which acrylonitrile (AN) and itaconic acid (IA) were used as the first and second monomer, azodiisobutyronitrile (AIBN) as initiator, and dimethylsulfoxide (DMSO) as solvent, the coagulation bath was DMSO/H₂O system. In this study, the nascent fibers were received from the coagulation bath under different temperatures, concentrations and minus stretch ratios.

Measurement of degree of crystallization and crystal size

Degree of crystallization and crystal sizes of the nascent fibers and PAN fibers were conducted on X-Ray diffractometer (Rigaku D/max-RA), made in Japan, the filter is Ni, radiation material is Cu K α , tube voltage is 40 kV, electric current is 40 mA, scanned range 2 θ was 5–50°. The degree of crystallization $C = S_c/S_t \times 100\% = S_c/(S_a + S_c) \times 100\%$. S_t is the

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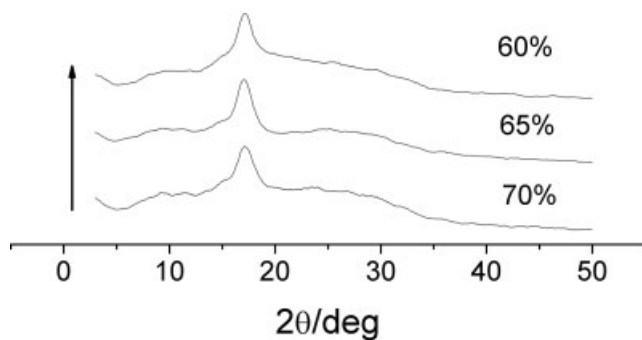


Figure 1 XRD patterns of nascent fibers under different coagulation bath concentration.

total peak area, S_a is the amorphous peak area, and S_c is the crystalline peak area. Crystal size $L = K\lambda/\beta \cos \theta$, where $\lambda = 1.541 \text{ \AA}$, K signifies the Scherrer constant (0.89 was used), β (arc) represents the half-width at mid height around $2\theta = 17^\circ$.

Measurement of sulfur content in nascent fibers

Elemental analyses (EA) were conducted in elemental analyzer (Vario EL III) to determine sulfur content in nascent fibers. Before this, the nascent fibers were dried at 30°C for an hour by desiccator.

Observation of nascent fibers' morphology

After freezing by liquid nitrogen, the specimens of nascent fibers were observed by a scanning electron microscope (SEM), Hitachi Model 8010, at 25 kV accelerating potential.

Mechanical properties

The denier and intensities of PAN fibers, the stress and strain of nascent fibers under different coagulation bath conditions have been measured by a XD-1 fiber fineness machine and a XQ-1 testing machine (both XD-1 and XQ-1 were made in Donghua University, Shanghai, China).

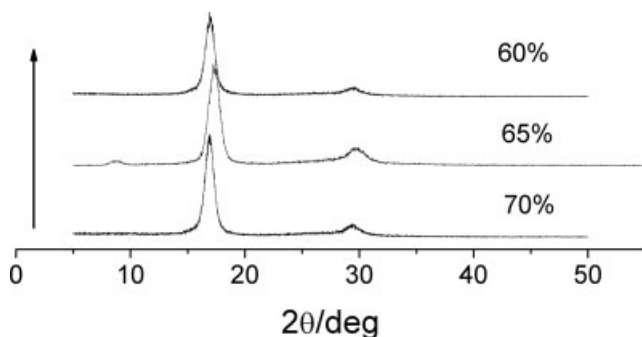


Figure 2 XRD patterns of PAN fibers under different coagulation bath concentration.

TABLE I
Degree of Crystallization and Crystal Size of Nascent Fibers and PAN Fibers Under Different Coagulation Bath Concentration

	Degree of crystallization (%)	Crystal size (nm)
Nascent fiber (60%)	44.1	5.32
Nascent fiber (65%)	45.3	5.08
Nascent fiber (70%)	39.6	6.48
PAN fiber (60%)	72.8	6.15
PAN fiber (65%)	75.2	5.99
PAN fiber (70%)	70.4	8.93

RESULTS AND DISCUSSION

Effect of coagulation bath conditions on the degree of crystallization and crystal size

Figures 1 and 2 show the XRD patterns of the nascent fibers and PAN fibers under different coagulation bath concentration, in which the temperature was 60°C , the minus stretch ratio was -10% , the three concentrations were 60, 65, 70%, namely, DMSO/ $\text{H}_2\text{O} = 60/40$ (wt/wt), DMSO/ $\text{H}_2\text{O} = 65/35$ (wt/wt), DMSO/ $\text{H}_2\text{O} = 70/30$ (wt/wt). It can be found that there are two apices in Figure 2, the one at 17° belongs to (100) diffraction, the other at 29.5° belongs to (110) diffraction. The typical diffraction peaks indicate that the crystallization of the fibers is not good and a number of amorphous phase exists in the PAN fibers. The degree of crystallization and crystal size are shown in Table I; it is clear that the nascent fibers with higher degree of crystallization are easier to receive PAN fibers with higher degree of crystallization, and when the coagulation bath concentration is 65%, the crystal size of the nascent fibers and PAN fibers is finer, the degree of crystallization is higher. When the coagulation bath concentration falls from 70 to 60%, the coagulation speeds up, the depth of coagulation pellicle increases, and the degree of crystallization in nascent fibers increases. But when the coagulation bath concentration is lower than a fixed value (about 65%), if the

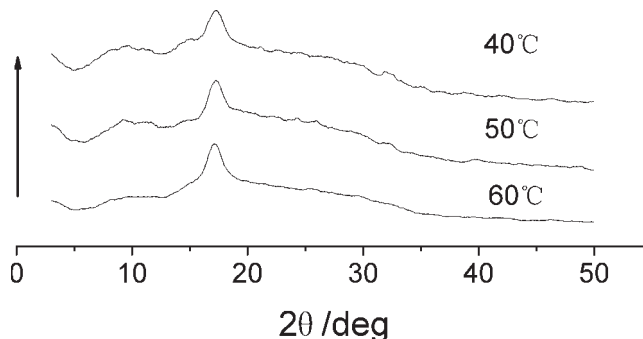


Figure 3 XRD patterns of nascent fibers under different coagulation bath temperature.

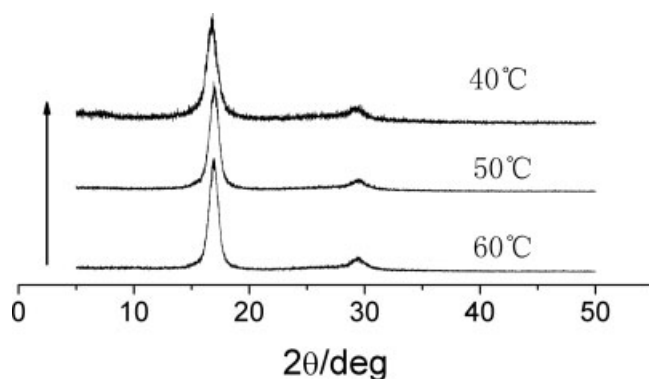


Figure 4 XRD patterns of PAN fibers under different coagulation bath temperature.

concentration continued lowering, the concentration grads between the inner and the outer of the fibers rise, the solidification will speed up, leading to the formation of hard surface pellicle in shorter time, which baffled the double-diffusion of solvent and water and decreased the degree of crystallization in nascent fibers.

Figures 3 and 4 are the XRD patterns of the nascent fibers and PAN fibers under different coagulation bath temperature, in which the concentration was 65% and the minus stretch ratio was -10%. From the calculation shown in Table II, it can be found that, when the temperature is 60°C, the degree of crystallization in nascent fiber and PAN fiber is the best. When the temperature ascends from 40 to 60°C, the big molecular chains in the fibers moves easier, the big molecules of PAN fibers arrange easier in the stretching direction and form an relatively ordered zone, so the degree of crystallization in nascent fibers and PAN fibers is higher and the crystal size is smaller.

Figures 5 and 6 show the XRD patterns of the nascent fibers and PAN fibers under different coagulation bath minus stretch ratios, in which the concentration was 65%, the temperature was 60°C, the minus stretch ratios were 0, -10, -20%. From the Table III, when the coagulation bath minus stretch ratio was -20%, the greater degree of crystallization

TABLE II
Degree of Crystallization and Crystal Size of Nascent Fibers and PAN Fibers Under Different Coagulation Bath Temperature

	Degree of crystallization (%)	Crystal size (nm)
Nascent fiber (40°C)	38.9	7.94
Nascent fiber (50°C)	42.2	5.88
Nascent fiber (60°C)	45.3	5.08
PAN fiber (40°C)	74.8	8.21
PAN fiber (50°C)	75	6.52
PAN fiber (60°C)	75.2	5.99

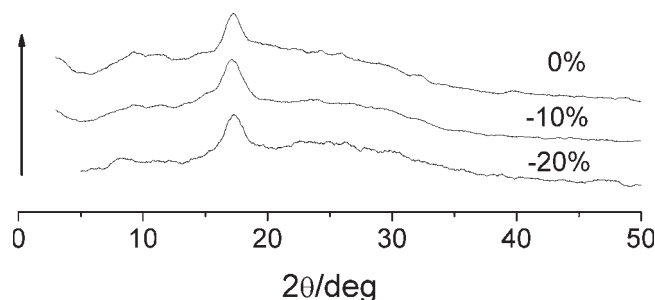


Figure 5 XRD patterns of nascent fibers under different coagulation bath minus stretch ratios.

of nascent fibers and PAN fibers can be received. With the rising of minus stretch ratio, the tropism of the nascent fibers is better, but the diffusion time is shortened, the coagulation pellicle becomes thinner, so that the degree of crystallization in nascent fibers reduces, the crystal size augments, and the PAN fibers represent the similar phenomenon. Comparing the crystallization degree and crystal size of -10% with -20%, we find that when the coagulation temperature and bath concentration are same, the change of minus stretch ratio from -20 to -10% is wee.

Effect of coagulation bath conditions on sulfur content in nascent fibers

Figure 7 is the sulfur content as a function of minus stretch ratio in coagulation bath, in which the temperature was 60°C, the concentration was 65%. And Table IV shows the relevant values of sulfur content. Since only solvent contains sulfur element in the polymer solution, the sulfur content in the nascent fibers reflects the residual solvent content in the nascent fibers in some sense. Because PAN fibers inherit some properties of the nascent fibers and the residual solvent in the PAN fibers affects the property of carbon fibers seriously, reducing the residual solvent

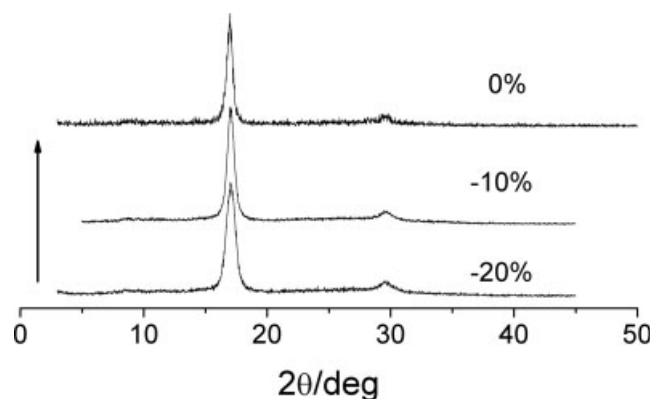


Figure 6 XRD patterns of PAN fibers under different coagulation bath minus stretch ratios.

TABLE III
Degree of Crystallization and Crystal Size of Nascent Fibers and PAN Fibers under Different Coagulation Bath Minus Stretch Ratio

	Degree of crystallization (%)	Crystal size (nm)
Nascent fiber (0%)	43.2	5.76
Nascent fiber (-10%)	45.3	5.08
Nascent fiber (-20%)	46.1	5.06
PAN fiber (0%)	72.3	6.85
PAN fiber (-10%)	75.2	5.99
PAN fiber (-20%)	75.6	5.87

content in nascent fibers is very necessary. From Figure 7, when the minus stretch rises, the fibers' diameter reduces, the diffusion in the fibers accelerates relatively, the solvent content in the fibers reduces, and the sulfur element content decreases accordingly. But when the minus stretch ratio reaches a determined value (about -10%), the diffusion of solvent and water approximately reaches equilibrium, the sulfur content reduces slowly. Considering simultaneously the effect of the degree of crystallization and the sulfur content in the nascent fibers, when the minus stretch ratio is -10%, the property of nascent fibers is better.

Figure 8 shows the sulfur content as a function of temperature under different coagulation bath concentrations, in which the minus stretch ratio was -10%. And Table V shows the relevant values of sulfur content. Because the diffusion velocity increases with the rise of temperature, the sulfur content decreases with the rise of temperature under different coagulation bath concentration. At the same time, when the coagulation bath concentration is 65%, the sulfur content in nascent fibers is the least. It is in agreement with the degree of crystallization

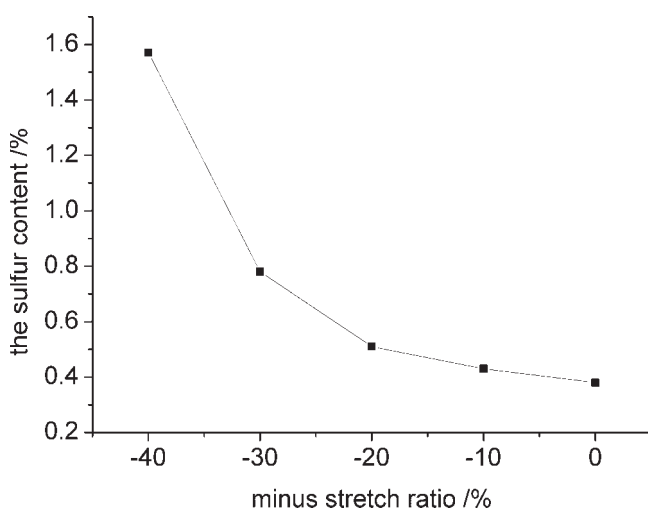


Figure 7 Sulfur content as a function of coagulation bath minus stretch ratio.

TABLE IV
The Sulfur Content Under Different Coagulation Bath Minus Stretch Ratio

Minus stretch ratio (%)	Mean sulfur content (%)	CV%
-40	1.591	4.1
-30	0.822	4.3
-20	0.593	3.5
-10	0.452	3.1
0	0.420	2.0

discussed above. When the concentration decreases, the concentration grads increase, the diffusion drive force increases, the residual solvent content reduces. But when the concentration is below 65%, the coagulation is expedited, the toughness-enforced effect of solvent on the fiber pellicles weakens, the surfaces become too hard to penetrate easily for solvent, so that the diffusion weakens, the residual solvent content in nascent fibers increases again.

Effect of coagulation bath conditions on microstructure of nascent fibers

Figure 9 shows the SEM of nascent fibers' cross section under different coagulation bath concentration, in which the temperature was 60°C, the minus stretch ratio was -10%. During wet-spinning, the coagulation of fibers is a double diffusion process, namely, solvent DMSO diffuses into the bath and the water diffuses into the fibers. The diffusion first takes place around the surface of the fibers, the surface pellicle is formed, which baffles the diffusion into the core of the fibers, so that the density of the surface and the core is different, the surface is compact and the core is loose. But if the process is controlled in a proper coagulation conditions,

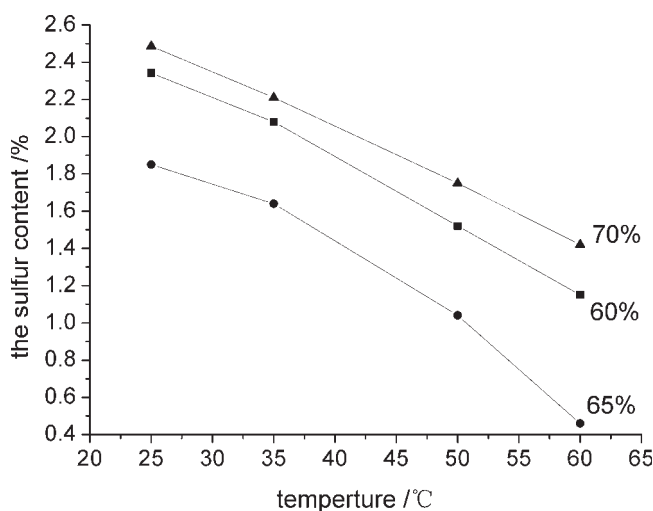


Figure 8 Sulfur content as a function of temperature under different coagulation bath concentration.

TABLE V
The Sulfur Content Under Different Coagulation Bath Temperature and Concentration

Concentration (%)	Temperature (°C)	Mean sulfur content (%)	CV%
60	25	2.341	3.9
60	35	2.084	4.2
60	50	1.523	4.1
60	60	1.152	4.3
65	25	1.854	3.3
65	35	1.642	3.4
65	50	1.043	2.6
65	60	0.420	2.0
70	25	2.485	4.2
70	35	2.213	3.5
70	50	1.752	3.2
70	60	1.421	3.6

symmetrical structure could be received. From Figure 9, we find that when the concentration is between 60 and 70%, especially 65%, the cross section of nascent fibers is circular, which are regular and symmetrical. But when the concentration is below 60%, concentration grads is so big that the inner force and outer force cannot reach equilibrium, the cross section becomes irregular and asymmetric

whose diameters and the shapes become anomalistic, as shown in Figure 9(a).

Figure 10 shows the SEM of nascent fibers' cross section under different temperatures, in which the concentration was 65%, the minus stretch ratio was -10% . From Figure 10, we find that when the temperature is 60°C , the nascent fiber is circular, the structure is more symmetrical. With the hoist of temperature, the coagulation accelerates, the pellicle is deeper, the diffusion is more symmetrical, the shapes of nascent fibers tend to regularity, but when the temperature reached 60°C , the interface tension of fibers and the inside shrinkage stress reached equilibrium. If the temperature is higher than 60°C , the coagulation rate is so great that the shapes of the cross section become irregular, the lacunas augments, as shown in Figure 10(d).

Figure 11 shows the SEM of nascent fibers' cross section under different minus stretch ratios, in which the concentration was 65%, the temperature was 60°C . No matter what the minus stretch ratio is, the structure of nascent fibers is compact. When the minus stretch ratio decreases from 0 to -30% , the shapes tend to irregularity, but the change is not obvious, indicating that when the coagulation bath

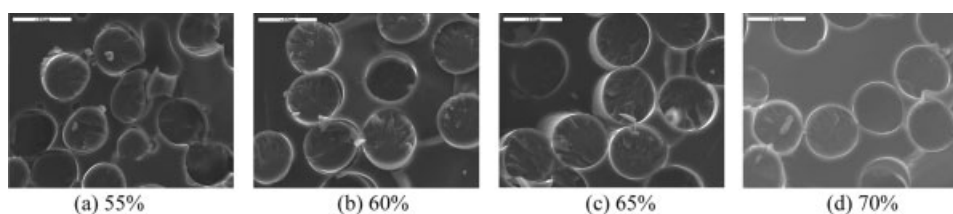


Figure 9 SEM of nascent fibers' cross section under different concentration.

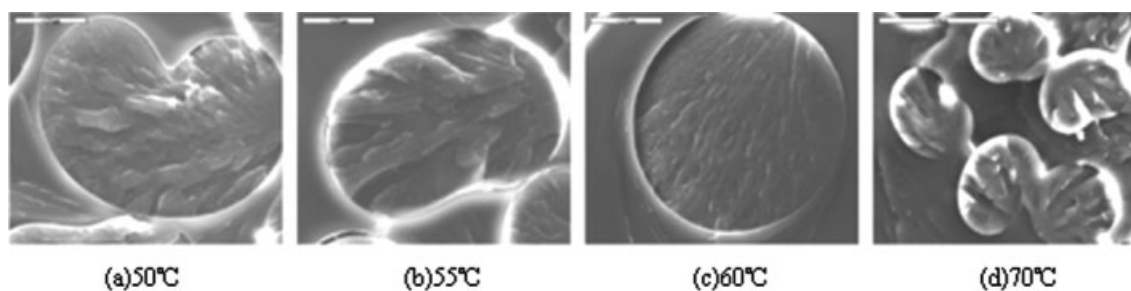


Figure 10 SEM of nascent fibers' cross section under different temperatures.

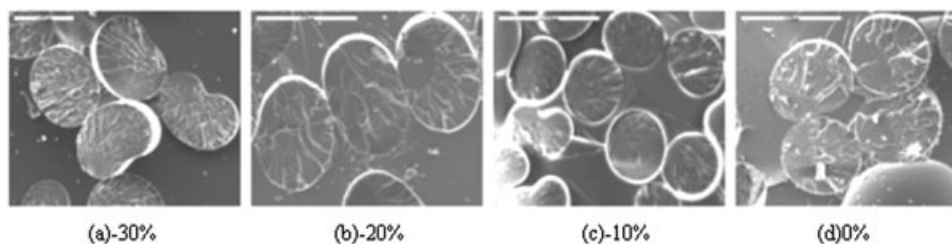


Figure 11 SEM of nascent fibers' cross section under different minus stretch ratios.

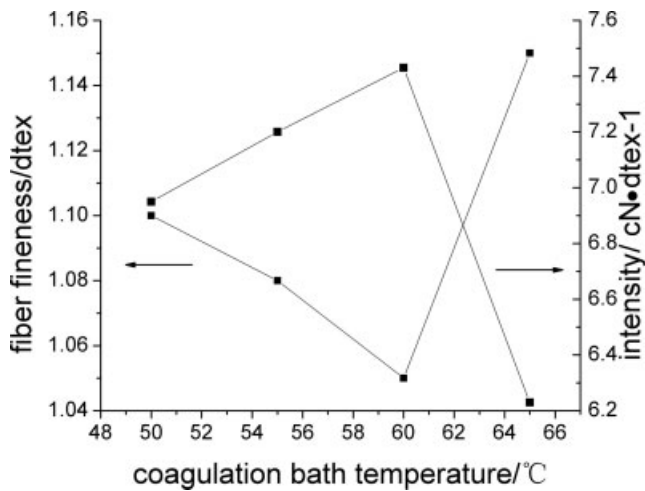


Figure 12 Fineness and intensity of PAN fiber as a function of temperature.

whose concentration is 65% is under 60°C, the minus stretch ratio is not a chief factor for the formation of fibers' shapes.

Effect of coagulation bath conditions on mechanical properties

Figure 12 shows the fineness and intensity of PAN fibers as a function of coagulation bath temperature, in which the minus stretch ratio was -10% and the temperature was 65°. Figure 13 shows the fineness and intensity of PAN fiber as a function of coagulation bath concentration, in which the minus stretch ratio was -10% and the concentration was 60°C. When the temperature is 60°C, the concentration is 65%, the fineness is smaller (about 1.04 dtex), and the intensity is higher (about 7.5 cN/dtex). During

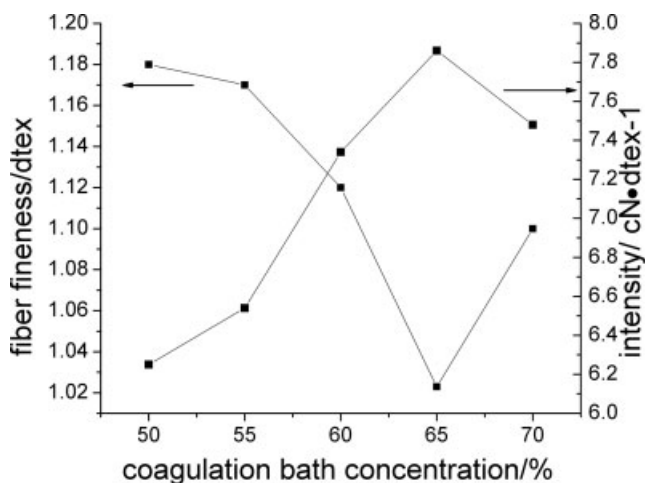


Figure 13 Fineness and intensity of PAN fiber as a function of concentration.

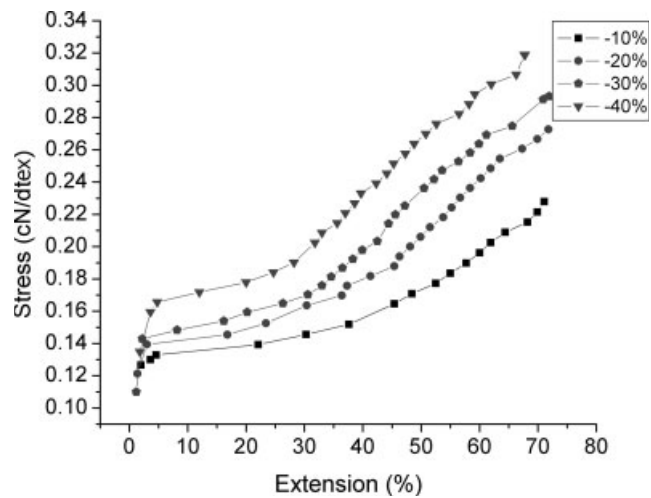


Figure 14 Stress versus extension curves of nascent fibers at different minus stretch ratios.

the manufacturing process of carbon fibers, high intensity and smaller fineness of PAN fibers is very important. If the fineness is too small, the tiny lacunas dispersed in the PAN fibers will occupy more space and will reduce the intensity of carbon fibers. If the fineness is too high, it is disadvantageous to penetrate for oxygen during the thermal stabilization, which affects the property of carbon fibers. So it is very important to control the coagulation bath temperature and concentration during wet-spinning.

Figure 14 shows the stress–strain curves of nascent fibers at different minus stretch ratios, in which the coagulation bath temperature was 60°C, the concentration was 65%. And the CV% of every minus stretch ratio from -40 to -10% was 2.5, 2.6, 2.5, 2.3%. In the drawing process whose coagulation temperature was 60°C, the stretch action showed necking. At the same time, the breaking point appears at the same elongation; despite the tension appreciably hoists with the decrease of minus stretch ratio, as shown in Figure 14. The orientation is a flabby process during the drawing process, which needs a period of time, so that the minus stretch ratio should be appropriate. If the stretch ratio is too low, the tropism is poor, and the intensity of the fibers formed is low. If the stretch ratio is too high, the orientation could not develop at so short time, which increase the inner tension. When the minus stretch ratio is -10% , the nascent fibers show the lower inner tension whose tenacity is better, which is advantageous to produce excellent PAN fibers.

CONCLUSIONS

During the preparation of polyacrylonitrile fibers in DMSO/H₂O coagulation, it is a primary step to

control the coagulation condition for the structure and property of nascent fibers and PAN fibers, especially the temperature, concentration, and the minus stretch ratio. According to the experimental results, the best coagulation condition is that the temperature is 60°C, the concentration is 65%, and the minus stretch ratio is -10%. Under these conditions, the crystal size of the nascent fibers and polyacrylonitrile fibers are smaller, the degrees of crystallization are higher, the residual solvents in the nascent fibers are less, the shapes of cross section of nascent fibers are circular, the inner stress in nascent fibers is less, and the intensity of polyacrylonitrile fibers is higher, which are advantageous for manufacturing ascendant carbon fibers.

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