

Study on the Coagulation Process of Polyacrylonitrile Nascent Fibers during Wet-spinning

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Summary

The coagulation process of polyacrylonitrile (PAN) precursor during wet-spinning was studied by chemical method based on the KMnO_4 titration. Experiments were performed with gelled solutions of PAN in dimethyl sulphoxide (DMSO) to determine the diffusion rate of solvent during the coagulation. The experimental data about solvent diffusion coefficient were calculated by using diffusion equation, which reflected the coagulation process of nascent fibers. At the same time, the effects of coagulation on the residual solvent content, the change of morphology of nascent fibers, the crystallization degree and the stress-strain curves were studied by use of X-ray diffraction, SEM, single fiber tensile test and so on. The results elucidated the relationship between coagulation process and the structure and property of PAN nascent fibers.

Introduction

As it is well known that the properties of carbon fibers are determined by the nature of precursor fibers, in which polyacrylonitrile precursors are usually used because of their higher molecular orientation, higher melting point and higher efficiency of carbon fibers[1-2]. Fiber formation by wet-spinning accounts for a significant fraction of production of today's man-made fibers. The coagulation mechanism of PAN fibers during wet-spinning is very complex, because of the coexistence of double diffusion and rheological phenomenon. Diffusion of solvent from the solidifying filament is an important part of fiber formation by the wet-spinning process and is a dominant factor in the coagulation process. Diffusion of solvent influences fibers' morphology and property by which design of the process is greatly affected[3]. Earlier studies referred just to the relationship between the actual spinning variables and the fibers' final property and the diffusion dynamics, and few to diffusion during the coagulation process and the combination with the structure and property of nascent fibers[4-6]. Most of the experiments in the past were performed with gelled rods that undergo no internal motion or only lasted filament which was studied. In this work experiments on the coagulation process which was studied by use of six length coagulation bath were performed to determine the diffusion rate of solvent during coagulation. DMSO was used as solvent for the polymer and the coagulation bath consisted of a mixture of

DMSO and water. At the same time the changes of rudimental solvent content, morphology of nascent fibers, crystallization degrees and stress-strain curves during coagulation were studied.

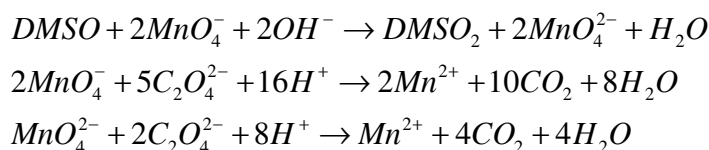
Experimental

Materials

The polyacrylonitrile nascent fibers were 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 which the coagulation bath temperature was 60°C, the coagulation bath concentration was 65% (namely, DMSO/H₂O=65/35(wt/wt)) and the coagulation bath minus stretch ratio was -10%. In this study, six different lengths of coagulation bath during the nascent fibers formation were designed, namely, coagulation bath was 15cm, 30cm, 45cm, 60cm, 75cm, 90cm, from which specimens were received.

Measurement of residual solvent and calculation of diffusion coefficient

The nascent fibers were composed of AN/IA copolymer, residual solvent DMSO and coagulate H₂O. The residual DMSO weight was obtained by the standard KMnO₄ solution, which only reacts with DMSO in nascent fibers, the reaction is represented as



At first the nascent fibers were boiled for one hour by pure water, so the solvent DMSO of nascent fibers was received. Secondly superfluous KMnO₄ solution was plunged into the DMSO solution, after reaction the residual KMnO₄ was consumed by superfluous Na₂C₂O₄. Finally residual Na₂C₂O₄ was consumed by appropriate KMnO₄ solution which was accurate, by which the DMSO residual contents were received. But before these all measurements, the DMSO and H₂O on the surface of nascent fibers were completely absorbed by absorption papers. Then, the diffusion coefficient of solvent DMSO under different coagulation time could be calculated using the double diffusion equation. When the nascent fiber is circular, the double diffusion equation[7] is represented as

$$\frac{M_t}{M_0} = 4 \sum_{n=1}^{\infty} \frac{1}{\lambda_n^2} \cdot e^{-D\lambda_n^2 t/R^2}$$

where M_t and M_0 ($M_0 = \pi R^2 c_0$) are weight fraction of DMSO at time t and time zero, in which c_0 (is equal to 12.1025mol/L in experiment) is the beginning mol concentration, D is the diffusion coefficient of DMSO, and λ_n is the fixed positive root satisfying the zero-order Bessel function. The solvent diffusion coefficient was calculated by the Matlab software.

Measurement of degree of crystallization and crystal size

Degree of crystallization and crystal sizes of the nascent fibers were conducted on X-ray diffractometer (Rigaku D/max-RA), made in Japan, the filter is Ni, radiation material is CuK α , tube voltage is 40kV, electric current is 40mA, scanned range 2 θ was 0~45°.

The degree of crystallization $C = \frac{S_c}{S_t} \times 100\% = \frac{S_c}{S_a + S_c} \times 100\%$.

S_t is the total peak area, S_a is the amorphous peak area, S_c is the crystalline peak area.

Crystal size $L = \frac{K\lambda}{\beta \cdot \cos\theta}$ where $\lambda=1.541\text{\AA}$, K signifies the Scherrer constant (0.89 was used), $\beta(\text{arc})$ represents the half-width at mid height around $2\theta=17^\circ$ [8].

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 25kV accelerating potential.

Measurement of mechanical property

The stress and strain of nascent fibers under different coagulation bath length 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). At the same time the breaking elongation ratio and breaking intensity was received by the stress-strain curves. Three or more experiments were performed at the same spinning condition, and the mean value of experimental data was used for the stress-strain curves.

Results and Discussion

Effect of coagulation process on the residual solvent and diffusion coefficient

Table 1. The residual solvent content of nascent fibers and diffusion coefficient of solvent under different coagulation bath length

Coagulation bath length /cm	Residual solvent content /%	Diffusion Coefficient ($\times 10^{-11}$)
15	76.2	4.8521
30	72.5	4.0125
45	70.3	3.6521
60	69.4	3.3684
75	66.1	3.0125
90	65.6	2.9657

Table 1 shows the residual solvent content of nascent fibers and diffusion coefficient of solvent under different coagulation bath length. 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. Because the diffusion coefficient

reflects the diffusion velocity, the coagulation is slowed by the reduction of diffusion coefficient. During the coagulation process the difference of solvent inside and outside was the diffusion drive, the concentration grads and the diffusion drive was gradually reduced in the coagulation process, so that change of the rudimental solvent contents in nascent fibers reflected the coagulation process, as shown in Figure 1. From Figure 1, we can find that when the coagulation bath length reached 75cm, the change of residual solvent was wee, which tallied with the diffusion coefficient, as shown in Table 1. It indicated that when the coagulation temperature was 60°C, the coagulation concentration was 65% and the coagulation bath stretch ratio was -10%, the coagulation bath length 75cm is enough for the sufficient diffusion of solvent during coagulation.

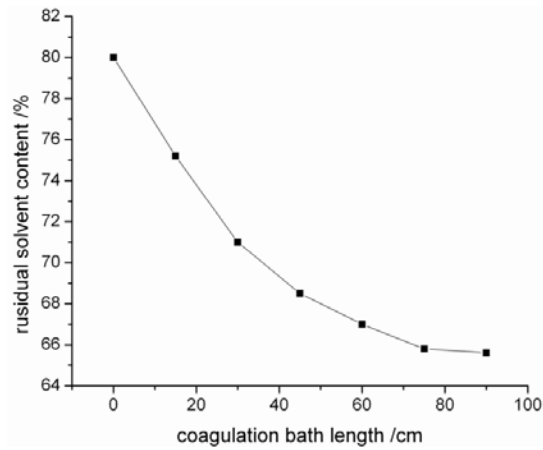


Figure 1. The residual solvent content of nascent fibers as function of coagulation bath length

Effect of coagulation process on the crystallization degree and crystal size

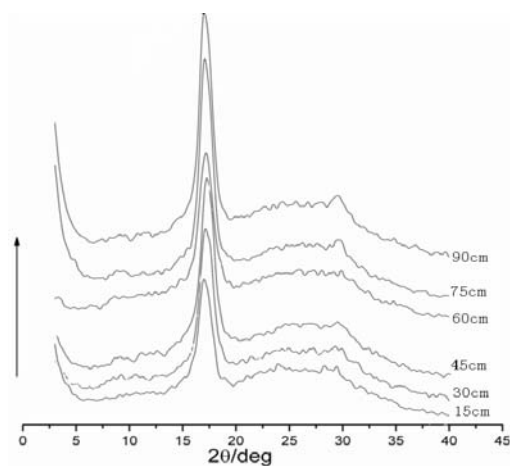


Figure 2. XRD patterns of nascent fibers under different coagulation bath length

Figure 2 shows the XRD patterns of the nascent fibers under different coagulation bath length. 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[9]. The typical diffraction peaks indicate that the crystallization of the fibers is not good and a number of amorphous phase exists in the nascent fibers. The crystallization degree and crystal size of nascent fibers under different coagulation bath length was shown in Table 2. It is clear that the crystallization degree of the nascent fibers increased with the augment of coagulation bath length. With the continuous diffusion the formed dense cuticle was ceaselessly increased, which affected the increase of crystallization degree. Contacted with the Table 1, we can find that when the coagulation bath length was from 15cm to 30cm, there are large changes of the diffusion coefficient and the crystallization degree. When the gelled polymer was sprayed into coagulation bath by spinneret, the filament was formed which swelled at first because of the “swell-effect” during exit[10]. So that when the bath length was under 15cm, the diffusion was easier in this swell zone, the drawing drive was not put on the filaments completely and the dense cuticle was not formed, which led to the lower crystallization degree and high diffusion coefficient. But when the bath length reached 30cm, the swell zone finished, the drawing drive took effect, the dense cuticle become thick, which brought the decrease of diffusion coefficient and the increase of crystallization degree.

Table 2. The crystallization degree and crystal size of nascent fibers under different coagulation bath length

Coagulation bath length /cm	Crystallization degree /%	Crystal size /nm
15	11.5	3.65
30	14.6	3.78
45	16.0	3.94
60	16.3	4.05
75	17.9	4.16
90	18.3	4.25

Effect of coagulation process on the morphology of nascent fibers

Although the coagulation bath conditions including coagulation bath temperature, concentration and minus stretch ratio play an important part in the factors that affect fiber formation, which have been studied by many scholars[11], during the coagulation process different coagulation bath lengths give birth to different morphologies of nascent fibers.

In wet-spun process, when the coagulation temperature, concentration and stretch ratio are fixed, the morphology of nascent fibers, especially the uniformity property, to a certain extent, depends on the values of diffusion coefficient. Figure 3 shows the SEM of nascent fibers at different coagulation bath length. With the increase of bath length, the diffusion drive, especially the concentration gradient reduced, diffusion coefficient became smaller, the diffusion became relaxative, the differences of nascent fibers decreased, which revealed similar or uniform morphology, as shown in Figure 3. At the same time contacted with the Table 3 we can find that the variance coefficients of fiber fineness became smaller with the increase of bath length, which was in accord with Figure 3.

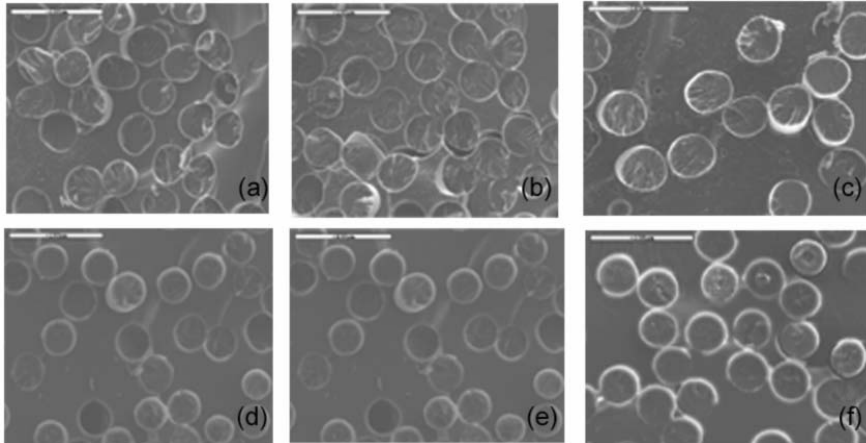


Figure 3. SEM of nascent fibers at different coagulation bath length ((a)15cm, (b)30cm, (c)45cm, (d)60cm, (e)75cm, (f)90cm)

Effect of coagulation process on the mechanical property

Figure 4 shows the stress-strain curves of nascent fibers at different coagulation bath length and Table 3 reveals the relationship between coagulation bath length and breaking extension and breaking intensity. In the coagulation process whose coagulation temperature was 60°C, which is under the glass-transition temperature of nascent fibers, the stretch action showed necking. At the same time, the succumbing point appears at the same elongation, despite the stress appreciably hoistes with the increase of cogulation bath length, as shown in Figure 4. As a crystal material, if the crystallization degree of poliacylonitrile nascent fibers is higher, the endured maximal drawing is higher, the breaking elongation ratio is higher, as shown in Figure 5. During the coagulation with the augment of coagulation bath length the DMSO residual contents decreased continuously, which is advantageous to improve the intensity and elongation[12], so that the nascent fibers revealed higher crystallization degree and higher breaking intensity.

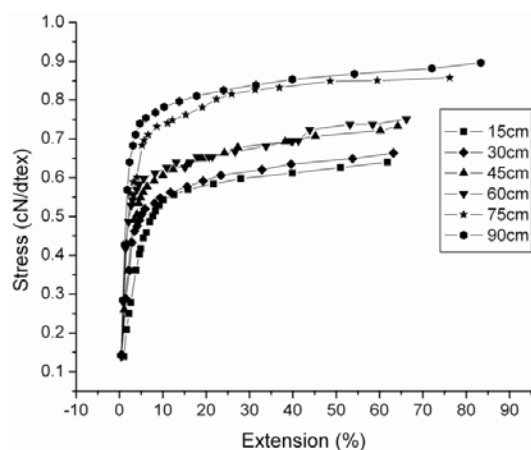


Figure 4. The stress-strain curves of nascent fibers at different coagulation bath length

Table 3. The relationship between coagulation bath length and breaking extension and breaking intensity

Coagulation bath length /cm	Fiber fineness of nascent fibers /dtex	Breaking extension ratios /%	Breaking intensity /cN
15	7.78±0.0396	61.8±3.51	4.98±0.0363
30	7.61±0.0350	63.2±3.45	5.05±0.0354
45	7.28±0.0328	64.2±3.25	5.33±0.0335
60	7.19±0.0314	66.2±3.12	5.47±0.0315
75	7.03±0.0255	76.2±2.71	6.17±0.0265
90	6.93±0.0223	81.2±2.65	6.21±0.0235

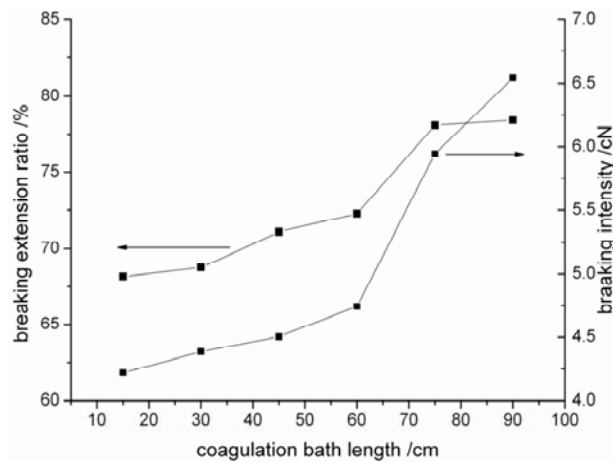


Figure 5. The relationship between coagulation bath length and breaking extension and breaking intensity

Conclusion

The coagulation process of PAN nascent fibers during wet-spinning have been studied, in which the coagulation bath temperature is 60°C, the coagulation concentration is 65%, the coagulation bath minus stretch ratio is -10%. The results have shown that with the increase of coagulation bath length the diffusion coefficients of DMSO reduce gradually, the residual solvent DMSO contents decrease continuously, in which the change is wee and diffusion finishes when the coagulation bath length is after 75cm. At the same time the changes of structure and property of nascent fibers during coagulation have indicated that with the augmentation of coagulation bath length the crystallization degree increases, in which the crystallization degree takes on a minimum when the coagulation bath length is 15cm because of the “swell-effect” during exit, the morphology of nascent fibers tends to uniformity and the breaking stress is higher which can endure higher stretch with the increase of bath length.

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