Study on the Formation Process of Polyacrylonitrile As-Spun Fiber

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ABSTRACT: In this article, the coagulation rate of PAN/DMSO dope was studied by observing the boundary movement of the gelled rods in different coagulation bath. Then the effect of the nature of solvent and coagulant and the coagulation conditions on the coagulation rate was discussed. It was found that the molecular size and molecular structure of coagulants is the most significant variable affecting the coagulation rate. The intermolecular affinity between coagulant and solvent determines the activation energy of coagulants, whereas the molecular volume is not a dominant factor. The coagulation rate depends not only on the diffusion coefficient of coagulants but also the nature of solvents. A solvent with strong polarity usually leads to a low-coagulation rate. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 328–333, 2008

Key words: moving-boundary model; coagulation rate; activation energy of coagulation; as-spun fiber

INTRODUCTION

Fiber formation by wet-spinning accounts for a significant fraction of the production of today's man-made fibers. In the first stage, a spinning dope is extruded through a spinneret orifice into a coagulation bath and a counter-diffusion phenomenon between solvent and coagulant takes place immediately and causes the polymer to solidify. This process is called coagulation. It is of great importance in fiber formation, and many scholars have carried out studies on this aspect.[1–4] The mathematical models used to explain the diffusion process in wet-spinning are mainly the Moving-Boundary Model and Constant-Flux Ratio Model proposed by Paul.[5,6] In addition, Rende,[7] Liu et al.,[8,9] and Knaul and Creber[10] also established similar models to describe the counter-diffusion phenomenon in wet-spinning and obtained similar result.

However, the coagulation process in wet-spinning is very complex and there are still many puzzles to be pendent. The reports on the coagulation rate of PAN/DMSO spinning system are few and inadequate. In this article, based on the moving-boundary model, the motion of the coagulating-boundary under various coagulation conditions was studied to release the effect of the coagulation variables on the coagulation rate, optimize and adjust the fiber formation progress to obtain excellent as-spun fibers with homogeneous and compact microstructure, and excellent mechanical properties.

EXPERIMENTAL

Fiber formation process

DMSO solution polymerization was used to synthesize AN polymer solution. The obtained dope was deaerated, filtered, and then pumped through a spinneret (1000 holes, 0.06 mm/hole, $L/D = 1.0$) to a coagulation bath. The as-spun fibers were obtained by adjusting the coagulation variables on wet-spinning system. The basic coagulation condition is set as follows: polymer content of the dope is 20 wt %, the coagulation bath temperature is 30°C, solvent content in bath is 60 wt %, and the jet stretch ratio is 0.7.

Measurement of the coagulation rate

According to the moving-boundary model, as illustrated in Figure 1, a very distinct interface is associated with the coagulation. One side of the boundary is hard, coagulated polymer, while the other side is the soft original gel. The boundary begins at the sample surface and moves inward with time until to the center.[6]

The PAN/DMSO dope were first poured into bottles and chilled into gels. By pushing a cylindric cork borer (0.9 cm diameter, 4.5 cm length) into them, as illustrated in Figure 2, the gelled solutions changed into gelled rods and were stored in a refrig-
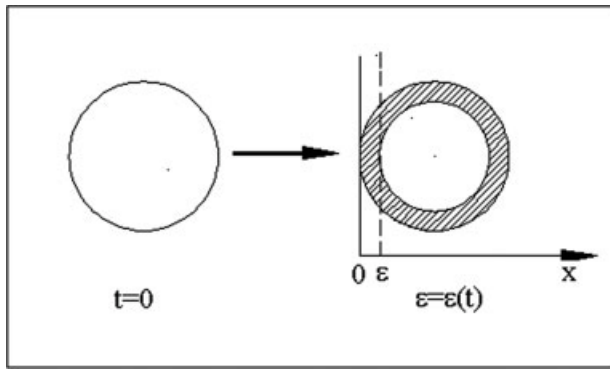
Figure 1 Scheme of boundary motion with time during the coagulation step.

erator. During the measurement, the gelled rod were brought to room temperature and immersed in various coagulation baths. At the prescribed time they were quickly removed from the baths and cross-sectioned by a razor blade. The depth of penetration of the boundary was observed with an optical microscope fitted with a calibrated scale.

Observation of morphology

The samples of as-spun fibers were put into liquid nitrogen to fix their structure. After being dipped in glue and brittle-ruptured their cross-sectional microstructure was observed by Electron Microprobe Analysis (Japan JXA-8800R type).

RESULTS AND DISCUSSION

Effect of the nature of the coagulants on the coagulation rate

Here, we adopt PAN/DMSO dope in the DMSO/coagulant mixture to study the effect of nature of coagulants on the coagulation rate. The concentration of polymer and DMSO in the dope is 20 and 80 wt %, respectively; the concentration of DMSO (solvent) and coagulant (nonsolvent) in the coagulation bath is 60 and 40 wt %, respectively. Figure 3 presents the relationship between the boundary position $\xi_{(t)}$ and coagulation time t during the coagula-
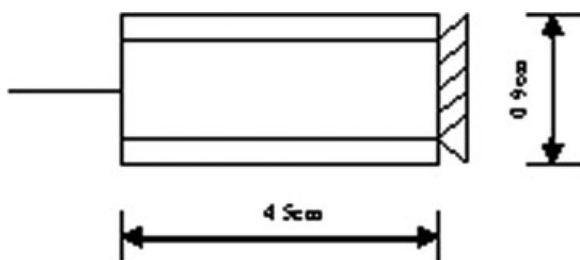

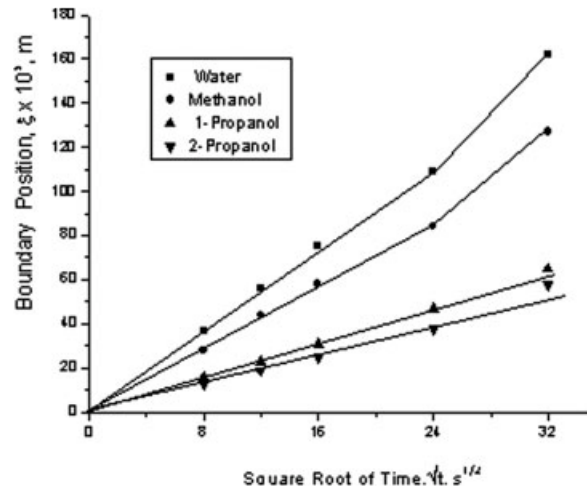**Figure 2** Scheme of a cork borer.

Figure 3 Curve of boundary position of various coagulants with time during coagulation step.

tion step of PAN/DMSO dope in various coagulants of water, methanol, 1-propanol and 2-propanol. It can be seen that $\xi_{(t)}$ is proportional to the square root of time in the initial period of coagulation. It can be explained as follows.

For a linear one-dimensional system, the Fick Second Law can be written as follows[11]:

$$\partial C_n / \partial t = D_n (\partial^2 C_n / \partial X^2) \tag{1}$$

Thereby the distribution expression of the concentration of the coagulant is obtained[12]:

$$C_n(x,t) = A \operatorname{erf}\left(\frac{x}{2\sqrt{D_n t}}\right) + B \tag{2}$$

where C_n is the concentration of coagulants at coagulation time t; D_n is the diffusion coefficient of the coagulant; x is the moving-boundary position at coagulation time t; erf is an error function; A and B are constants of integration.

Then via the boundary condition, $C_n(x,t) = C_{n,0}$ when $x = 0$, and $C_n(x,t) = C_{n,\text{eq}}$ when $x = \xi$, we can get:

$$A = \frac{C_{n,\text{eq}} - C_{n,0}}{\operatorname{erf}\left(\frac{\xi}{2\sqrt{D_n t}}\right)} \tag{3}$$

Thereby $\xi/\sqrt{t}$ is a constant and is called "coagulation rate," which reflects the growth rate of the outer coagulated-layer during the coagulation process.[13] The larger the coagulation rate, the thicker is the coagulated layer formed in the same coagulation time and the more rapidly and acutely the coagulation process. It reflects the effect of coagulation condition on the coagulation process and is valid only at the very early stage of the coagulation process.

Coagulants	Water	Methanol	1-Propanol	2-Propanol
$V \times 10^6$ (m^3/mol)	18.0	40.4	74.8	76.2
$\xi/\sqrt{t} \times 10^5$ (m/s$^{1/2}$)	4.62	3.59	1.92	1.57

Table I shows the coagulation rate of four coagulants obtained from Figure 2. It showed that the coagulation rate decreases with the increasing molecular volume of coagulants.

This result indicates that the diffusion process is mainly controlled by the diffusion of the coagulant.[9] According to the "Cavity Theory,"[14] the coagulation rate will be determined by the molecular volume of coagulant. Liu considered that the molecular volume of coagulant mainly affected the diffusion coefficient of coagulant.[15] Usually the diffusion coefficient descends with the increase of the molecular volume, and a large diffusion resistance will be encountered during the course of migration. Thus the coagulation rate becomes low.

In addition, the characteristic of functional groups and molecular structure of coagulants may also affect the coagulation rate. As the steric arrangement of the macromolecular chains between 1-propanol and 2-propanol is different, the presence of the side group (—CH$_3$) near the hydroxyl on the macromolecular chains of 2-propanol reduces their accessibility to the solvent molecules in the polymer solution and also weakens the mobility migrating through the gel solution, which results in a low-diffusion rate into the solution and consequently a low-coagulation rate than that of 1-propanol.

The minimum coagulation rate acquired for complete coagulation

The selected coagulants should provide sufficient coagulation rate to fully coagulate the polymer dope. Otherwise defects such as inner microvoids will occur. Neglect the effect of the die-swell and the jet stretch, and assume the diameter of as-spun fibers is equal to that of the spinneret orifice, then the minimum coagulation rate acquired for complete coagulation is as follows[9]:

$$\left(\xi/\sqrt{t}\right)^* = 0.7(D/2)(\overline{V}/L)^{1/2} \qquad (4)$$

where D is the diameter of the spinneret orifice, and L and V is the immersion distance and average velocity, respectively.

The minimum coagulation rate reflects the growth rate of the coagulated layer and does not control its

composition, which is the key factor affecting the structure and properties of as-spun fibers. However, it is very useful in predicting a suitable coagulant or coagulation condition for a certain spinning system. If the coagulation rate of one coagulant is less than the minimum coagulation rate, then the coagulation is insufficient and inner voids are easy to form. Hence it can be used to select a coagulant suitable for a certain spinning system. As per the spinning system used in our laboratory, the diameter of the spinneret orifice $D = 60$ μm, the immersion distance $L = 150$ cm, the average velocity $V = 4.59$ cm/s, then the minimum coagulation rate acquired for complete coagulation is 0.367 [$\times 10^{-5}$ m/s$^{1/2}$] based on formula 4. The coagulation rate of water, methanol, 1-propanol and 2-propanol at 30°C is, respectively: 4.62, 3.59, 1.92, and 1.57 [$\times 10^{-5}$ m/s$^{1/2}$], all of which are bigger than the minimum coagulation rate, thus they can all be used as coagulant.

The variety of coagulants determines greatly the morphology of as-spun fibers, as shown in Figure 4. As a higher coagulation rate implies the coagulation that occurs sharply and usually leads to a rigid skin-layer at the very early stage, which hinders the diffusion of coagulant into the dope stream, and thus some voids form in the inner and a rough cross-section appears, as shown in Figure 4(a). On the contrary, as for the coagulant of 1-propanol with a lower coagulation rate, the coagulation takes place in a steady and even state, so the skin layer formed at first is soft and thin, which favors diffusion of coagulant and leads to a more compact structure with a regular cross-section.

Effect of the nature of solvents on the coagulation rate

The diffusion of solvent is an important part in PAN fiber formation, and it has dominant effect on the structure and properties of as-spun fibers. To discuss the effect of solvent on the coagulation rate we adopt DMSO and DMF as solvent, H$_2$O as coagulant, and measure their coagulation rate using the same method as earlier. As per PAN/DMSO in DMSO/H$_2$O system, the concentration of polymer and DMSO in the dope is 20 and 80 wt %, respectively, the concentration of DMSO and H$_2$O in the coagulation bath is 60 and 40 wt %, respectively. As per PAN/DMF in DMF/ H$_2$O system, the concentration of polymer and DMF in the dope is 20 and 80 wt %, respectively, the concentration of DMF and H$_2$O in the coagulation bath is 60 and 40 wt %, respectively. The result is shown in Figure 5.

It is reported that the intermolecular force between solvent and coagulant is a significant factor determining the value of coagulation rate. As the polarity of DMSO molecules is weaker than that of DMF, the
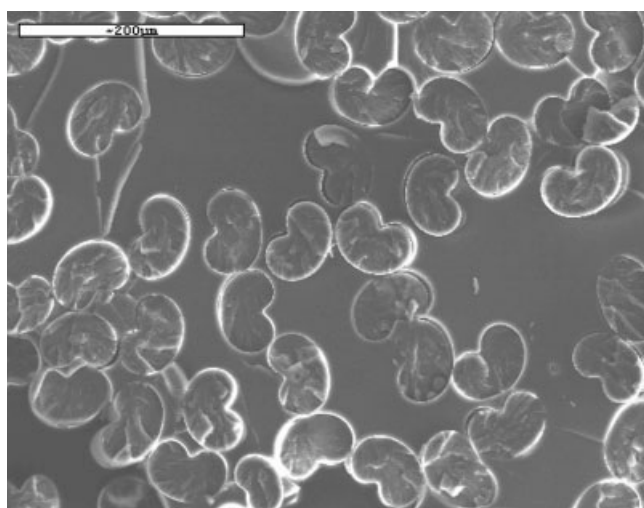
(a)
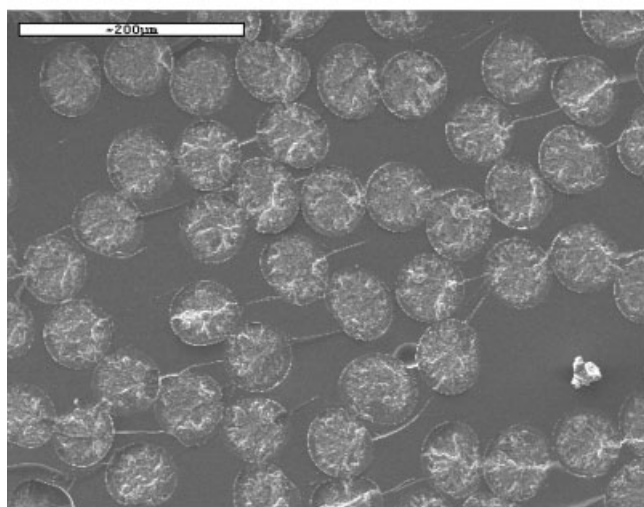
(b)

Figure 4 Morphology of the as-spun fibers with different coagulants (a) water; (b) 1-propanol.

intermolecular force between DMSO and coagulant is smaller than that of DMF, so the driving force for it to diffuse out of the solution is also smaller and it has to overcome a higher energy barrier before being activated. Moreover, the viscosity of PAN/DMSO dope is bigger than that of DMF, so there is a large resistance for the DMSO molecules to diffuse through the dope. Thereby the coagulation rate of PAN/DMSO in DMSO/H_2O is lower than that of PAN/DMF in DMF/H_2O.

Activation energy of coagulation

The coagulation of the polymer in a coagulation bath is a rate process. According to the ''Cavity Theory,''[14] the mobility of diffusion species (coagulant) is determined by its molecular volume and void size of the medium into which it will diffuse.

The ability to diffuse of coagulant increases with the temperature. The relationship between the coagulation rate and the temperature is in accordance with the following Arrhenius equation:

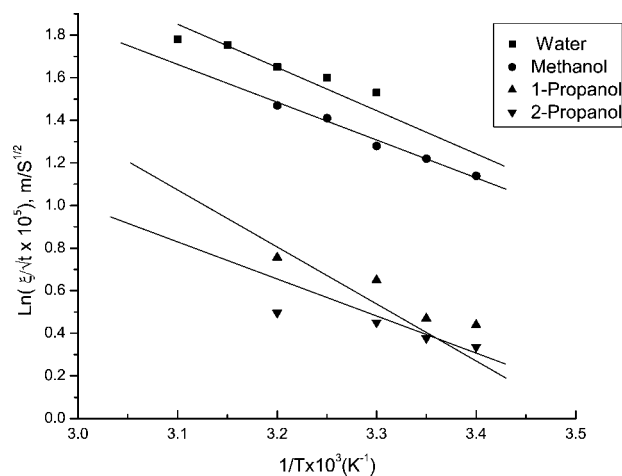$$\ln(\xi/\sqrt{t}) = \ln A - \frac{E_a}{RT} \qquad (5)$$

where $\xi/\sqrt{t}$ represents the coagulation rate, T is the coagulation bath temperature, E_a is the activation energy of coagulation, and A is the intercept.

Here, we adopt PAN/DMSO dope in the DMSO/coagulant mixture to study the effect of coagulation bath temperature on the coagulation rate. The concentration of polymer and DMSO in the dope is 20 and 80 wt %, respectively; the concentration of DMSO (solvent) and coagulant (nonsolvent) in the coagulation bath is 60 and 40 wt %, respectively. Figure 6 is the Arrhenius plot of coagulation rate of different coagulants versus the coagulation bath temperature. The activation energy of water, methanol, 1-propanol and 2-propanol calculated by Figure 5 is shown in Table II. They are within the same order of magnitude as those reported for other coagulation systems such as cellulose/NH_3/NH_4SCN in methanol, 1-propanol and 2-propanol (5.146–16.024 kJ/mol); PAN/DMF solution in an aqueous DMF bath (15.899–25.941 kJ/mol); and cellulose xanthate/NaOH in aqueous H_2SO_4 bath (7.896 kJ/mol).[9]

The activation energy of coagulation depends on the variety of coagulant, its molecular volume, the steric arrangement of the macromolecular chains, and the affinity between coagulant and solvent, not depending on the coagulation conditions such as temperature and concentration, etc. A free energy of activation acquired for the movement of a diffusion species from one site to another site in medium
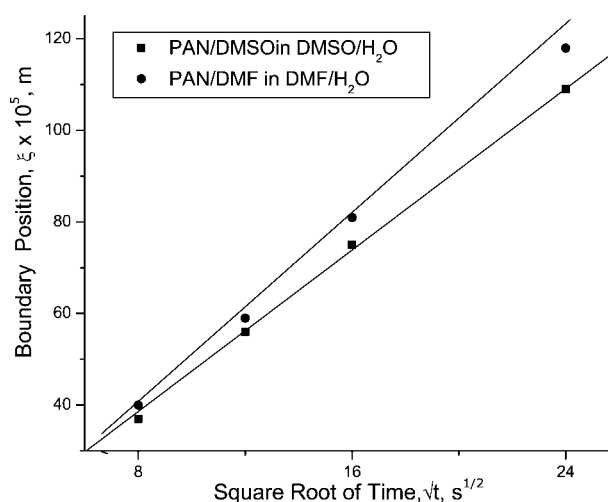
Figure 5 Curve of boundary motion of different solvents with time during coagulation step.

Figure 6 Arrhenius plot of coagulation rate versus the coagulation bath temperature.

must be gained before diffusion can take place. According to "Cavity Theory" the activation energy should increase with the increasing molecular volume of the coagulant. But in fact it is opposite, that is, E_a [Water] $> E_a$ [Methanol] $> E_a$ [1-Propanol] $> E_a$ [2-Propanol]. It is because that this theory only considered the effect of molecular volume of diffusion species but not includes the interaction between diffusion species, which is a more dominant factor determining the energy barrier. The species with strong polarity will cause stronger affinity with solvent molecules, which will hinder the free movement of the diffusing species, thus the activation energy enhances. The molecular polarity of water and methanol is larger than that of 1-propanol and 2-propanol, thus their activation energy is also larger than the latter two.

As the hydroxyl locates in the middle of the macromolecular chains of 2-propanol, its polarity is not strong as that of 1-propanol that possesses straight macromolecular chains, so the affinity between it and solvent molecules is weaker than that of 1-propanol and its diffusion molecules can move much freely. In addition, the steric arrangement of the molecular chains of 2-propanol is unstable and easy to be activated, thus its activation energy is lower than that of 1-propanol.

Effect of solvent content in coagulation bath on the coagulation rate

Here, we adopt PAN/DMSO dope in the DMSO/ H_2O mixture to study the effect of jet stretch on the coagulation rate. The concentration of polymer and DMSO in the dope is 20 and 80 wt %, respectively.

From Figure 7 it can be seen that with the increase of the solvent concentration the coagulation rate descends gradually to the lowest value and then rises slightly. With the increase of the solvent con-

TABLE II
The Regression Equation for the Relationship Between $\ln \xi / \sqrt{t}$ and $1/T$.

Coagulant	$\ln \xi / \sqrt{t}$—$1/T$ regression equation	E_a (kJ/mol)
Water	$\ln(10^5 \times \xi / \sqrt{t}) = 3.20 - 0.46(10^3 \times 1/T)$	16.17
Methanol	$\ln(10^5 \times \xi / \sqrt{t}) = 2.67 - 0.45(10^3 \times 1/T)$	15.71
1-Propanol	$\ln(10^5 \times \xi / \sqrt{t}) = 1.58 - 0.34(10^3 \times 1/T)$	11.68
2-Propanol	$\ln(10^5 \times \xi / \sqrt{t}) = 0.88 - 0.16(10^3 \times 1/T)$	5.54

centration the dilution effect of solvent content on the coagulant concentration in the bath became prominent. As the solvent content increases, the concentration of coagulant decreases in the bath, accordingly the driving force for the coagulant to diffuse into the stream reduced and led to a descent coagulation rate. The coagulation rate drops to the lowest point and then presents a slight rise. Because at this solvent concentration the gel becomes fluffy and swollen and makes the osmosis easy to occur, so the skin layer containing a large portion of solvent becomes soft and loose and leads to a swollen structure. Correspondingly, there is a higher value for the boundary position.

Effect of the jet stretch ratio on the coagulation rate

Here, we adopt PAN/DMSO dope in the DMSO/ H_2O mixture to study the effect of jet stretch on the coagulation rate. The concentration of polymer and DMSO in the dope is 20 and 80 wt %, respectively; the concentration of DMSO (solvent) and coagulant (nonsolvent) in the coagulation bath is 60 and 40 wt %, respectively. As illustrated in Figure 8, the coagulation rate of PAN/DMSO dope in DMSO/H_2O mixture reduced with the increasing jet stretch ratio. It
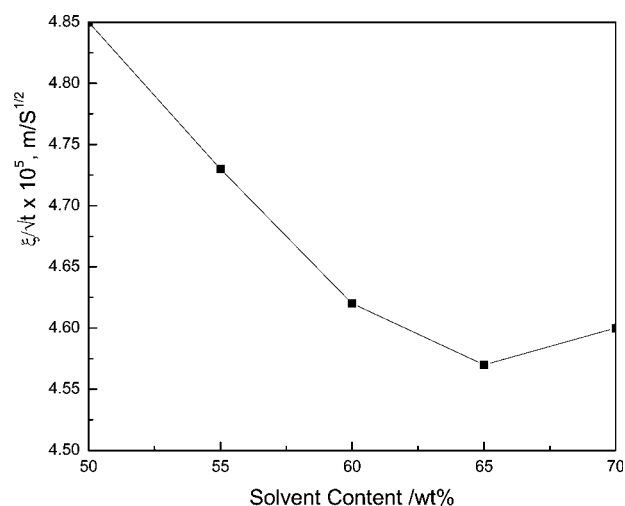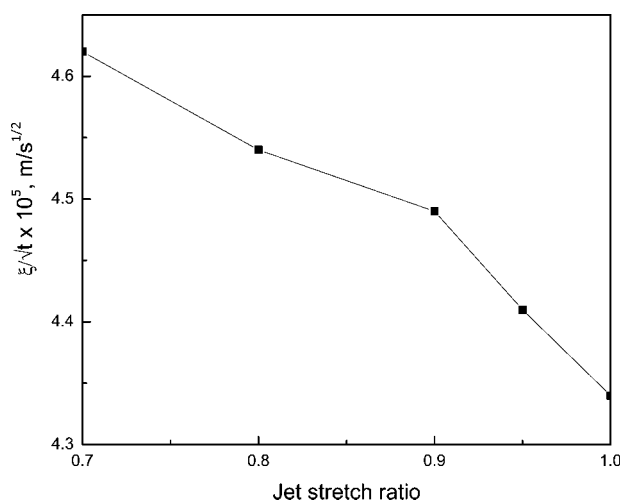

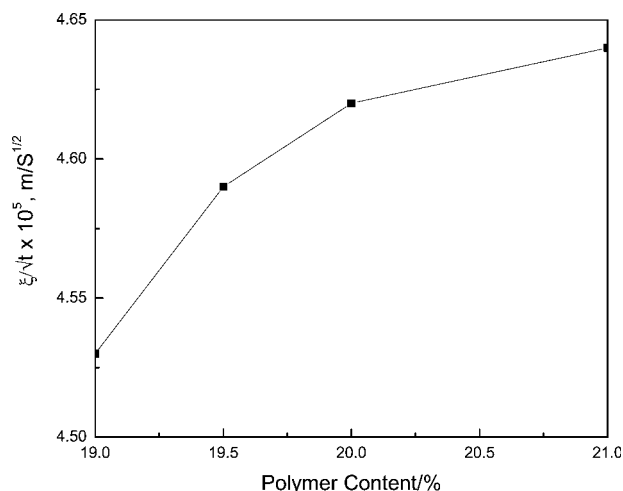**Figure 7** Effect of solvent content on the coagulation rate.

can be explained as follows. With the increasing jet stretch ratio the die-swell ratio of the dope reduced and the fineness of as-spun fibers became smaller, so the inner microvoids became less and the orderly arrangement of the macromolecular chains enhanced. As the diffusion ability of coagulant is controlled by the isotacticity of polymer molecular chains and the mobility of segments, which is greatly determined by the crystallinity and the inner porous structure.[16,17] The decrease of the amount of inner voids and increase of the crystallinity made the osmosis difficult. In addition, the higher the jet stretch ratio is, the bigger is the tension applied to the spinning line, which hinders the mobility of the polymer chains, and the diffusion of coagulant is impeded.[18] Accordingly the coagulation rate reduced.

Effect of polymer content of the dope on the coagulation rate

Here, we adopt PAN/DMSO dope in the DMSO/H_2O mixture to study the effect of polymer content on the coagulation rate. The concentration of DMSO (solvent) and coagulant (nonsolvent) in the coagulation bath is 60 and 40 wt %, respectively. From Figure 9 it can be seen that the increase of polymer content of the dope will cause a prominent increase of the coagulation rate. Polymer content of the dope has double effects on the coagulation rate. On one hand, the increase of polymer content accompanies the increase of the viscosity and a reduced mobility of solvent and coagulant, resulting in a lower coagulation rate; on the other hand, the higher polymer content enhances the intermolecular affinity caused by the high density of polymer chains and further enhances the driving force for coagulation. The latter has dominant affect on the coagulation rate.

Figure 8 Effect of the jet stretch ratio on the coagulation rate in DMSO/H_2O mixture.

Figure 9 Effect of polymer content on the coagulation rate.

CONCLUSION

1. The nature of coagulants including molecular sizes as well as molecular structure is the most significant variable affecting the coagulation rate of PAN/DMSO dope. Of all the four coagulants, water has the most effective coagulation ability.
2. The intermolecular affinity between coagulant and solvent determines the energy barrier of the activation energy of coagulants, whereas the molecular volume is not a dominant factor.
3. The coagulation rate depends not only on the diffusion coefficient of coagulants but also the nature of solvents. A solvent with strong polarity usually leads to a low coagulation rate.

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