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Effect of Bath Concentration on Coagulation Kinetics at the Early Stage during Wet Spinning of PAN Copolymer Nascent Fibers

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A mathematical model was proposed to simulate the effect of bath concentration on coagulation kinetics at the early stage of wet spinning for the poly(acrylonitrile-co-vinyl acetate)/dimethylsulfoxide (DMSO)/water system. The dependence of critical precipitation time, components concentration distribution, and the radius of nascent fibers on the concentration of DMSO in the DMSO/water coagulation bath were estimated by solving the model equation numerically. The experimental results indicated the model was suitable to simulate the dynamic features of the early stage of the coagulation process. The critical precipitation time was found to increase with bath concentration. The mode of phase separation was changed from instantaneous demixing to delayed demixing as DMSO bath concentration increased. The simulation results showed that bath concentration influenced the phase separation path which determined the polymer concentration distribution in the spinning solution. As a result, nascent fibers with different structures would form in wet spinning and a radial homogeneous structure would be obtained when the DMSO bath concentration increased to some extent.

Keywords carbon fibers, diffusion, mathematical model, PAN copolymer, phase diagram, wet spinning

Introduction

Polyacrylonitrile (PAN) copolymer fibers are considered as important precursors for the production of carbon fibers. Wet spinning is one of the methods to produce PAN copolymer precursor fibers.1 In wet spinning, a viscous polymer solution is extruded through small holes of a spinneret immersed in a coagulation bath. Then a diffusional interchange between the spinning solution jet and the coagulation bath causes the spinning solution to solidify. During the diffusional interchange, one or more of the bath components diffuse into the jet, while solvent diffuses out of it.2 Then the structure of nascent fibers forms. Due to the dependence of the properties of subsequent carbon fibers on its precursor structure, particularly on the section shape, the external skin, and the void structures, an accurate understanding of the phenomena is of great importance to regulate these features.

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Extensive works have been carried out on the relationship between the spinning conditions and properties of PAN fibers.\(^3\)–\(^{12}\) The influence of coagulation conditions on the coagulation process during the wet spinning of PAN nascent fibers have also been reported.\(^{13}\)–\(^{16}\) However, the mechanisms of the coagulation during wet spinning are not yet well understood. Because of the rapid complex coagulation kinetics, it is very difficult to obtain information of the coagulation process. The development of computer technology aids in simulating experimental phenomena. General modeling techniques to understand the mechanisms of the coagulation processes have been reported by Oh et al.\(^{17}\) and Chen et al.\(^{18}\) Although the models presented general coagulation mechanisms, they cannot provide detailed information of the early stage of the coagulation process.

The goal of the research reported here was to investigate the effect of bath concentration on the early stage of coagulation kinetics during wet spinning for the PAN copolymer/dimethylsulfoxide/water system by both experiments and a mathematical model.

**Experiments**

**Wet Spinning**

PAN copolymer solution was obtained by free-radical solution copolymerization, in which acrylonitrile (AN) and vinyl acetate (VAc) were monomers (AN:VAc = 93:7), azodiisobutyronitrile (AIBN) was the initiator, and dimethylsulfoxide (DMSO) as solvent. After removal of unreacted monomers, the solution was deaerated, filtered, and then pumped through a spinneret (1000 holes, 0.06 mm/hole, L/D = 1.2) into a DMSO/water coagulation bath system of varying DMSO/water ratio. The PAN copolymer nascent fibers were obtained from the coagulation bath using different DMSO bath concentrations, holding other factors constant. The polymer concentration was 20 wt% in the spinning solution. The coagulation bath temperature was 50°C and the apparent stretch ratio was 0.9. Dry PAN copolymer nascent fibers were obtained by freeze-drying technology to preserve the structure of nascent fibers.

**Characterization**

The section morphology of the PAN copolymer nascent fibers was examined by field emission scanning electron microscopy (FESEM) (JSM-6700F, JEOL Ltd.) with 1 nm point-to-point resolution operating with a 10-kV accelerating voltage under vacuum conditions. The samples were fractured in liquid nitrogen to preserve the structure of the nascent fibers. All samples were then coated with a thin layer of gold before the FESEM observation.

**Measurement of Phase Diagram**

The phase diagram of the ternary system PAN copolymer/DMSO/water was constructed using the linearized cloudpoint curve correlation (LCP) approach according to a previous literature.\(^{19}\) Figure 1 shows a plot of ln(% water/% copolymer) vs. ln(% DMSO/% copolymer), derived from the cloudpoint compositions. The binodal curve for the PAN copolymer/DMSO/water system is presented in Fig. 2.

**Measurement of the Critical Precipitation Time**

An optical microscope (Nikon YS100) equipped with a liquid cell and a video camera (Canon PowerShot A620) was applied for detecting the coagulation process of PAN
copolymer films (Fig. 3). A film of PAN copolymer solution was prepared by spreading the solution onto a glass slide, covered with another slide, and then put in the liquid cell. The liquid cell holder was placed horizontally on the sample stage and the optical image of the interface between the air and polymer solution obtained. Then the liquid cell was filled with a DMSO/water solution by a syringe and the coagulant introduced into the thin space between the two slides. The coagulation process of PAN copolymer films was recorded by the camera at a rate of one frame per 30 ms.

The critical precipitation time is the interval between the first contacting with the coagulant and the beginning of the precipitation for the spinning solution. To investigate the critical precipitation time of the interface between DMSO/water and PAN copolymer solution during the coagulation process, coagulation experiments with the film were carried out as DMSO concentration in coagulation bath was varied from 0 to 80 wt%. Figure 4(A) shows an optical microscopy image of PAN copolymer solution which was formed by spreading the PAN copolymer solution in the liquid cell. An interface between air and

Figure 1. LCP plot for the PAN copolymer/DMSO/water system.

Figure 2. Phase diagram for the PAN copolymer/DMSO/water system and interfacial compositional trajectories at different bath concentrations.
PAN copolymer solution was formed which was visible because of the different refractive indexes. When DMSO/water was injected into the liquid cell and contacted with the copolymer solution, the interface between air and the copolymer solution disappeared while a new interface between the solution of DMSO/water and copolymer solution formed, as shown in Fig. 4(B).

**Mathematical Model**

During the coagulation process, the spinning solution is extruded through a spinneret immersed in a coagulation bath, and then a diffusional interchange occurs between the spinning solution jet and the coagulation bath. Solvent leaves the spinning solution while nonsolvent enters.[2] Normally, the spinning solution jet during the coagulation process is considered as a cylinder of infinite length, as shown in Fig. 5, in which mass transfer in the axial direction can be neglected. Therefore, only mass diffusion in the radial direction is considered.[18] Solvent and nonsolvent are transported by molecular diffusion during the coagulation process. Diffusions of solvent and nonsolvent in the coagulation bath can be regarded as diffusion in an immobile medium because of the dynamic boundary layers of the coagulation bath around the filaments. Besides, although it is formally a tricomponent (polymer/solvent/nonsolvent) system, in view of the low mobility of the macromolecules of the polymer, it should actually be considered as a bicomponent system with the mutual diffusion coefficient of solvent and nonsolvent.[20] Based on the basic assumptions, the mass transfer of component \(i\) within the phase \(j\) in the radial direction can be given by

![Figure 3. Schematic representation of sample apparatus for the film coagulation experiment.](image)

![Figure 4. The optical microscopy observation of PAN copolymers/DMSO solution (A) Not contacted with the coagulant and (B) contacted with the coagulant.](image)
Fick’s second law as

\[
\frac{\partial C_{(i,j)}}{\partial t} = \frac{1}{r} \left\{ \frac{\partial}{\partial r} (r \cdot D_{(i,j)} \frac{\partial C_{(i,j)}}{\partial r}) \right\}, \quad i = 1, \ 2, \ \ldots \ \text{for } j = 1, \ 2, \ \ldots 
\]  

(1)

where \( C_{(i,j)} \) represents the molar concentration of component \( i \) in phase \( j \) at time \( t \) (mol/m\(^3\)), \( D_{(i,j)} \) is the diffusion coefficient of component \( i \) in phase \( j \) (m\(^2\)/s), \( t \) is the diffusion time (s), \( r \) is the diffusion distance in radial direction (m), and components 1, 2, and 3 are the solvent, nonsolvent, and polymer, respectively. To solve the equation, boundary conditions are given by

\[
\frac{\partial C_{(i,1)}}{\partial r} \bigg|_{r=0} = 0, \quad i = 1, \ 2; \ \text{for } j = 1, 
\]

(2)

\[
\frac{\partial C_{(i,2)}}{\partial r} \bigg|_{r=R+L} = 0, \quad i = 1, \ 2; \ \text{for } j = 2, 
\]

(3)

\[
C_{(i,1)} \big|_{r=R} = k_{(i)} \cdot C_{(i,2)} \big|_{r=R}, \quad i = 1, \ 2, 
\]

(4)

\[
D_{(i,1)} \cdot \frac{\partial C_{(i,1)}}{\partial r} \bigg|_{r=R} = D_{(i,2)} \cdot \frac{\partial C_{(i,2)}}{\partial r} \bigg|_{r=R}, \quad i = 1, \ 2, 
\]

(5)

where \( R \) is the radius of the filament at time \( t \) (m), \( k_{(i)} \) is the partition coefficient of component \( i \), and \( L \) is the thickness of boundary layers in the coagulation bath around the filaments (m). Equations (2) means that there is no mass exchange through the left boundary of the system and Eq. (3) means the component concentration remains constants at the right boundary of the system. Equation (4) describes the local thermodynamic equilibrium at the interface between the spinning solution phase and the coagulation bath phase, and Eq. (5) describes the mass transfer continuity at the phase interface of spinning solution and coagulation bath.

Assuming that the initial solution is homogeneous, initial conditions are given by

\[
C_{(i,j)} \big|_{t=0} = C_{0(i,j)}, \quad i = 1, \ 2 \ \text{for } j = 1, \ 2, 
\]

(6)
where $C_{0(i,j)}$ is the initial molar concentration of component $i$ in phase $j$ (mol/m$^3$). The global mass balance equation may be expressed as

$$\sum_{i=1}^{NC} \Phi_{(i,j)} = 1, \quad j = 1, 2,$$

(7)

where NC is the number of chemical components, being equal to 3. $\Phi_{(i,j)}$ is the volume fraction of component $i$ in the phase $j$, defined as

$$\Phi_{(i,j)} = \frac{C_{(i,j)}}{M_{(i,j)}} \cdot \left[1 - \Phi_{(1,1)} - \Phi_{(2,1)}\right],$$

(8)

where $M_{(i,j)}$ is the molecular weight of component $i$ (kg/mol) and $\rho_{(i,j)}$ is the density of component $i$ (kg/m$^3$), so the molar concentration of polymer composition in the spinning solution is

$$C_{(3,1)} = \frac{\rho_{(3,1)}}{M_{(3,1)}} \cdot \left[1 - \Phi_{(1,1)} - \Phi_{(2,1)}\right],$$

(9)

whereas the solvent concentration in coagulation bath is

$$C_{(1,2)} = \frac{\rho_{(1,2)}}{M_{(1,2)}} \cdot \left[1 - \Phi_{(2,2)}\right]$$

(10)

Finally, the radius change can be derived from the global mass balance equation of the polymer component. The polymer mass is assumed to be constant and completely contained in the filament. Thus

$$m_{(3,1)} = \int_{0}^{R} 2\pi r \cdot C_{(3,1)} \cdot dr$$

(11)

where $m_{(3,1)}$ is the total polymer mass in the filament per unit length (kg/m). If Eq. (11) is differentiated with respect to time and made equal to zero, then

$$\frac{dR}{dt} = -\frac{1}{2\pi R \cdot C_{(3,1)}|_{r=R}} \cdot \int_{0}^{R} 2\pi r \cdot \frac{dC_{(3,1)}}{dt} \cdot dr$$

(12)

which is the filament radius changing with time. Equations (1–12) constitute a mathematical model of the early stage of the coagulation process during wet spinning. The binodal curve for the PAN copolymer/DMSO/water system is presented in Fig. 2. It was assumed that precipitation would occur when the dynamic trajectory crossed the system binodal curve. Figure 2 illustrates the procedure. According to the mathematical model, the components concentration distribution and the radius of the filament at time $t$ could be obtained.

To create a model of the coagulation process, it was necessary to know the mutual diffusion coefficients and partition coefficients for all the chemical components involved. According to the literature,[21] the mutual diffusion coefficient of solvent and nonsolvent in the PAN copolymer solution was taken equal to $9 \times 10^{-11}$ m$^2$/s. No reported value for the corresponding diffusivity in the DMSO/water system can be applied directly. The mutual diffusion coefficient of solvent and nonsolvent in the coagulation bath was taken equal to $1 \times 10^{-9}$ m$^2$/s and typical values for the partition coefficients of solvent and nonsolvent...
were 1.0 and 0.5, respectively.\cite{22} In agreement with previous literature,\cite{17,18} the model was built without taking the flow field into consideration.

There are many factors which affect the coagulation process in wet spinning. Here only the bath concentration was studied with the others unchanged. The effect of the DMSO concentration in coagulation bath on the polymer concentration distribution, critical precipitation time, interfacial polymer concentration distribution, and radius of nascent fibers were all investigated. The spinning solution was assumed to contain 20 wt% copolymer and 80 wt% DMSO solvent. The initial radius of the spinning solution jet was 30 \(\mu m\). The solutions of these equations were obtained with the aid of Matlab software.\cite{18}

**Results and Discussion**

For the surface of the copolymer solution that first contacted the DMSO/water solution, the coagulation time recorded by the optical image was short. When the DMSO concentration in the coagulation bath was below 70 wt\%, the coagulation time was shorter than 30 ms, but the coagulation time was between 30 ms and 60 ms when the DMSO concentration in the coagulation bath was over 70 wt\%. Due to the equipment capacity, it was difficult to obtain an accurate value of coagulation time for both concentrations. In the simulation, the critical precipitation times increased from 0.333 ms to 52.4 ms as DMSO concentration in coagulation bath was varied from 0 to 80 wt\%, as shown in Fig. 6. The critical precipitation time obtained from the model was thus in good agreement with the experiment. This indicated that the model was suitable to simulate the dynamic features of the early stage of the coagulation process. Therefore we can use the model to research the coagulation process in the early stage during wet spinning to some extent.

The critical precipitation time was found to increase slightly with DMSO concentration in coagulation bath up to 70 wt\%, after which it increased rapidly, as shown in Fig. 6. Therefore, the mode of phase separation would change from instantaneous demixing to delayed demixing as DMSO bath concentration increased.\cite{14} In other words, phase separation was delayed by addition of DMSO solvent to the coagulation bath. This was expected since the driving force for diffusion would be reduced when the amount of solvent in the coagulation bath increased. Furthermore, the results indicated that delayed demixing could be easily

![Figure 6. The plot of critical precipitation time vs. bath concentration.](image-url)
obtained by raising the concentration of solvent within the coagulation bath. Many studies have led to a rather general conclusion that delayed demixing was better than instantaneous demixing during wet spinning to obtain high-performance precursor fibers. Therefore, increasing bath concentration was quite beneficial for obtaining high performance precursor fibers, which is in good agreement with the previous reports.

Nascent fibers were obtained under different bath concentration, as shown in Fig. 7. There was a relatively dense skin on the surface of the nascent fibers and a relatively loose sublayers structure at 50 wt% bath concentration, while the structure became more homogeneous at 60 wt% bath concentration. In addition, the core of nascent fibers became denser when the bath concentration was sufficiently high. It indicated that nascent fibers with different structures may be formed depending on the bath concentration. This was because the phase separation path was transformed when the bath concentration was changed, as shown in Fig. 2. The phase separation path determined the PAN copolymer concentration distribution in the spinning solution, and then resulted in different structures of the nascent fibers. The interfacial PAN concentration increased from 0.19 to 0.23 with water as coagulant whereas it decreased from 0.19 to 0.13 with 80 wt% DMSO as coagulant, as shown in Fig. 8. Figure 9 shows that the PAN copolymer concentration gradients at precipitation became smaller as DMSO concentrations in coagulation bath increased from 0 to 80 wt%. Low DMSO concentration in coagulation bath led to high interfacial polymer concentration and a sharp polymer concentration gradient at the interfacial boundary. These caused a decrease in thickness and an increase in density of the skin of nascent fibers, which led to large radial heterogeneity.

Figure 10 shows how the radius responded to DMSO bath concentration. The radius of nascent fibers shrank from 30 \( \mu m \) to 29.93 \( \mu m \) with water as coagulant whereas it swelled...
from $30 \mu m$ to $31.07 \mu m$ with $80$ wt% DMSO as coagulant. The interfacial PAN copolymer concentrations were lower than the initial concentration in spinning solution when DMSO concentration in coagulation bath was above $60$ wt%, as shown in Fig. 8. These results indicated that too high a concentration led to the spinning solution jet swelling. It has been explained in terms of a greater influx of water than outflow of solvent.\textsuperscript{14} Furthermore, the results suggested that too high a concentration hindered the coagulation of the spinning solution. These implied that the structure of nascent fibers may form with some defects, as reported in the previous literature.\textsuperscript{12} In conclusion, bath concentration influenced the structure of nascent fibers.
The bath temperature is as important as bath concentration in wet spinning. The model was utilized to simulate the effect of bath temperature on the coagulation process with all parameters assumed to be known. However, after the formation of the skin of the nascent fibers the model becomes invalid. The spinning solution jet splits into two different parts: a solidified layer and a uniform solution phase. The solidified layer increased in thickness during the coagulation process while the uniform solution phase decreased. Therefore, a further development of the mathematic model will be needed to describe this process.

Conclusions

The effect of bath concentration on the early stage of the coagulation process during wet spinning for PAN copolymer/DMSO/water system was investigated by both experiments and the mathematical model. The experiments confirmed that the model was suitable to simulate the dynamic features of the early stage of the coagulation process. The critical precipitation time was found to increase slightly with the DMSO bath concentration then increase rapidly when DMSO concentration in coagulation bath was above 70 wt%. As a result, the mode of phase separation was changed from instantaneous demixing to delayed demixing as DMSO bath concentration increased. In addition, delayed demixing could be more easily obtained by raising the concentration of DMSO solvent within the coagulation bath. The simulation results indicated that the bath DMSO concentration influenced the phase separation path which determined the polymer concentration distribution in the spinning solution, and then resulted in that nascent fibers with different structures was formed. A more homogeneous sublayers structure of nascent fibers was obtained at high bath concentrations. However, when the bath concentration is too high, the spinning solution jet may swell, hence hindering the coagulation of the spinning solution.

References
