Study on the Coagulation Mechanism of Wet-Spinning PAN Fibers

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Abstract

The mechanism of coagulation process of polyarylonitrile (PAN) wet-spinning was studied based on the numerical analysis of the coagulation of viscous polymer solution by diffusional interchange with a bath. Experiments were performed in order to determine the diffusion coefficient of solvent and non-solvent. The numerical solutions of Fick's second law equations for diffusion were obtained by using the MOL method. The microstructure of nascent fibers is investigated by Transmission Electron Microscope (TEM) and Electron Probe Microanalyser (EPMA). It is found that the speed of outflow solvent is more rapid than that of influent non-solvent. The speed of concentration change of solvent and non-solvent is rapid in outside layers of filament (0.2R) and slow in inner layers. The solvent concentration is keeping a high value at the center of filament. TEM and EPMA show that the microstructure is a typical layered structure. The thickness of dense skin is about 0.2R. The core region of fiber is very loose.

Introduction

Fiber formation by wet-spinning accounts for a significant fraction of the production of today's man-made fibers [1]. In this process a viscous polymer solution is extruded through the small holes of a spinneret immersed in a liquid bath. A diffusional interchange between the freshly formed fluid filament and the bath causes the polymer to solidify. This process is called coagulation. There are two diffusional motions that carry the solvent out of the filament to the bath and non-solvent from the bath to the filament. When the concentrations of polymer, solvent, and non-solvent overcome the phase equilibrium conditions, precipitation of the polymer in fibrillar form takes place [2]. Because of the dependency of structure, particularly on the regularity of the cross-sectional shape, the integrity of the external skin, and the number and size of voids, accurate knowledge of the phenomena regulating these features is of great importance [3].

Early studies were just empirical attempts to correlate the actual spinning variables with the final properties of the fibers [4–6]. Few investigators studied on the dynamics of the phenomena [7, 8], and to the best of our knowledge, there is almost no reports studied on the mechanism of coagulation process. The development of computer facilitates calculation and simulation to the experiment phenomenon, thus study mechanism of coagulation process deeply. In this work experiments on the spinning process were performed to determine the diffusion coefficient of solvent and non-solvent during coagulation. A H$_2$O/dimethl sulfoxide (DMSO) mixture was used as the coagulation bath of the wet-spinning process, and polyarylonitrile (PAN) solution (DMSO as solvent) was used as spinning dope. The concentration profile of solvent and non-solvent in a moving filament was computed by using a MOL (method of lines) method [9], which is well-known as a method to solve the partial difference equation with effect [9].

Theoretical analysis

For a cylinder of infinite length where diffusion occurs in the radial direction, Fick's second law for diffusion is given by:

$$\frac{\partial c}{\partial t} = \frac{1}{r}\left\{\frac{\partial}{\partial r}\left(rD\frac{\partial c}{\partial r}\right)\right\} = D\left(\frac{\partial^2 c}{\partial^2 r} + \frac{1}{r}\frac{\partial c}{\partial r}\right) \quad (1)$$

Where c represents solvent or non-solvent concentration (mol/l), D is the diffusion coefficient (m^2/s), t is the time(s), and r is normal to the surface of the filament. To solve the equation, initial and boundary conditions for a cylinder with radius R are given by:

$$
\begin{array}{llll}
c = c_0 & \text{for } 0 \le r \le R & \text{at} & t = 0 \\
c = c_\infty & \text{for } t \ge 0 & \text{at} & r = R \\
\frac{\partial c}{\partial r} = 0 & \text{for } t \ge 0 & \text{at} & r = 0
\end{array} \quad (2)
$$

Where c_0 represents the initial concentration of component inside the filament, and c_∞ represent the equilibrium concentration.

In the case of wet spinning, the diffusion of non-solvent and solvent in and out the filament may be taken as two independent processes. In order to obtained the diffusion coefficients, a number of authors solved Equation (1) [10–13], and the following is the results.

The equation for solvent diffusing out of the filament is given by:

$$\frac{M_t}{M_\infty} = 1 + 4\left(\frac{c_0}{c_\infty} - 1\right)\sum_{n=1}^{\infty}\frac{1}{\lambda_n^2}\cdot e^{-D\lambda_n^2 t/R^2} \qquad (3)$$

where M_t is the amount of this component inside the filament at time t, M_∞ is the amount when equilibrium, and λ_n is the positive root satisfying the zero-order Bessel function.

For non-solvent diffusing into the filament, the equation is given by:

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

The M values of the left side of the equations can all be experimentally determined. The values of the right side of Dt/R^2 can be calculated with the aid of a computer, and the D values corresponding to a definite value of t can be finally ascertained.

After the D value was ascertained, the numerical solution of Equation (1) can be obtained using various methods such as finite difference method, finite element method, Method of lines (MOL), etc.

The MOL is a general technique for solving PDE by typically using finite difference relationships for the spatial derivatives and ordinary differential equations for the time derivative. The numerical solution of PDE can be solved when this technique is implemented in conjunction with a convenient ODE solver package such as Matlab. Consider the diffusion occurs in the radial direction of filament, the finite difference of radius is shown in Figure 1. For this problem, the radius is divided into 10 sections with 11 node points. And according the initial and boundary conditions,

$$c_n = c_0 \qquad \text{for} \quad n = 2, 3, \ldots, 11 \quad \text{at} \quad t = 0 \qquad (5)$$

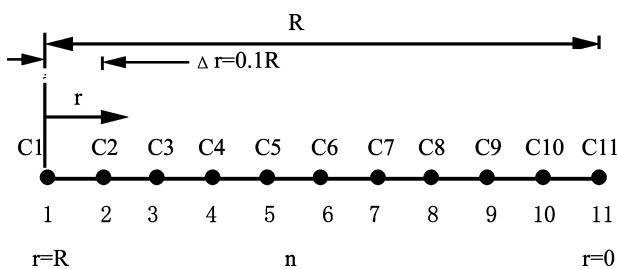$$c_1 = c_\infty \qquad \text{for} \quad t \geq 0 \qquad (6)$$

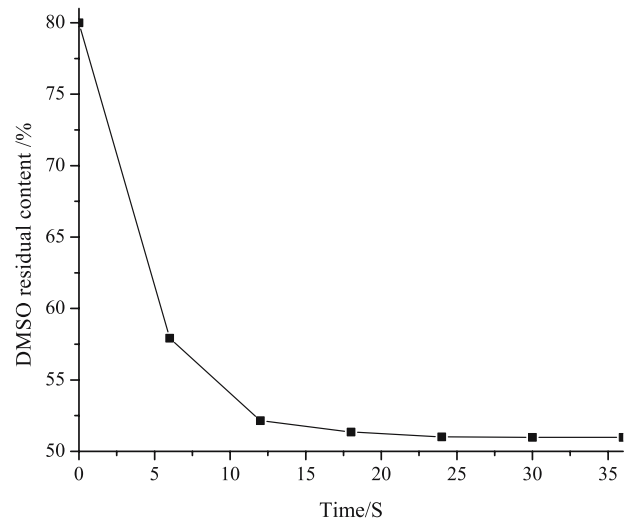*Figure 1.* Diffusion in a one-dimensional radius direction.

Figure 2. Plot of DMSO residual content versus time.

$$\frac{\partial c_{11}}{\partial r} = 0 \qquad \text{for} \quad t \geq 0 \qquad (7)$$

Experiment

Filament formation process

The resulting PAN solution made by solution polymerization was used as spinning dope after removal of excess solvent and uncreated monomers. Then, the dope was deaerated, filtered, and then pumped through a spinneret (1,000 holes, 0.06 mm/hole) to a coagulation bath. After a definite time, the coagulated nascent spinning filaments were obtained.

Characterization

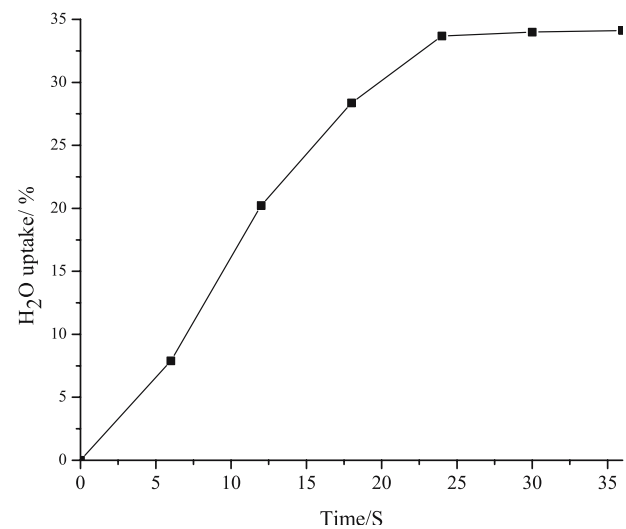The weight of the filament consisted of PAN weight, solvent DMSO, and non-solvent H_2O. The weight of

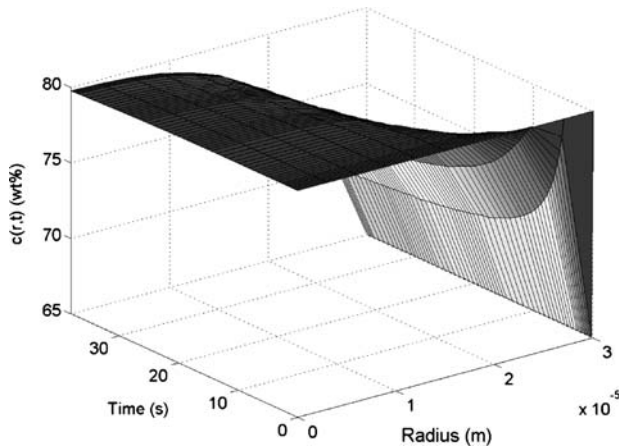

Figure 3. Plot of H_2O uptake versus time.

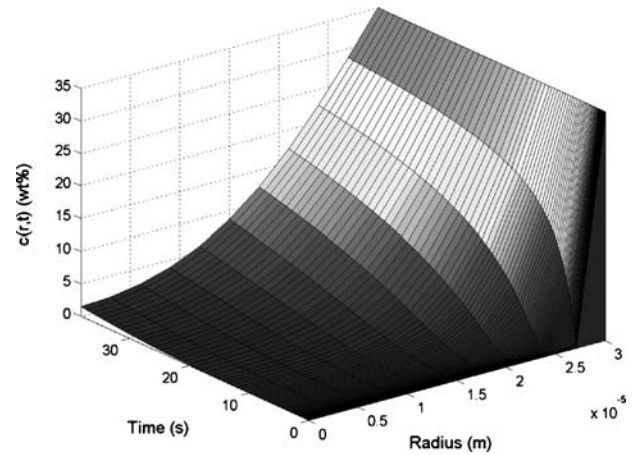*Figure 4.* DMSO concentrations versus time and radius.

Figure 6. H$_2$O concentrations versus time and radius.

solvent in filaments was measured by the following method. The bath solution smeared on the filament surface was carefully removed by moisture absorption paper, and filament was dipped in water and boiled for 1 h to diffuse the solvent from the filament sufficiently. The solvent concentration in water was measured by means of KMnO$_4$ back titration method. PAN weight was obtained by dry the filament in vacuum. Then, the remainder is the uptake weight of H$_2$O in the filament.

The diffusion coefficient (D_{DMSO}) of DMSO was calculated using Equation (3) by measuring DMSO weight in the filament with time intervals of t in the coagulation bath. Diffusion coefficient (D_{H2O}) of H$_2$O was calculated using Equation (4) by calculating H$_2$O weight in the filament with time intervals of t in the coagulation bath.

The microstructures of nascent fibers were studied by a HITACHI H-800 (Japan) Transmission Electron Microscope (TEM) operated at 150 kV. The samples of the fibers were ion-plasma etched in oxygen for 10–60 min. Then they were coated with a layer of gold (10–15 nm thick) in vacuum.

The nascent fiber specimen was embed in epoxy, ruptured in liquid nitrogen and coated with a layer of carbon (10–15 nm thick) in vacuum. Then the cross-

sectional microstructure was observed by an Electron Probe Microanalyser (EPMA) JXA-8800R (Japan) operated at 20 kV.

Results and discussion

Calculation of diffusion coefficient

A H$_2$O/DMSO mixture was used as the coagulation bath. The H$_2$O uptake and DMSO residual content in the filament was investigated under conditions when PAN concentration in the polymer solution was 20%, DMSO concentration in the coagulation bath was 65 wt.%, the coagulation bath temperature was 60°C, and jet stretch minus ratio was 40%. Figure 2 shows DMSO residual content in the nascent fibers versus time. Figure 3 shows H$_2$O uptake in the nascent fibers versus time. The nascent fibers reached equilibrium DMSO residual content values within 18 s, and reached maximum H$_2$O uptake values within 24 s. It can be seen that the speed of outflow solvent is more rapid than that of influent non-solvent.

Diffusion coefficients of DMSO and H$_2$O were calculated using Equations (3) and (4), with a time interval of
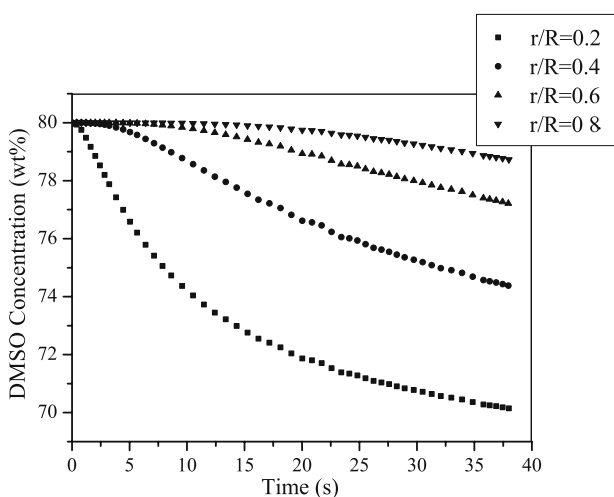

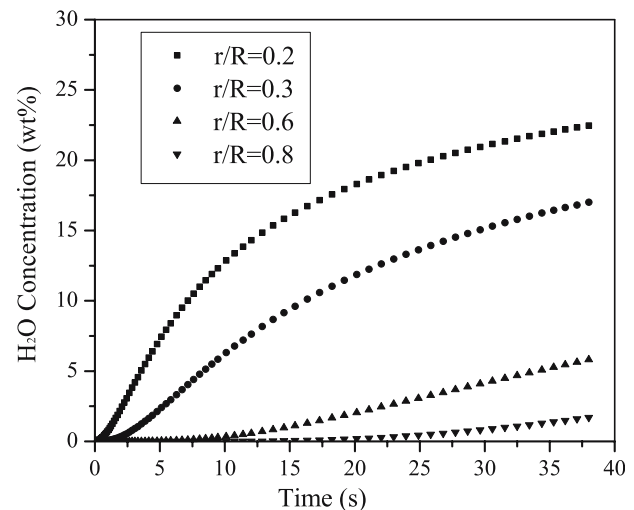*Figure 5.* DMSO concentrations in various layers versus time.

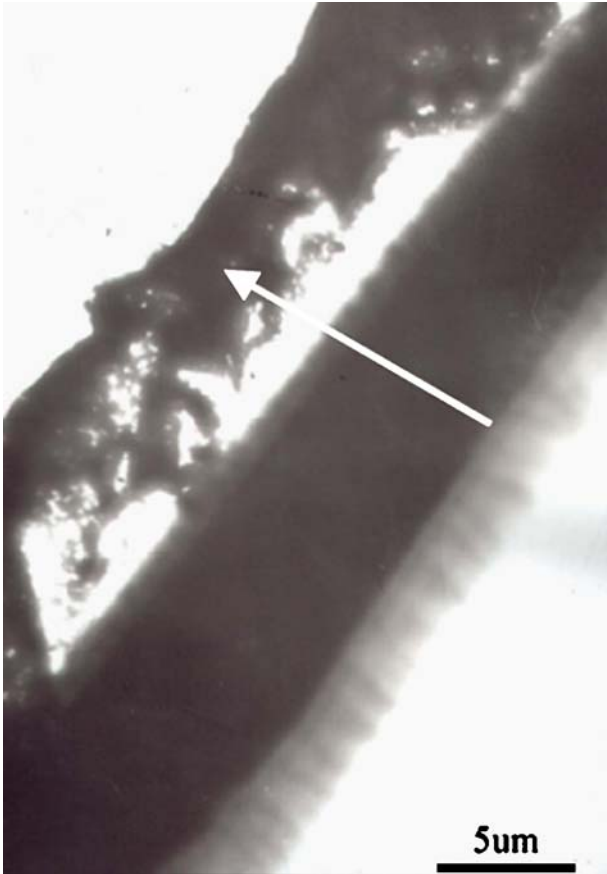*Figure 7.* H$_2$O concentrations in various layers versus time.

Figure 8. The TEM images of PAN nascent fiber.

6 s in the coagulation bath. The diffusion coefficient of DMSO was 2.39×10^{-12} m$^2 \cdot$s^{-1}, and H$_2$O was 2.02×10^{-12} m$^2 \cdot$s^{-1}. This is consonant with the experimental results. Early authors [6–8] have reported that the diffusion coefficients of solvent and non-solvent in wet spinning are controlled by varies factors, including the polymer concentration in spinning solution (dope), the concentration and temperature of coagulation bath, draw ratio. The effect of these factors on diffusion coefficient and structure of fibers have been investigated in detail.

Simulation of coagulation process

The numerical solution of Equation (1) was obtained using MOL method based on the experimental conditions mentioned above and the diffusion phenomenon was simulated.

For this problem with $N = 10$ sections of length $\Delta r = 0.1R = 3 \times 10^{-6}$ m, Equation (1) can be rewritten using a central difference formula for the second derivative as:

$$\frac{\partial c}{\partial t} = D\left(\frac{1}{(\Delta r)^2} + \frac{1}{r_n \Delta r}\right)c_{n+1}$$
$$- D\left(\frac{2}{(\Delta r)^2} + \frac{1}{r_n \Delta r}\right)c_n + \frac{D}{(\Delta r)^2}c_{n+1} \quad (8)$$

$$\text{for } (2 \leq n \leq 10)$$

The boundary condition represented by Equation (7) can be written using a second-order backward finite difference as:

$$\frac{\partial c_{11}}{\partial t} = \frac{3c_{11} - 4c_{10} + c_9}{2\Delta r} = 0 \quad (9)$$

that can be solved for c_{11} to yield:

$$c_{11} = \frac{4c_{10} - c_9}{3} \quad (10)$$

The problem then requires the solution of Equations (6), (8), and (9) which result in nine simultaneous ordinary differential equations and two explicit algebraic equations for the 11 concentrations at the various nodes. This set of equation can be solved with aid of Matlab.

The three-dimension graph of DMSO concentration in radial direction versus times is shown in Figure 4. Figure 5 shows the DMSO concentrations versus time in various layers. It is found that for the diffusion of solvent out of the filaments, the DMSO concentration in outside layers of filament $(0.2R)$ decrease rapidly in short time and the concentration of inner layers decrease slowly with time.
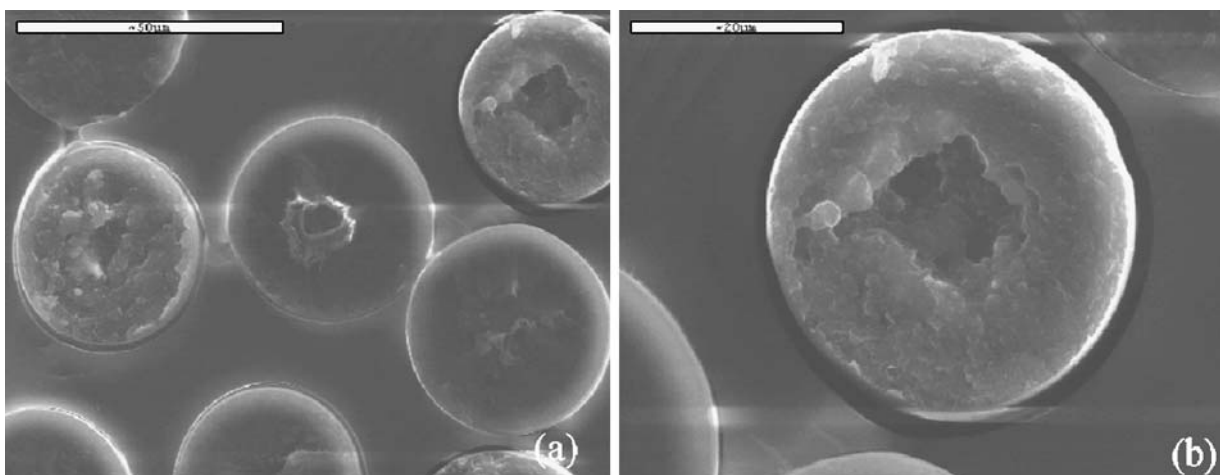

Figure 9. EPMA photographs of PAN nascent fibers.

The DMSO concentration is keeping a high value at the center of filament (0.6–$0.8R$). In outside layers of filament, the outflow speed of DMSO is rapid initially due to the differential concentration, which results in polymer precipitated and a dense layer is formed at a very short time in the coagulation bath. This coagulated dense layer has an effect on the following diffusion of DMSO to some extent, so the diffusional speed of inner layers is decreased.

The three-dimension graph of H_2O concentration in radial direction versus times is shown in Figure 6. Figure 7 shows the H_2O concentrations versus time in various layers. It is found that the diffusion of non-solvent is similar to the solvent. The H_2O concentration in outside layers of filament ($0.2R$) increase rapidly in short time and the concentration of inner layers increase slowly with time. H_2O is concentrated in outside layers. As mentioned above, a dense layer is formation at a very short time in the coagulation bath. This coagulated dense layer has an effect not only on the following diffusion of DMSO, but also on H_2O, so the speed of inner layers diffusion is decreased.

Microstructure of PAN nascent fiber

Figure 8 shows the microstructure of PAN nascent fiber investigated by TEM, the arrow, perpendicular to the fiber axis, points from the skin to the core. It can be seen that its transverse microstructure is a typical layered structure and clear interfaces exist between the single layers. The thickness of skin is about $0.2R$. The skin composed of stacked layers is a sheet-like structure. And the structure is dense and homogeneous. The core region of fiber is very loose which leads to big holes. The experimental phenomenon is consistent with the simulation results.

The 'skin-core' structure is an important defect structure of wet-spinning PAN fiber, which puzzled lots of authors [14]. The cross-sectional profiles are illustrated in Figure 9. The 'skin-core' structure in fibers is obvious. The results of simulation work can explain the cause of 'skin-core' structure formed. The mass transport process concentrates in outside layers. A dense layer is formation at a very short time in the coagulation bath. The speed of inner layers diffusion is slow. The solvent concentration is keeping a high value at the center of filament. There is not coagulated polymer solution in the center of the filament when the filament leaving the coagulation bath. As spinning process, the structure, with dense outside layer and loose center, is keeping in filament and voids formed as the outflow of inner solvent later. As a result, 'skin-core' structure is formed in final PAN fibers.

Conclusion

The coagulation process of polyarylonitrile (PAN) wet-spinning was studied numerically and experimentally. The speed of outflow solvent is more rapid than that of influent non-solvent. It is found from simulations that the diffusion speed of solvent and nonsolvent is rapid in outside layers ($0.2R$) of filament and the speed is slow in inner layers. The solvent concentration is keeping a high value at the center ($0.6 - 0.8R$) of filament. The TEM and EMPA image of nascent fibers shows that the microstructure is a typical layered structure. The thickness of dense skin is about $0.2R$. The core region of fiber is very loose. The experimental phenomenon confirmed the simulation result.

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