Determination of the Diffusion Coefficient of H_2O in Polyacrylonitrile Fiber Formation

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Abstract

An H_2O/dimethyl sulphoxide (DMSO) mixture was used as the coagulation bath of a wet-spun process. The diffusion coefficient of H_2O in the protofibers prepared by acrylonitrile homopolymers was determined. It was found that the diffusion coefficient of H_2O in the protofibers prepared by homopolymers synthesized by solution polymerization was highest compared with those of homopolymers synthesized by H_2O/DMSO mixture suspension polymerization and aqueous suspension polymerization. With an increase of polyacrylonitrile concentration in the dope, the diffusion coefficient of H_2O decreased continuously. The diffusion coefficient of H_2O increased along with the bath temperature, but the changes of diffusion coefficient values were less prominent as the temperature went beyond 60 °C. When the DMSO concentration in the coagulation bath was 55%, the value of the diffusion coefficient of H_2O was minimal. The diffusion coefficient of H_2O increased with increasing jet stretch minus ratio. When the protofiber radius was increased, there was a corresponding increase of the diffusion coefficient of H_2O.

Introduction

Wet spinning is one of many methods of producing polyacrylonitrile precursors [1]. The mechanism of the acrylic fiber formation by the wet-spinning technique is quite complex and involves a combination of rheological and diffusional phenomena. As the very viscous dope leaves the spinneret to enter the coagulation bath, there are two diffusional motions, which carry solvent out of the protofiber to the bath and coagulate from the bath to the protofiber; and when the concentrations of polymer, solvent and coagulate overcome the phase equilibrium conditions, precipitation of the polymer in fibrillar form takes place [2]. Because of the dependence of subsequent textile properties of the fiber on its 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]. To our knowledge, early studies were just empirical attempts to correlate the actual spinning variables with the final properties of the fibers [4, 5], without any investigation of the dynamics of the phenomenon, and there are almost no reports on the diffusion coefficient of coagulate in the polyacrylonitrile fiber formation process. In this study, an H_2O/dimethyl sulphoxide (DMSO) mixture was used as the coagulation bath; acrylonitrile (AN) homopolymers were used to prepare the spinning dopes. For estimating the diffusion coefficient of the coagulate, many possible technical designs of wet spinning techniques for the fiber formation process were applied. The effect of coagulation variables on the diffusion coefficient of the coagulate was contrastively studied.

Experimental

Spinning Dope and its Preparation

Suspension polymerization, H_2O/DMSO mixture suspension polymerization and DMSO solution polymerization were used to synthesize homopolymers [6]. After a definite reaction time, the resultant mixture made by suspension polymerization and H_2O/DMSO mixture suspension polymerization were poured into a large amount of methanol for precipitation and washed with methanol several times. The solvent and unreacted monomer in the resultant mixture were removed by the suction pump. The polymers were dried at 60 °C under vacuum, and then weighed. The polymers were dissolved in DMSO to get a clear dope. The resulting polymer solution made by solution polymerization could be directly used as the spinning dope after the removal of excess solvent and unreacted monomers by the suction pump.

The viscosities of the polymers were measured at 35 °C in dimethyl formamide by using an Ubbelohde viscometer [7], and the molecular weight was calculated from the following equation [8]:

$$[\eta] = 2.78 \times 10^{-4} M_w^{0.76}.$$

Table 1. Characterization of the AN homopolymer

Sample	Polymerization technique	$M_w/10^4$	Isotacticty
PAN1	DMSO solution	10.32	0.267
PAN2	H$_2$O/DMSO mixture suspension	28.25	0.308
PAN3	aqueous suspension	41.28	0.351

Nuclear magnetic resonance (NMR) measurements were carried out using a Bruker-DPX300 spectrometer (German) operating at 75 MHZ. Analysis was made according to the manner of inoue and the isotacticty discussed here is defined by three monomer units (triad tacticty).

The polymers code and the isotacticty are given in Table 1.

Fiber Formation Process

The obtained dope was deaerated, filtered, and then pumped through a spinneret (1000 holes, 0.06 mm/hole, $L/D = 1.2$) into a coagulation bath. The protofibers were then obtained. The cross section of the protofibers were observed under a high resolution scanning electron microscope JXA-840 (Japan).

Characterization

The trace of DMSO and H$_2$O on the protofibers surface was completely absorbed by the filter paper after the spinning process. The residual weight of the protofiber was composed of the polymer weight, the solvent DMSO weight and the coagulate H$_2$O weight. The H$_2$O weight was immediately determined by evolved gas analysis (EGA) on a DT40 thermal analyzer. EGA studies were performed at a heating rate of 5 °C/min in N$_2$ with the highest temperature being 130 °C.

The diffusion coefficient (D_a) of H$_2$O was calculated using Crank's method [9] by measuring the H$_2$O weight of the protofibers with time intervals of t in the coagulation bath. Crank's equation is represented as

$$D_a = \frac{\pi a^2}{16t}\left(\frac{C_t}{C_\infty}\right), \qquad (1)$$

where D_a is the diffusion coefficient of H$_2$O, C_t is the H$_2$O weight in the protofibers at time t, C_∞ is the equilibrium H$_2$O weight in the complete coagulated protofiber, a is the radius of the protofiber, and t is the coagulation time.

Results and Discussion

Calculation of the Diffusion Coefficient

The H$_2$O/DMSO mixture was used for the coagulation bath. The effect of time on H$_2$O uptake was assessed when the DMSO concentration in the coagulation bath was 60 wt%, the coagulation bath temperature 60 °C, the jet stretch minus ratio 50%, the concentration of AN homopolymers prepared by DMSO solution polymerization, and the H$_2$O/DMSO
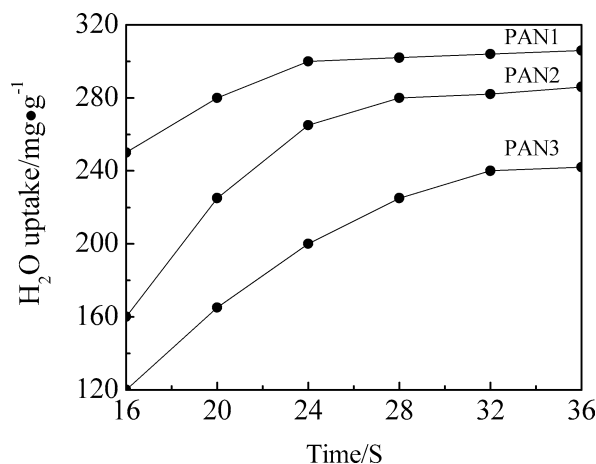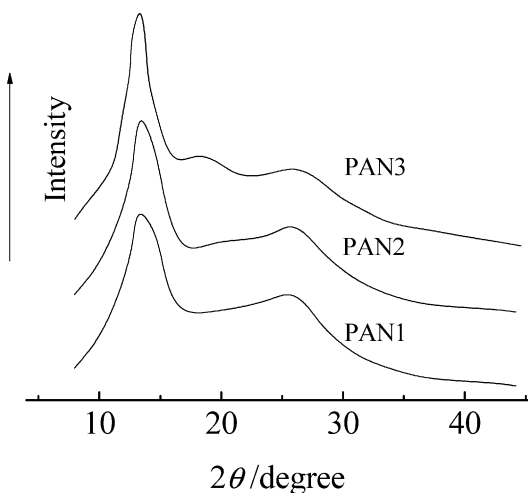

Figure 1. Plot of H$_2$O uptake versus time.

Figure 2. XRD patterns of the protofibers.

mixture suspension polymerization and aqueous suspension polymerization in the dope was controlled at 20, 18, 15 wt%, respectively. Figure 1 shows the H$_2$O uptake in the protofibers versus time. The protofibers prepared by the DMSO solution polymerization reached maximum H$_2$O uptake values in 24 seconds, whereas the protofibers prepared by the H$_2$O/DMSO mixture suspension polymerization and aqueous suspension polymerization took 28, 32 seconds to reach equilibrium, respectively. Diffusion coefficients of H$_2$O in protofibers prepared by PAN1, PAN2, PAN3 was 5.23×10^{-11}, 4.48×10^{-11} and 3.92×10^{-11} m^2·s^{-1}, respectively. It is reported [10–12] that the diffusion of H$_2$O into the protofibers is controlled by the stereo-tacticity and segmental mobility of the polymer chain, and to a considerable extent the crystallinity and void structure in the protofibers. From Table 1 it can be seen that the fraction value of the stereospecific sequence of AN homopolymers prepared by the aqueous suspension polymerization technique can reach 0.351. With an increase of DMSO concentration in the H$_2$O/DMSO mixture, the extent of the stereospecific sequence of AN homopolymers decreases. Comparison of the crystallinity of the protofibers prepared by the homopolymers in Figure 2 shows that there is a marked decrease in crystallinity in the protofibers prepared by the solution
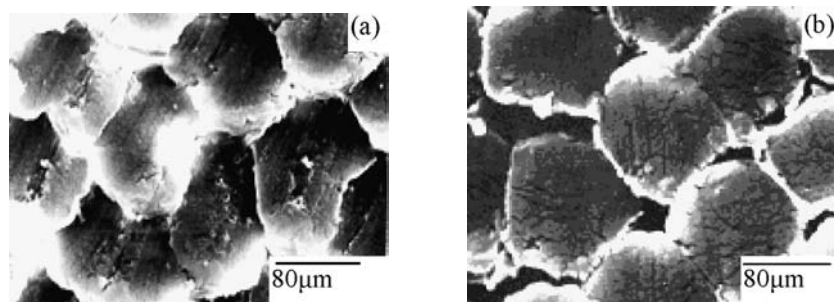
Figure 3. Comparison of sem images of the protofibers prepared by different polymerizations: (a) DMSO solution polymerization; (b) the aqueous suspension polymerization.

Table 2. Comparison of the protofibers

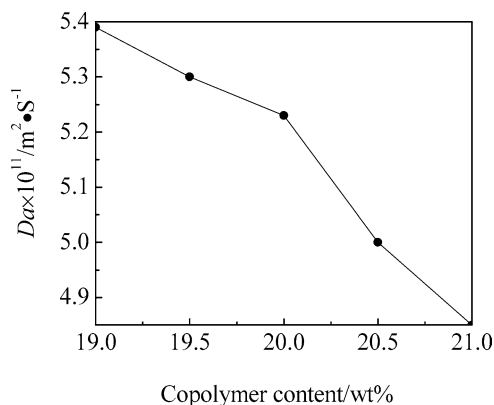| Sample	Polymerization technique	Density of the precursors/g·cm⁻³	Number of voids
PAN1	DMSO solution	1.132	Few
PAN2	H₂O/DMSO mixture suspension	1.138	Less
PAN3	Aqueous suspension	1.141	Least

Figure 4. Relationship between homopolymer concentration and the diffusion coefficient of H₂O.

Figure 5. Effect of the coagulation bath composition and temperature on the diffusion coefficient of H₂O.

polymerization. Comparison of the sem images of the cross-section of the protofibers prepared by the homopolymers in Figure 3 shows that there are prominent voids in the protofibers prepared by solution polymerization. It is evident from Table 2 that the density of the precursors manufactured by the protofibers prepared by the aqueous suspension polymerization is highest. Thus the protofibers prepared by solution polymerization reached equilibrium faster because of the presence of the voids and low crystallinity.

Effect of Polymer Concentration on the Diffusion Coefficient of H₂O

The effect of polymer concentration on the diffusion coefficient of H₂O was studied by varying the concentration of AN homopolymers prepared by solution polymerization from 19 to 21 wt% while keeping other factors constant. Figure 4 shows the changes of diffusion coefficient of H₂O as a function of polymer concentration in the dope. Diffusion coefficient of H₂O decreases continuously with an increase of polymer concentration up to 21 wt%. As the polymer concentration increases, the viscosity of the dope increases quickly, the concentration gradient of DMSO between the spinning dope and the coagulation bath decreases, osmosis of DMSO is more difficult, and an unexpected desolvatation of the outer layer of the protofiber occurs slowly, so that the diffusion coefficient of H₂O shows a trend of decrease.

Effect of Bath Temperature and Concentration on the Diffusion Coefficient of H₂O

Because bath temperature and concentration also play an important role in the factors that affect the diffusion coefficient of H₂O, it is necessary to study the diffusion coefficient of H₂O at the different bath temperatures and concentrations.

The effect of the bath temperature on the diffusion coefficient of H₂O of the protofibers prepared by homopolymers synthesized by solution polymerization while keeping other experimental parameters constant was assessed by varying the temperature in the range of 45–70 °C. As shown in Figure 5, the diffusion coefficient of H₂O increases continuously with an increase of temperature, but the changes of diffusion coefficient values are less prominent as temperature goes beyond 60 °C, which shows a few disagreements with the values reported [11]. This can be explained by taking into account the glass-transition temperatures of these protofibers. It has been reported that the glass-transition temperatures of the protofibers with addition of DMSO sol-
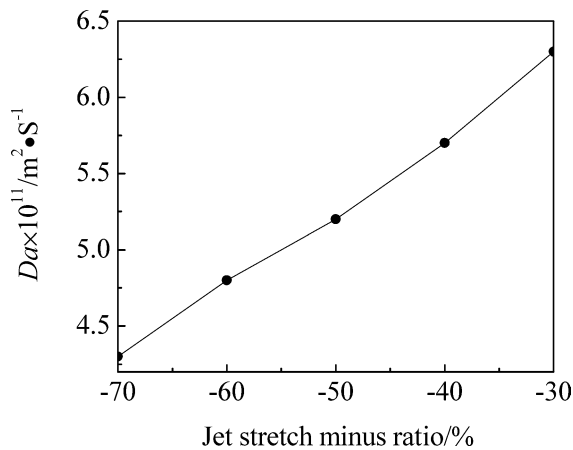
Figure 6. Relationship between the diffusion coefficient of H$_2$O and jet stretch minus ratio.

vent decrease to 63 °C [13]. This is presumably because of a reduction in dipole interaction due to the irregularly-disposed pendant groups. As bath temperature increases about 60 °C, the lower glass-transition temperature eases the H$_2$O diffusion and provides more sites. As temperature goes beyond 60 °C, there are no obvious factors which favor good diffusion of H$_2$O molecules and the increase of diffusion coefficient values is less obvious.

In the wet-spun process, the values of the diffusion coefficient of the coagulate always varies with changes of bath concentration. The effect of bath concentration on the diffusion coefficient of H$_2$O of the protofibers prepared by homopolymers synthesized by solution polymerization while keeping other experimental parameters constant was studied. It is evident from Figure 5 that there is a great drop in the diffusion coefficient of H$_2$O as the concentration of DMSO rises up to 55 wt%, and then the coefficient appears to increase. The bath concentration at which the values of the diffusion coefficient of coagulate is minimal is governed by the gel formed in the protofibers. With an increase of DMSO concentration, the gel density becomes higher which makes the osmosis of H$_2$O more difficult. As DMSO concentration goes beyond 55 wt%, the gel becomes swollen [14] and its density becomes lower, the diffusion of H$_2$O becomes easier.

Effect of the Jet Stretch Minus Ratio on the Diffusion Coefficient of H$_2$O

The ease of fiber formation under continuous spinning conditions is decided by the jet stretch minus ratio. The jet stretch ratio is generally accepted as a comprehensive index of the rheology and hydrodynamic process of wet spinning [15]. This term is defined as the ratio of the linear take-up rate at which protofibers are taken out of the coagulation bath to the linear rate at which spinning dope is extruded through the spinnerette holes. According to Han and Segal the jet stretch ratio can be expressed as:

$$\phi = \frac{V_1 - V_2}{V_2},$$

where ϕ is the jet stretch ratio, V_1 is the linear velocity of the spinning dope in the spinnerette hole, V_2 is the linear

velocity of the filament at the take-up roller. The effect of the jet stretch minus ratio on the diffusion coefficient of H$_2$O of the protofibers prepared by homopolymers synthesized by solution polymerization while keeping other experimental parameters constant was studied. Figure 6 shows that the diffusion coefficient of H$_2$O increases from 4.3 to 6.3 × 10^{-11} when the jet stretch minus ratio rises from −70 to −30%. According to Knudsen [16], decreasing the values of the jet stretch minus ratio is accompanied by decreasing the bulk density and increasing the numbers of voids. Increasing the numbers of voids in the protofibers eases H$_2$O diffusion and the diffusion coefficient of H$_2$O shows a trend of increase.

Conclusions

Laboratory studies of the fiber formation process have shown that the diffusion coefficient of H$_2$O into the protofibers prepared by homopolymers synthesized by solution polymerization was highest compared with those of homopolymers synthesized by an H$_2$O/DMSO mixture suspension polymerization and aqueous suspension polymerization. The diffusion coefficient of H$_2$O decreased continuously with an increase of polymer concentration in the dope. The diffusion coefficient of H$_2$O increased continuously with an increase of the bath temperature, but the changes of the diffusion coefficient values were less prominent as temperature went beyond 60 °C. There was a great drop in the diffusion coefficient of H$_2$O as the concentration of DMSO went up to 55 wt%, and then the coefficient appeared to increase. The diffusion coefficient of H$_2$O increased as the jet stretch minus ratio increased. As the protofiber radius progressively increased, there was a corresponding increase of the diffusion coefficient of H$_2$O.

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