

Diffusion Coefficient of DMF in Acrylic Fiber Formation

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Received 12 November 2004; accepted 1 June 2005

DOI 10.1002/app.22696

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A H₂O/dimethyl formamide (DMF) mixture was used as the coagulation bath of wet-spun process for acrylic fibers. Diffusion coefficient of DMF in the protofibers prepared by acrylonitrile/acrylamide copolymers was determined. It has been found that diffusion coefficient of DMF outflow of the protofibers prepared by acrylonitrile/acrylamide copolymers synthesized by solution polymerization is highest compared with those of acrylonitrile/acrylamide copolymers synthesized by H₂O/DMF mixture suspension polymerization and aqueous suspension polymerization. With an increase of copolymer concentration in the dope, diffusion coefficient of DMF decreases continuously. Diffu-

sion coefficient of DMF increases along with the bath temperature, but the changes in diffusion coefficient values are less prominent as temperature goes beyond 55°C. When DMF concentration in the coagulation bath was 50%, the value of the diffusion coefficient of DMF was minimal. Diffusion coefficient of DMF increases along with jet stretch minus ratio increase. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3616–3619, 2006

Key words: diffusion coefficient; fiber formation; wet spinning

INTRODUCTION

Wet-spun process is one of the main methods of producing acrylic precursors.¹ Mechanism of the acrylic fiber formation by 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; 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 on the protofibers' 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 on the dynamics of this phenomenon. There is almost no report on the diffusion coefficient of solvent and there is almost no report on

acrylamide as a comonomer in acrylic fiber formation process. In this study, a H₂O/dimethyl formamide (DMF) mixture was used as the coagulation bath, and acrylonitrile (AN)/acrylamide (AM) copolymers synthesized by different polymerization technologies were used to prepare the spinning dopes. For estimating the diffusion coefficient of DMF, many possible technical designs of wet-spinning techniques in fiber formation process were applied. Effect of coagulation variables on the diffusion coefficient of DMF was studied in contrast.

EXPERIMENTAL

Spinning dope and its preparation

Aqueous suspension polymerization, H₂O/DMF (70/30 w/w) mixture suspension polymerization, and DMF solution polymerization were used to synthesize AN/AM copolymers.⁶ After a definite reaction time, the resultant mixtures made by aqueous suspension polymerization and H₂O/DMF mixture suspension polymerization were poured into a large amount of methanol for precipitation and washed with methanol several times. The solvent and the unreacted monomer in the resultant mixture were removed by the suction pump. AN/AM copolymers were dried at 60°C under vacuum and then weighed. Copolymers were then dissolved in DMF to get a clear dope. The resultant AN/AM copolymer solution made by solution polymerization can be directly used as the spinning dope after removal of excess solvent and unreacted monomers by the suction pump.

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Contract grant sponsor: Project of Natural Science Foundation of Yantai Normal University; contract grant number: 042920.

TABLE I
Characterization of AN/AM Copolymers

Sample	Polymerization technique	Molecular weight/ 10^4	Isotacticity (<i>mm</i>)
PAN1	DMF solution	9.18	0.243
PAN2	H ₂ O/DMF mixture suspension	24.76	0.298
PAN3	aqueous suspension	43.12	0.342

Viscosities of copolymers 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

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

The triad tacticities [(*mm*), (*mr*), (*rr*); *m* and *r* mean *meso* and *racemo* diad sequences, respectively] of AN/AM copolymers were determined on the basis of the Schaefer's assignment⁹ from the ratio of intensities for the three nitrile carbon peaks in the ¹³C NMR spectra. ¹³C NMR spectra were recorded on a Bruker-DPX300 spectrometer (German) in 2.5 wt % solution in deuterated dimethylsulfoxide (DMSO-d₆) at 80°C under the following operating conditions: complete decoupling mode; pulse delay time, 1.745 s; acquisition time, 0.655 s; pulse width, 5.5 μs (45° pulse); accumulation, more than 3000 times. The polymers code and the isotacticity are given in Table I.

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) to a coagulation bath. The protofibers were obtained by the complete coagulation.

Characterization

The trace of DMF and H₂O on the protofiber surface was completely absorbed by the filter paper after the spinning process. The residual weight of the protofiber was composed of AN/AM copolymer weight, the solvent DMF weight, and the coagulate H₂O weight. Copolymer weight was immediately obtained by drying the protofibers in vacuum. H₂O weight was immediately determined by evolved gas analysis (EGA) on a DT40 thermal analyzer, and then the remainder was the residual weight of DMF in the protofibers. EGA studies were performed at a heating rate of 5°C/min in N₂, with the highest temperature of 130°C.

Diffusion coefficient (D_a) of solvent DMF was calculated using the Crank's method,¹⁰ by calculating DMF weight outflow of the protofibers with time in-

tervals of t in the coagulation bath. Crank's equation⁷ is represented as

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

where D_a is the diffusion coefficient of DMF, C_t is the outflow weight of DMF from the protofibers at time t , C_∞ is the equilibrium DMF outflow weight from the complete coagulated protofibers, a is the radius of the protofiber, and t is the coagulation time.

RESULTS AND DISCUSSION

Determination of diffusion coefficient of DMF

H₂O/DMF mixture was used as the coagulation bath. Effect of time on DMF residual content in the protofibers was discussed when DMF concentration in the coagulation bath is 55 wt %, the coagulation bath temperature is 60°C, the jet stretch minus ratio is -50%, and concentration of AN homopolymers prepared by DMF solution polymerization, H₂O/DMF mixture suspension polymerization and aqueous suspension polymerization in the dope is controlled at 20, 18, and 15 wt %, respectively. Figure 1 shows DMF residual content in the protofibers versus time. The protofibers prepared by DMF solution polymerization reach equilibrium values in 7 s, whereas the protofibers prepared by H₂O/DMF mixture suspension polymerization and aqueous suspension polymerization takes 10 and 16 s to reach equilibrium, respectively. Diffusion coefficients of DMF in the protofibers prepared by PAN1, PAN2, and PAN3 were 1.79×10^{-10} , 1.25×10^{-10} , and $0.783 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, respectively. It is reported¹¹⁻¹³ that the diffusion of DMF out of the protofibers is controlled by the stereo-tacticity and segmental mobility of the polymer chain, and to a considerable extent, the gel and void structure in the protofibers. From Table I, the fraction value of ste-

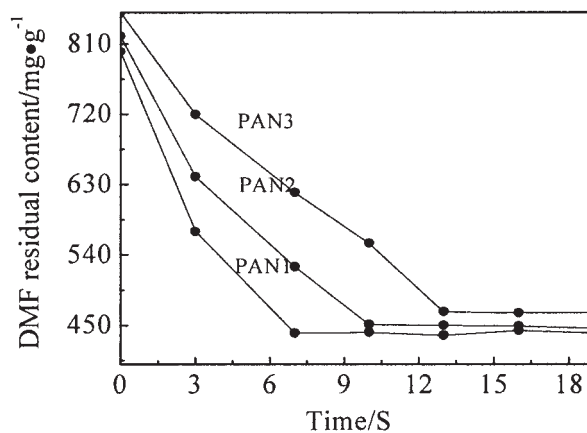


Figure 1 Plot of DMF residual content vs time.

TABLE II
Comparison of the Protofibers

Sample	Polymerization technique	Density of the precursors/g cm ⁻³	Number of voids
PAN1	DMF solution	1.128	few
PAN2	H ₂ O/DMF mixture suspension	1.132	less
PAN3	aqueous suspension	1.139	least

reospecific sequence of AN/AM copolymers prepared by aqueous suspension polymerization technique can reach 0.342. With an increase of DMF concentration in H₂O/DMF mixture, the extent of stereospecific sequence of AN/AM copolymers decreases. It is evident from Table II 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 reach equilibrium faster because of the presence of the voids and the least isotacticity.

Effect of copolymer concentration on diffusion coefficient of DMF

Effect of AN/AM copolymer concentration on diffusion coefficient of DMF was studied by varying the concentration of AN/AM copolymer prepared by solution polymerization from 19 to 21 wt % while keeping other factors constant. Figure 2 shows the changes of diffusion coefficient of DMF as a function of copolymer concentration in the dope. Diffusion coefficient of DMF decreases continuously with an increase of polymer concentration up to 21 wt %. As the polymer concentration increases, the DMF concentration gradient between the protofibers and the bath decreases, the viscosity of the dope increases quickly, and the free volume in the AN/AM copolymer solution is

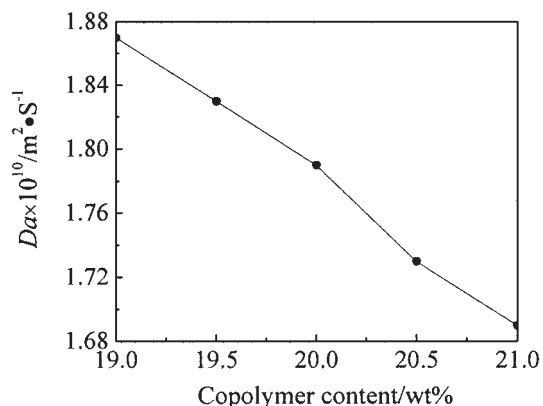


Figure 2 Relationship between of AN/AM copolymer concentration and diffusion coefficient of DMF.

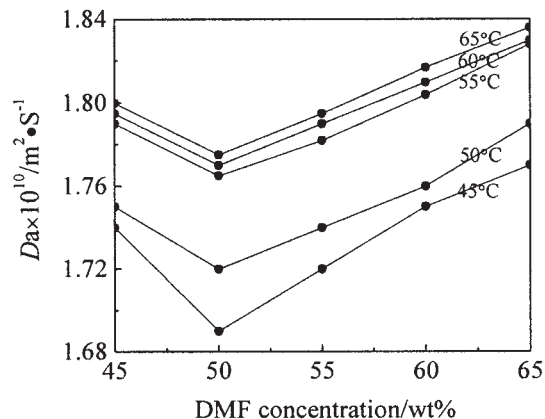


Figure 3 Effect of the coagulation bath composition and temperature on the diffusion coefficient of DMF.

mostly occupied, so that osmosis of DMF is more difficult.

Effect of bath temperature and composition on diffusion coefficient of DMF

Because bath temperature and composition also play an important role in the factors that affect diffusion coefficient of DMF, it is necessary to study diffusion coefficient of DMF at different bath temperature and composition. Effect of the bath temperature on the diffusion coefficient of DMF out of the protofibers prepared by AN/AM copolymers synthesized by solution polymerization while keeping other experimental parameters constant was discussed by varying temperature in the range of 45–65°C. As shown in Figure 3, diffusion coefficient of DMF increases continuously with an increase of temperature, but the changes of diffusion coefficient values are less prominent as temperature goes beyond 55°C, which show a few disagreements with the values reported.¹² This can be explained by taking into account the glass-transition temperatures of these protofibers. The values of glass-transition temperature of AN/AM copolymers dissolved into DMF solvent decrease greatly.¹⁴ This is presumably because of a reduction in the dipole interaction due to the irregularly-disposed pendant groups. As bath temperature increases to about 55°C, the lower glass-transition temperature eases DMF diffusion. As temperature goes beyond 55°C, there are no obvious factors which favor good diffusion of DMF molecules, and increase of diffusion coefficient values is less obvious.

In wet-spun process, value of diffusion coefficients of solvent always varies with changes of bath concentration. Effect of bath composition on diffusion coefficient of DMF out of the protofibers prepared by AN/AM copolymers synthesized by solution polymerization while keeping other experimental param-

eters constant was studied. It is evident from Figure 3 that there is a great drop in diffusion coefficient of DMF as the bath concentration of DMF goes up to 50 wt %, and then the coefficient appears to increase. The bath concentration of DMF at which the values of diffusion coefficient of coagulate is minimal is governed by the gel formed in the protofibers.⁹ With an increase of DMF concentration in the bath, the gel density becomes higher, which makes the osmosis of DMF more difficult; as DMF concentration goes beyond 50 wt %, the gel becomes swollen and its density becomes lower, and the diffusion of DMF outflow of the protofibers becomes easily.

Effect of jet stretch minus ratio on diffusion coefficient of DMF

The ease of fiber formation under continuous spinning conditions is decided by 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 spinneret 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 spinneret hole, V_2 is the linear velocity of the filament at the take-up roller. Effect of jet stretch minus ratio on diffusion coefficient of DMF out of the protofibers prepared by AN/AM copolymers synthesized by solution polymerization while keeping other experimental parameters constant was studied. Figure 4 shows that the diffusion coefficient of DMF increases from 1.58 to 1.92×10^{-10} when jet stretch minus ratio rises from -70 to -30% . According to Knudsen,¹⁶ decreasing the values of jet stretch minus ratio is accompanied by decreasing bulk density and increasing numbers of voids. Increasing numbers of voids in the protofibers ease DMF diffusion and diffusion coefficient of DMF shows a trend of increase.

CONCLUSIONS

Laboratory studies of the fiber formation process have shown that diffusion coefficient of DMF out of the protofibers prepared by AN/AM copolymer synthesized by solution polymerization is highest compared

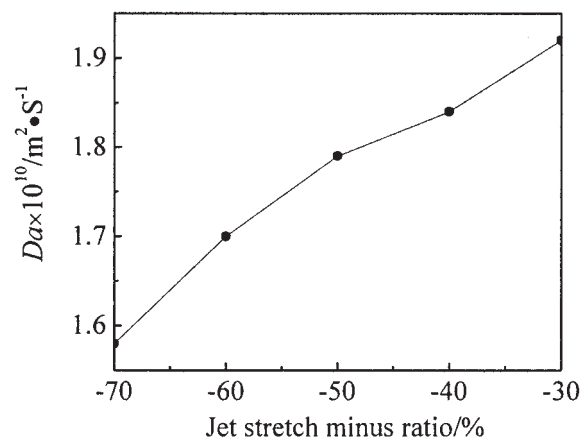


Figure 4 Relationship between diffusion coefficient of DMF and jet stretch minus ratio.

with those of AN/AM copolymer synthesized by H_2O/DMF mixture suspension polymerization and aqueous suspension polymerization. Diffusion coefficient of DMF decreases continuously with an increase of polymer concentration in the dope. Diffusion coefficient of DMF increases continuously with an increase of the bath temperature, but the changes of diffusion coefficient values are less prominent as temperature goes beyond $55^\circ C$. There is a great drop in diffusion coefficient of DMF as the concentration of DMF in the bath goes up to 50 wt %, and then the coefficient appears to increase. When the jet stretch minus ratio was increased, there is a corresponding increase of diffusion coefficient of DMF.

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