

Effect of Deaeration Processing on the Behavior of an Acrylonitrile–Acrylamide Copolymer and Carbon Fiber Precursors

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ABSTRACT: The effect of the deaeration process on the behavior of acrylonitrile–acrylamide copolymer solutions was demonstrated experimentally in detail. The corresponding mechanical properties and morphology of the resultant precursors were also been examined. It was found that the viscosity of the copolymer solutions at rest increased continuously with the deaeration time prolonged at every fixed temperature stage, but it considerably increased when the deaeration temperature decreased. The changes in the viscosity of the solutions at 80°C were less prominent than those of the solutions at 20°C in the beginning stage; beyond 60 min, the changes became remarkable. In concentrated copolymer solutions, the dimethyl sulfoxide composition weight percentage decreased with an increase in the deaeration temperature; the increasing temperature reduced the

solvent power continuously at a high deaeration temperature, so more solid–elastic gels were formed in the solutions with an increase in time. At the same degree of vacuum, when the temperature varied from 20 to 80°C and, in particular, the deaeration temperature was beyond 60°C, the products from the copolymer seemed to have slightly narrower molecular weight distributions. With the deaeration temperature increasing, the tensile strength, elongation at break, and bulk density of the resultant precursors increased, but their fineness and coefficient of variation decreased. The morphology of the precursors was more compact and more round beyond 60°C than below 60°C. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1616–1620, 2008

Key words: copolymerization; fibers; viscosity

INTRODUCTION

It is important to select a suitable technique and optimize the conditions of spinning to satisfy the requirements for high-tenacity acrylic fibers.^{1–10} The free-radical solution copolymerization of acrylamide (AM), acrylonitrile (AN), dimethyl sulfoxide (DMSO), and azodiisobutyronitrile (AIBN) was carried out with ultrapure nitrogen under continuous agitation; there were lots of bubbles of different sizes in the polymerization solutions, and the viscosity of the AN/AM copolymer solutions was high. Spinning dopes are also usually required for the settlement of the deaeration process; the deaeration process for solutions of macromolecules in the wet spinning of chemical fibers is important. Air bubbles larger than half of the diameter of the spinneret hole must be removed from the spinning solution to ensure stable spinning because the air bubbles that enter these holes can prevent the fiber from being formed; moreover, even very small bubbles can cause the formation of defects

in the filament, dissolve air can affect the structure formation, even the performance of the resultant carbon fiber. It is necessary to remove the dispersed air and prevent it from being released in the subsequent stages of the producing process. Elimination of air by boiling implies heating of the spinning solution to a high temperature in a deep vacuum, which is technologically unsuitable in many cases because of volatilization of the solvent; continuous deaeration in a vacuum, which is a degree of vacuum with –0.1 MPa of residual pressure, must be carried out to ensure high efficiency of the spinning process. To the best of our knowledge, this is the first time a detailed investigation has been reported of the effect of continuous deaeration of spinning solutions on the properties of polyacrylonitrile (PAN) copolymer solutions with AM and even the resultant precursors.

EXPERIMENTAL

Materials

AN (Tianjin Chemical Reagent Plant, Tianjin, China) was distilled at 76–78°C under atmospheric pressure before use. Acrylamide (AM), used as the second monomer, was supplied in an extrapure grade by Tian-

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TABLE I
Important Parameters of Copolymerization

AN/AM (w/w)	Oxygen concentration in the copolymer (wt %)	AM concentration in the copolymer (wt %)	Conversion (%)	$M_w \times 10^{4a}$
99/1	0.48	2.02	96	16

Conditions: DMSO/(AM + AN + AIBN + DMSO) = 78.5% w/w; [AN] = 4.5 mol/L; [AIBN] = 0.007 mol/L; time = 6 h; temperature = 60°C.

^a M_w was calculated as follows: $[\eta] = 2.83 \times 10^{-4} M_w^{0.758}$, where $[\eta]$ is the intrinsic viscosity.¹¹

jin Chemical Resin Industry (Tianjin, China) and distilled to remove inhibitors before use. AIBN (Shandong Xueyin Chemical Fiber Co., Zibo, China) as an initiator was recrystallized at a lower temperature twice from absolute ethanol before use. Deionized water (self-made) and DMSO (Liaoning Panjin Chemical General Plant, Panjin, China) were used as solvents.

Copolymerization

Required amounts of AM, AN, DMSO, and AIBN were used for free-radical solution copolymerization in a 20-L pilot-scale stainless reactor that was continuously flushed with ultrapure nitrogen. The polymer solution was provided with heat jackets to keep the solution at the desired temperature of 60°C. Some important parameters and polymerization conditions of the copolymer are shown in Table I. The composition of the AN/AM copolymers was determined from the oxygen concentration in the copolymers.

Deaeration process

The resulting 20% (w/w) polymerization solution was deaerated into a 20-L pilot-scale stainless deaerator connected to a vacuum pump; the degree of vacuum could be pumped up to -0.1 MPa. There was a pump metering the amount of the spinning solution by 1.2 cc/r between the reactor and deaerator.

Characterization

Elemental analysis of the copolymers was carried out with a PE 2400 elemental analyzer (PerkinElmer, Inc., Waltham, MA) to determine the oxygen in these copolymers.

The viscosity of copolymer solutions of the same copolymer content was measured with an NDJ-4 rotary viscosimeter (Shanghai Leigu Instrument Company, Shanghai, China) under different conditions.

The hydrophilicity of the copolymers was determined with the contact angle. The contact angle was calculated with the following equation:¹²

$$\cos \theta = 1 - \rho g h_m^2 / 2\sigma \quad (1)$$

where θ is the contact angle, h_m is the maximal height of the liquid, σ is the surface tension, ρ is the density of the liquid (here water), and g is a constant.

The molecular weight distribution (MWD) and polydispersity index [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were obtained by gel permeation chromatography with a train of five columns with the following specifications: column 1, deactivated Porasil; column 2, deactivated Porasil; column 3, deactivated Porasil; column 4, Styragel; and column 5, Styragel. The carrier solvent was dimethylformamide containing 0.05M lithium bromide at a flow rate of 2.5 mL/min at room temperature.

The bulk density of the fibers was determined by means of a density gradient column maintained at 25°C; the columns were prepared in 250-mL graduated cylinders.

The resultant precursors were examined with a Hitachi (Tokyo, Japan) model 8010 scanning electron microscope at an accelerating voltage of 25 kV.

The titer was measured with an XD-1 fiber fineness machine; all the fibers were measured with an XQ-1 testing machine (both machines were made at Donghua University, Shanghai, China) at a cross-head speed of 0.5 mm/min with a testing length of 20 mm and a load cell of 15 g. In each case, at least 30 sample filaments were tested, and the average of 30 filaments was taken for each experiment.

RESULTS AND DISCUSSION

Effect of the deaeration time and temperature on the viscosity of copolymer solutions

Before the deaeration process, the concentration of the AN/AM copolymer in the solutions was kept at 20 wt %. The deaerator was provided with a heat jacket to control the deaeration temperature, which was defined as 20, 40, 60, or 80°C. In every temperature stage, the corresponding deaeration time for the fixed quantitative spinning solution could be attained through the control of the rotation speed of the meter pump. The time was 20, 40, 60, 80, 100, 120, or 140 min. Figure 1 illustrates the effect of time, which picks up the suction, on the viscosity-time characteristics for AN/AM copolymer solutions. The viscosity of the copolymer solutions at rest increased continuously with time at every fixed temperature stage but considerably increased with the temperature being reduced. The changes in the viscosity of the solutions at 80°C were less promi-

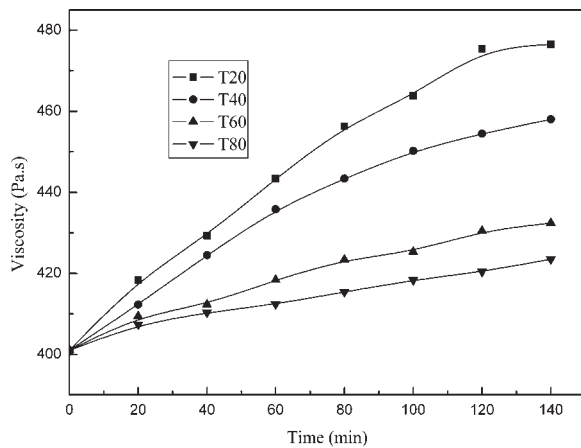


Figure 1 Effect of time and temperature on the viscosity of copolymer solutions.

ment than those of solutions at 20°C and at the beginning stage; beyond about 60 min, the changes became remarkable. The temperature increase apparently prevented the formation of aggregates and stabilized the original structure of the solutions.

Effect of the deaeration time and temperature on the composition of copolymer solutions

The deaeration time and temperature for the solvent used in the preparation of copolymer solutions can considerably affect the composition and stability of the copolymer solutions. The effects of the deaeration time and deaeration temperature on the solvent of the copolymer solutions was studied by the time being varied from 20 to 160 min at a constant temperature and at a constant degree of vacuum of -0.1 MPa. The deaeration temperature was defined as 20, 40, 50, 60, 70, 80, or 90°C. The DMSO composition weight percentage in the solution was a function of a series of factors, such as the temperature, external pressure, and mechanical stress. Figure 2 illus-

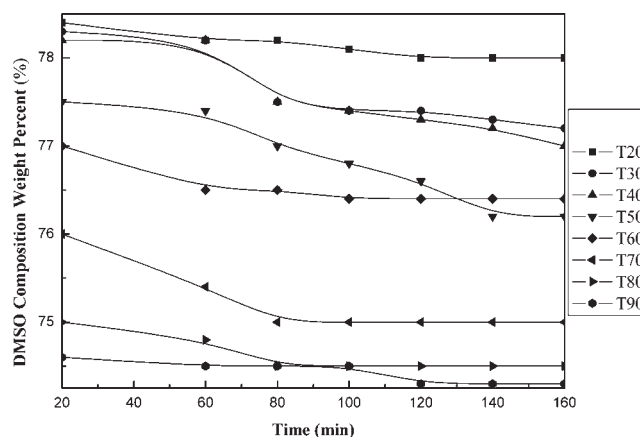


Figure 2 Effect of time and temperature on the DMSO composition weight percentage of copolymer solutions.

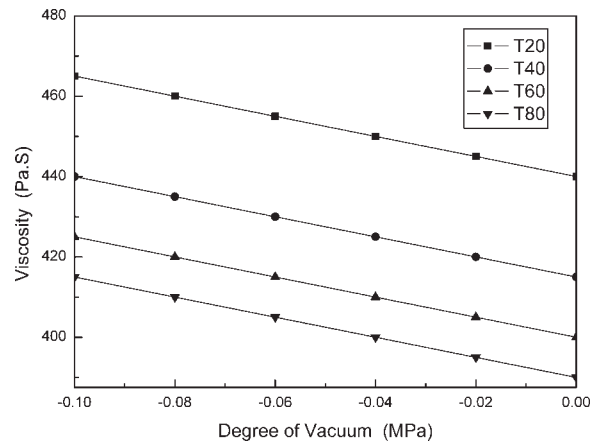


Figure 3 Effect of the degree of vacuum on the viscosity of copolymer solutions.

trates the DMSO composition weight percentage of copolymer solutions as a function of time. In the solutions, the DMSO composition weight percentage decreased with an increase in the deaeration temperature. On the one hand, some shrinkage of molecular coils reduced viscosity. On the other hand, the reduction of solvent power led to increased polymer–polymer interactions, promoted aggregation, and generally destabilized the solutions. Increasing the temperature reduced the solvent power continuously at high deaeration temperatures, so more solid–elastic gels were formed in the solutions with an increase in time.

Effect of the degree of vacuum on the copolymer solutions

The influence of the deaeration pressure on the viscosity of the AN/AM copolymer solutions was studied by the degree of vacuum being varied from -0.1 to 0 MPa at a constant deaeration time of 100 min; the mixture was kept at 20, 40, 60, or 80°C. Figure 3

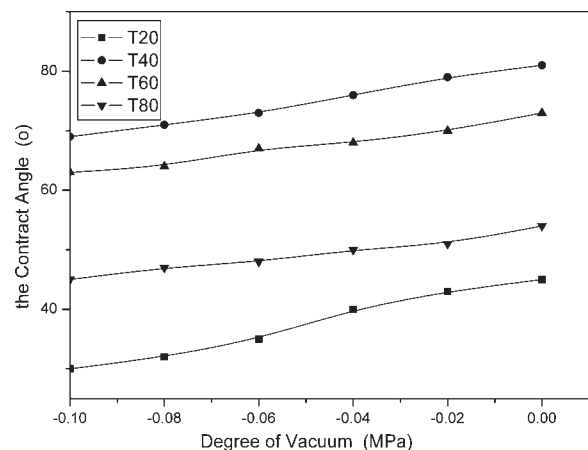


Figure 4 Contact angle of hydrophilicity in the deaeration process.

TABLE II
Effect of Deaeration Processing on MWD of Copolymer Solutions

Degree of vacuum (MPa)	MWD (M_w/M_n)			
	20°C	40°C	60°C	80°C
-0.10	3.12	2.44	2.21	2.10
-0.08	3.19	3.12	3.07	3.05
-0.06	3.33	3.28	3.13	3.07
-0.04	3.68	3.56	3.33	3.15
-0.02	4.65	4.12	3.87	3.54
0	4.89	4.71	4.16	4.02

shows changes in the viscosity with a reduction of the degree of vacuum. The viscosity of the copolymer solutions decreased continuously as the degree of vacuum varied from -0.1 to 0 MPa.

In the literature,⁴ factors have been reported that affect the viscosity of a copolymer solution at a constant shearing rate. The first includes the extent of high molecular entanglement. The second is the free volume in the copolymer solution. There are many bubbles when bubbles are dissolved in the solution. Intermolecular interaction is reduced by more bubbles, and this leads to a decrease in the association degree of high molecular entanglement. Entanglement networks of high molecular chains are destroyed.

At one time, the contact angle between a polymer layer and water can be used to demonstrate the hydrophilicity of the polymer.¹³ The effect of the deaeration process on the hydrophilicity of the copolymer is shown in Figure 4. By consideration of the changes in the values of the contact angle, it was found that the hydrophilicity of the copolymer showed an obvious trend of decreasing with the degree of vacuum varying from -0.1 to 0 MPa. To some extent, the increase of the copolymer's hydrophilicity was proportional to the spinning processes of the precursor fibers, namely, the coagulation and stretching processes, causing the dope to be converted to gel fibers because of the phase separation, and it was easy to infuse with water, which could act as a plasticizer of molecular section movement.

Effect of the deaeration process on the MWD of copolymer solutions

The gel permeation chromatography chromatograms obtained for the dope at four different temperature

with the degree of vacuum varying from -0.1 to 0 MPa are shown in Table II. As plotted in Table II, at the same temperature, the polydispersity indices (M_w/M_n) of PAN showed an increasing trend with the degree of vacuum varying from -0.1 to 0 MPa, but at the same degree of vacuum, there was a decreasing trend when the temperature varied from 20 to 80°C. In particular, the trend leveled off beyond 60°C; this suggests that these products had slightly narrower MWDs. In general, the physical properties of the precursor fibers that developed from the dope with narrow MWDs were excellent. That is, narrow MWDs could improve the homogeneity of the fiber structure by reducing the incidence of larger voids.

Effect of the deaeration process on the mechanical properties and morphology of the resultant precursors

The effect of the deaeration process on the mechanical properties of the precursor fibers from the copolymers attained at different temperatures and at the same degree of vacuum of -0.1 MPa was recorded and is shown in Table III.

As shown in Table III, with other experimental parameters kept constant and with the deaeration temperature increasing, the tensile strength increased from 5.88 to 8.07 cN/dtex, the elongation at break varied from 9.44 to 12.21%, and the bulk density varied from 1.134 to 1.172 g/cm³, but the fineness and coefficient of variation decreased from 1.32 to 1.12 dtex and from 34.22 to 12.43%, respectively. Increasing the temperature reduced the solvent power continuously at high deaeration temperatures; some solvent and monomer that did not take part in the free-radical solution copolymerization were eliminated, and more solid-elastic gels were formed in the solution with an increase in time, so a less loosely packed microstructure in the protofibers resulted. In other words, it appeared that an improvement in the density of the protofiber also resulted in an improvement in the tensile strength of the protofiber. As shown in Figure 5, this can be supported by scanning electron microscopy images of the cross sections of precursor fibers, which were attained from copolymers attained at different temperatures and at a degree of vacuum of -0.1 MPa.

TABLE III
Effect of Deaeration Process on the Mechanical Properties of the Precursors

Sample code	Fineness (dtex)	Tenacity (cN/dtex)	Elongation at break (%)	Bulk density (g/cm ³)	Coefficient of variation (%)
T20	1.32	5.88	9.44	1.134	34.22
T40	1.24	6.42	9.58	1.145	26.77
T60	1.22	7.55	11.23	1.169	13.56
T80	1.12	8.07	12.21	1.172	12.43

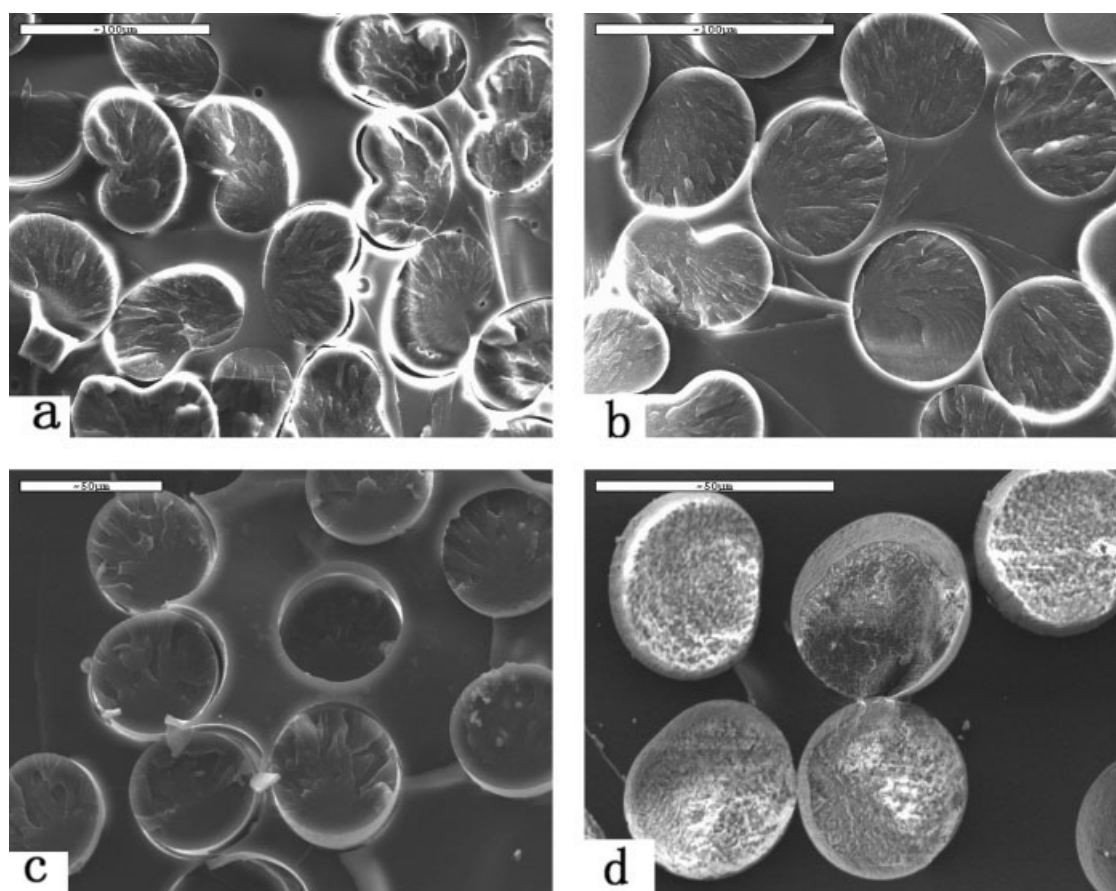


Figure 5 Effect of the deaeration process on the morphology of the resultant precursors at different temperatures and at the same degree of vacuum of -0.1 MPa: cross sections at deaeration temperatures of (a) 20, (b) 40, (c) 60, and (d) 80°C .

CONCLUSIONS

After the free-radical solution copolymerization of required amounts of AM, AN, DMSO, and AIBN in a 20-L pilot-scale stainless reactor, the subsequent deaeration process became an important stage to get a well-behaved dope, to enhance the spinnability of the dope, and to attain excellent performance from the precursors for producing the carbon fibers. The deaeration temperature increase apparently prevented the formation of aggregates and stabilized the original structure of the solution. Increasing the temperature reduced the solvent power continuously at a high deaeration temperature, so more solid-elastic gels were formed in the solution with an increase in time. Intermolecular interaction was reduced by more bubbles, and this led to a decrease in the association degree of high molecular entanglement. When the deaeration temperature was beyond 60°C , the copolymerization solution seemed to have slightly narrower MWDs. At one time, with the deaeration temperature increasing, the tensile strength, elongation at break, and bulk density of the resultant precursors increased, but the fineness and coefficient of variation decreased. The morphologies of the

precursors beyond 60°C were more compact than those below 60°C .

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