

NOTE

Stability of Acrylonitrile–Acrylamide Copolymer Solutions

Chen Hou,¹ Cheng-Guo Wang,¹ Liang Ying,² Hua-Su Cai¹

¹Carbon Fiber Center, College of Materials Science and Engineering, Shandong University, Jinan 250061, China

²Shandong Institute of Metrology, Jinan 250014, China

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INTRODUCTION

The stability of spinning dopes for the spinning of acrylic fibers is an important problem.¹ Spinning dopes are usually prepared at temperatures considerably higher than extrusion temperatures, and long periods are required for the settlement of deaeration. In fiber technology, acrylonitrile (AN) polymer solutions that rapidly cool to the processing temperature tend gradually to the equilibrium state, which is accompanied by variations of the viscosity properties. Concentrated polar AN polymer solutions exhibit intense molecular interactions, and some examples illustrating the aging phenomena of acrylic polymers have been observed and reported in the literature;^{2,3} the addition of additives may vary the viscosity of AN polymer solutions.^{4,5} To our knowledge, there are only a few reports on dilute AN copolymer solutions, but there are almost no reports on concentrated AN copolymer solutions with acrylamide (AAM) as a comonomer. With this in mind, we studied the stability of AN/AAM copolymers. In this study, a solvent water suspension technique was used to synthesize a copolymer. The viscosity was controlled and determined with an NDJ-4 rotary viscosimeter. The effects of mechanical mixing, the composition of the solvent, and the additives on the viscosity of AN/AAM copolymer solutions were contrastively studied.

EXPERIMENTAL

Materials

Extra-pure-grade AN and AAM were supplied by Tianjin Chemical Resin Industry (Tianjin, China) and were distilled for the removal of inhibitors before use. Azobisisobutyronitrile (AIBN), supplied by Shanghai Chemical Resin Industry (Shanghai, China), was used as an initiator and was recrystallized from ethanol before use.

Poly(vinyl alcohol) (PVA) was obtained from Shanghai Chemical Resin Industry and used as a suspending agent. Deionized water (self-made) and dimethyl sulfoxide (DMSO), supplied by Taigu Chemical Plant (Taigu, China), were adopted as the polymerization media.

Copolymerization

The required amounts of AN, AAM, PVA, AIBN, deionized water, and DMSO were placed in a glass flask, which was continuously flushed with ultrapure nitrogen. The flask was wholly immersed in a temperature-controlled water bath and was shaken from time to time. After 2 h, the resultant mixture was poured into a large amount of methanol for precipitation, washed with methanol several times, and dried at 60°C *in vacuo* until it reached a constant weight. Copolymer samples were obtained.

Characterization

An elemental analysis of the copolymers was carried out with a PE 2400 elemental analyzer to determine the oxygen content. The viscosity of copolymer solutions with the same copolymer content was measured with the NDJ-4 rotary viscosimeter under different conditions.

RESULTS AND DISCUSSION

Copolymer composition

The H₂O/DMSO suspension technique was used to synthesize the AN/AAM copolymer. Some important parameters and polymerization conditions of the copolymer are shown in Table I. Pure AN/AAM copolymer were synthesized by this technique. The composition of the AN/AAM copolymers was determined from the oxygen concentration.

Flow action of the copolymer solutions

The viscosity of the AN/AAM copolymer solutions at different shearing rates at 40°C was determined with the NDJ-4 rotary viscosimeter. The AN/AAM copolymer was dissolved in the DMSO solvent, and this yielded an 18 wt % solution. The solution was stirred for 2 h at 40°C until a transparent and viscous complex was obtained. The shearing rate was proportional to the rotor speed. The shearing rate was calculated as follows:

$$\gamma = 2wR^2 / (R^2 - r^2) \quad (1)$$

where γ is the shearing rate; w is the rotor speed; and r and R are the radii of the rotor and beaker, respectively. The experimental results are given in Table II. The changes in the

Correspondence to: C. Hou (chenhou0825@163.net).

TABLE I
Important Parameters of Copolymerization

H ₂ O/DMSO (v/v)	AN/AAM (w/w)	Oxygen concentration in the copolymer (wt %)	AAM concentration in the copolymer (wt %)
90/10	98/2	0.45	1.997

Conditions: [AN] = 4.15 mol/L; [AIBN] = 0.008 mol/L; [PVA] = 0.22 g/L; time = 2 h; temperature = 60°C.

viscosity became less prominent with an increase in the rotor speed. This agreed with the character of Newtonian flow. Roychen et al.⁷ reported the same result. It can be concluded that the copolymer solutions showed Newtonian flow at lower shearing rates and that the viscosity was independent of the shearing rate.

Effect of the stirring rate on the viscosity of the copolymer solutions

The influence of the mechanical mixing on the viscosity of the copolymer solutions was studied through variations in the stirring rate from 0 to 40 rpm at a constant rotor speed of 6 rpm, and the copolymer solution was kept at 40°C. The concentration of the AN/AAM copolymer in the solutions was kept at 18 wt %. Figure 1 illustrates the effect of mechanical mixing (i.e., the stirring rate) on the viscosity–time characteristics of AN/AAM copolymer solutions. The viscosity of the copolymer solutions at rest increased continuously with time, but the increase in the viscosity of the copolymer solutions was considerably reduced by mechanical mixing. The changes in the viscosity of the solutions with a stirring rate of 40 rpm were less prominent than those of solutions with a stirring rate of 20 rpm. THE addition of mechanical mixing apparently prevented the formation of aggregates and stabilized the original structures of the solutions.

Effect of the solvent composition on the viscosity of the copolymer solutions

The composition of the solvent used in the preparation of the copolymer solutions considerably affected the viscosity properties and stability of the copolymer solutions. Dimethylformamide (DMF) and H₂O were good and poor solvents, respectively, for the AN/AAM copolymer, and they were used as additives. The effect of the solvent composition on the viscosity of the copolymer solutions was studied through variations in the contents of additives in DMSO (from 0 to 10 wt %) at a constant rotor speed of 6 rpm, and the mixture was kept at 40°C. The concentration of the AN/AAM copolymer in the solutions was kept at 18 wt %. Figure 2 illustrates the viscosity of the copolymer solutions

as a function of the additive content in DMSO. When DMF was used as an additive, the solution viscosity decreased monotonically, as expected from the stronger solvent power of DMF (with respect to DMSO). When H₂O was used as an additive, the viscosity of the copolymer solutions decreased continuously as the concentration of H₂O increased to 3 wt % and then increased. In concentrated copolymer solutions, two opposite effects of the solvent power on the viscosity were expected. On the one hand, some shrinkage of molecular coils would reduce viscosity. On the other hand, the reduction of the solvent power would lead to increased polymer–polymer interactions, promote aggregation, and generally destabilize the solution.⁸ The addition of increasing amounts of H₂O to DMSO reduced the solvent power continuously, and the viscosity minima reflected the competition between chain coiling and polymer interaction effects. At high concentrations of H₂O, the solutions formed solid and elastic gels.

Effect of the alkali salts on the viscosity of the copolymer solutions

The influence of the alkali salts on the viscosity of the AN/AAM copolymer solutions was studied through variations in the concentrations of the alkali salts from 0 to 0.035 mol/L at a constant rotor speed of 6 rpm, and the mixture was kept at 40°C. The concentration of the AN/AAM copolymer in the solutions was kept at 18 wt %. Figure 3 shows the changes in the viscosity with the addition of KCl and NaCl. The viscosity of the copolymer solutions decreased continuously as the concentrations of KCl and NaCl increased to 0.025 mol/L and then increased. The changes in

TABLE II
Effect of the Rotor Speed on the Viscosity of the Copolymer Solutions

Rotor speed (rpm)	1.5	3	6	12
Viscosity (Pa, S)	398.6	395.2	397.4	396.5

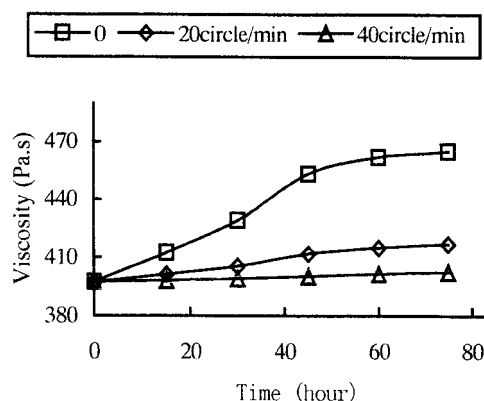


Figure 1 Effect of the stirring rate on the viscosity of the copolymer solutions.

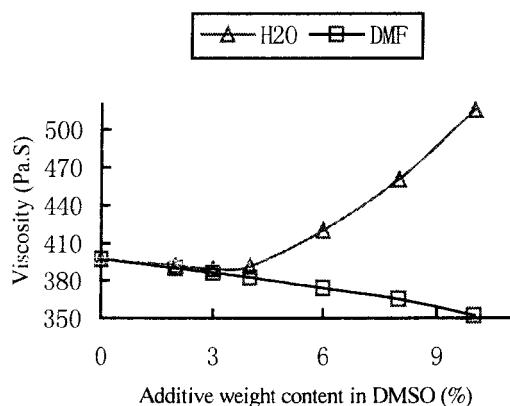


Figure 2 Effect of the additives on the viscosity of the copolymer solutions.

the viscosity of the solutions containing KCl were less prominent than those of solutions containing NaCl.

In the literature,⁹ factors have been reported that affect the viscosity of copolymer solutions at a constant shearing rate. These factors can be divided into two different groups. The first includes the extent of high molecular entanglement. The second is the free volume in the copolymer solution. There are significant salt effects when alkali salts are placed in a DMSO solvent. Alkali salts decompose into ions because of a solvation effect (i.e., Na⁺, K⁺, and Cl⁻). Intermolecular interactions are reduced by Na⁺ and K⁺, and this leads to a reduction of the association degree of high molecular chains. Entanglement networks of high molecular chain are destroyed. Disentanglement and slippage of entanglement crosslinking begin to occur. With an increase in the alkali salt concentration, the rate of disentanglement and slippage is faster than that of entanglement, and slippage among the high molecular chains becomes easy. The introduction of alkali salts KCl and NaCl produced a decrease in the viscosity of the copolymer solutions. When the alkali salt concentration was greater than 0.025 mol/L, the free volume in the copolymer solution was mostly occupied. The free area in which high molecular chains relatively moved became smaller. The viscosity of the copolymer solutions rose slowly.

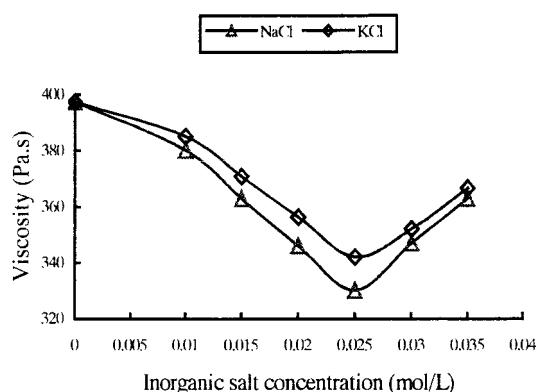


Figure 3 Effect of the alkali salts on the viscosity of the copolymer solutions.

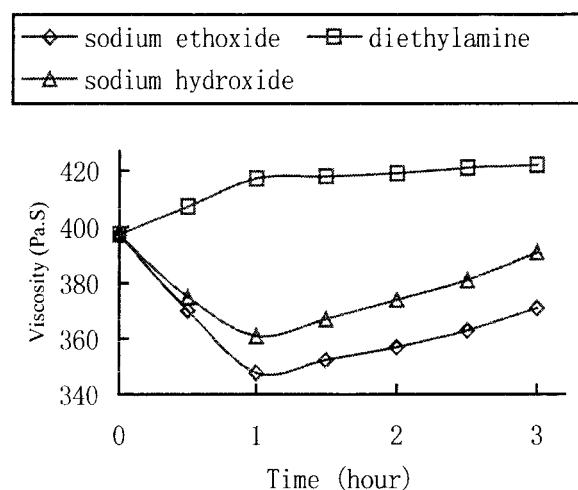


Figure 4 Effect of the base on the viscosity of the copolymer solutions.

Effect of the bases on the viscosity of the copolymer solutions

For our initial experiments, two strong bases, sodium ethoxide and sodium hydroxide, and a weak base, diethylamine, were used. As soon as the AN/AAM copolymer was added to a DMSO–base mixture, the copolymer dissolved, and coloration occurred simultaneously. The solution containing diethylamine did not become as dark as the solution containing sodium ethoxide and sodium hydroxide. The influence of the alkali salts on the viscosity of the AN/AAM copolymer solutions was studied with a base concentration of 0.02 mol/L and a constant rotor speed of 6 rpm; the mixture was kept at 40°C. The concentration of the AN/AAM copolymer in the solutions was kept at 18 wt %. Figure 4 shows a plot of the viscosity against time. Within the first hour, there was a great drop in the viscosity of the copolymer solutions containing a strong base, and then the viscosity appeared to increase. Batty and Guthrie¹⁰ indicated that the rapid viscosity drop was due to random chain scission and that the polymer chains coiled tightly. Bashir et al.¹¹ also reported an increase in the viscosity with sodium hydroxide after an initial drop. The viscosity increase was probably due to a limited amount of crosslinking. Gelation was observed, and a dark red-black gel was formed 15 h later.

The viscosity of the copolymer solutions containing a weak base did not drop but instead increased in the first hour. After a period of a few hours, changes in the solution viscosity became less prominent, and this agreed with the literature.^{11,12}

Effect of acetic acid on the viscosity of the copolymer solutions

As an extension of the viscometric studies, the effect of acetic acid on the viscosity of the copolymer solutions was studied. For this work, the copolymer was dissolved in DMSO, and the acetic acid was carefully added to give the required composition of the mixed solvent. The effect of the solvent composition on the viscosity of the copolymer solutions was studied through variations of the contents of the additives in DMSO from 0 to 24 wt % at a constant rotor speed of 6 rpm,

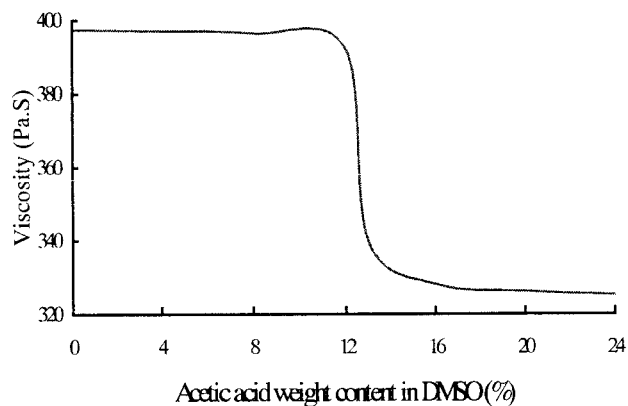


Figure 5 Effect of acetic acid on the viscosity of the copolymer solutions.

and the mixture was kept at 40°C. The concentration of the AN/AAM copolymer in the solutions was kept at 18 wt %. The results are given in Figure 5. The viscosity of the copolymer solutions suddenly dropped at 13 wt % acetic acid in DMSO. The composition with 13 wt % acetic acid in DMSO

can be considered a θ solvent¹³ for the AN/AAM copolymer.

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