Rheological Behavior of Acrylonitrile/Ammonium Acrylate Copolymer Solutions

Liang Ying,[1] Chen Hou,[2] Wang Qun[2]

[1]Office of Science and Technology, Yantai Normal University, Yantai 264025, People's Republic of China
[2]College of Chemistry and Materials Science, Yantai Normal University, Yantai 264025, People's Republic of China

ABSTRACT: Ammonium acrylate was first used as a comonomer to copolymerize with acrylonitrile. The viscosity behavior of dimethyl formamide solutions of acrylonitrile/ammonium acrylate copolymer was studied, and the rheological kinetics of the solutions were studied for comparison. It was shown that the solutions behaved the same as a Newtonian flow as the rotor speed increased beyond 12 rpm. With an increase in temperature, the apparent viscosity of acrylonitrile/ammonium acrylate copolymer solutions showed a trend of decreasing. The changes in the apparent flow-activation energy of solutions (E_η) calculated by the Arrhenius equation became less prominent along with the changes in the molecular weight of the acrylonitrile/ammonium acrylate copolymers. E_η increased continuously with an increase in copolymer concentration. The viscosity of copolymer solutions decreased continuously as the concentrations of KCl and NaCl increased up to 0.015 mol/L, and then it increased. The E_η showed an obvious trend of decreasing with the addition of alkali salts, and the changes in the E_η containing NaCl were more prominent than those of solutions containing KCl. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2320–2324, 2007

Key words: additives; viscosity; rheology

INTRODUCTION

In fiber technology, selection of a suitable dope viscosity for spinning of acrylic fibers is an important step.[1] Spinning dopes are usually prepared in temperatures considerably higher than extrusion temperatures, and long periods are required for settlement of deaeration. Acrylonitrile (AN) polymer solutions rapidly cooled to the processing temperature tend to gradually reach the equilibrium state, which is accompanied by variation in viscosity properties.[2] Increasing the molecular weight of an AN polymer and the solid content of spinning dope can improve the mechanical properties of precursors and the resulting carbon fiber, always leading to increasing dope viscosity, which is disadvantageous and dangerous for preparation and transportation. Many reagents have been reported in the literature[3,4] as pretreatments for decreasing the viscosity of AN polymers and moderating the stabilization exotherm. In one case, the addition of LiCl to the spinning dope decreases the viscosity of the dopes and moderates the stabilization exotherm of the precursors.[5] To our knowledge, there have been only a few reports on the viscosity behavior of ordinary AN copolymer dilute solutions, but almost nothing has been reported on the rheological kinetics of the solutions of high-molecular-weight AN copolymer with ammonium acrylate (AAT) as a comonomer. With this in mind, a study was undertaken of the rheological kinetics of dimethyl formamide (DMF) solutions of high-molecular-weight AN/AAT copolymer. In this study, AAT was first used to successfully copolymerize with acrylonitrile using various polymerization techniques. The apparent flow-activation energy of DMF solutions of AN/AAT copolymer was calculated, and the effects of additives on the rheological kinetics of AN/AAT copolymer solutions were studied for comparison. Such viscosity measurements and the rheological kinetic study of DMF solutions of AN/AAT copolymer can be used to adjust the spinning process and improve the mechanical properties of AN precursors.

EXPERIMENTAL

Materials

Monomer AN was supplied as extrapure grade by the Tianjin Chemical Resin Industry (Tianjin, China) and distilled to remove inhibitors before use. AAT

WILEY
InterScience®
DISCOVER SOMETHING GREAT

TABLE I
Comparison of the Viscosity-Average Molecular Weight of AN/AAT Copolymers

Sample code	Polymerization technology	AN/AAT ratio in the feed (w/w)	M_η ($\times 10^4$)	AAT concentration in copolymer (wt %)
poly(AN/AAT)1	DMF solution	98 : 2	9.04	1.99
poly(AN/AAT)2			11.8	1.97
poly(AN/AAT)3	Aqueous suspension		34.2	1.89
poly(AN/AAT)4			41.7	1.86

was obtained by neutralization of acrylic acid supplied as extrapure grade by Tianjin Chemical Resin Industry (Tianjin, China) and NH_3. DMF was supplied by Shanghai Chemical Resin Industry (Shanghai, China). High-molecular-weight AN/AAT copolymer was prepared by the aqueous suspension polymerization technology. The details of the polymerization technology were given previously.[6,7] For comparison, ordinary AN/AAT copolymer synthesized by DMF solution polymerization[8] technology was also used.

Characterization

The molecular weight (M_η) of AN/AAT copolymer was determined by intrinsic viscosity measurements. The intrinsic viscosity [η] of AN/AAT copolymer was measured at 25°C in dimethyl formamide using an Ubbelohde viscometer,[9] and the molecular weight was calculated from eq. (1):

$$[\eta] = 3.92 \times 10^{-4} M_\eta^{0.75} \tag{1}$$

Elemental analysis of the copolymers was carried out using a PE 2400 elemental analyzer to determine the oxygen in these copolymers, and then the AAT concentration in copolymer could be calculated. The composition and characteristics of the AN/AAT copolymers are given in Table I.

The apparent viscosity of AN/AAT copolymer solutions with the same solids content at a constant temperature was measured using a NDJ-4 rotary viscosimeter.

The apparent flow-activation energy of DMF solutions of AN/AAT copolymers were calculated by Arrhenius equation [eq. (2)]:[10]

$$\eta = Ae^{E_q/RT} \tag{2}$$

where η is the apparent viscosity of AN/AAT copolymer solutions, E_η is the apparent flow-activation energy of AN/AAT copolymer solutions, and A is an equation parameter. The plot of ln η versus T^{-1} gave a straight line.

RESULTS AND DISCUSSION

Flow action of AN/AAT copolymer solutions

The apparent viscosity of AN/AAT copolymer solutions using a NDJ-4 rotary viscosimeter at different shear rates at 35°C was determined. The concentration of the AN/AAT copolymer in the solutions was kept at 10 wt %. The shear rate, which was proportionate to the rotor speed, could be calculated from eq. (3):[11]

$$\dot{\gamma} = \frac{2wR^2}{(R^2 - r^2)} \tag{3}$$

where $\dot{\gamma}$ is the shear rate, w is the rotor speed, and r and R are the radii of the rotor and the beaker, respectively. The experimental results are given in Figure 1. The apparent viscosity of the AN/AAT copolymer solutions decreased prominently as the rotor speed increased to 12 rpm, and the solutions showed non-Newtonian flow behavior, with less and less shear force. The changes in the viscosity of the solutions lessened as the rotor speed increased beyond 12 rpm, and its behavior was in accord with behavior characteristic of Newtonian flow. Roychen et al.[12] reported the same result. It may be concluded that AN/AAT copolymer solutions show Newtonian flow at a high shear rate and that the apparent vis-
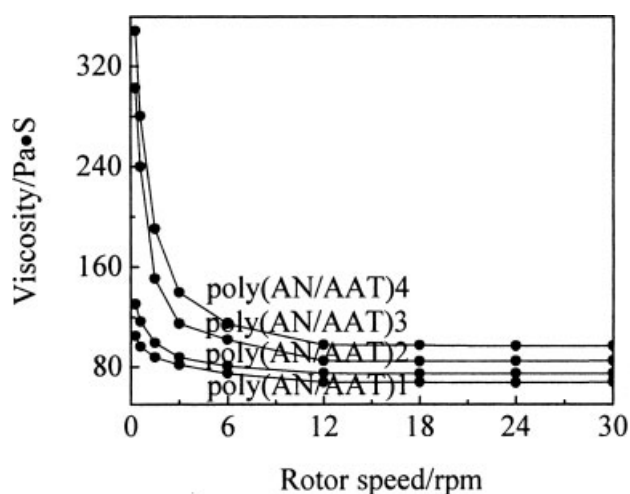

Figure 1 Viscosity curve of AN/AAT copolymers.

TABLE II
Effect of Temperature on Apparent Viscosity of Poly(AN/AAT)2 Solutions

	Temperature (°C)				
	30	35	40	45	50
Apparent viscosity (pa s)	88.1	75.2	64.3	55.4	47.8

cosity is independent of the shear rate. It is also evident from Figure 1 that the effects of the rotor speed on the apparent viscosity of solutions containing low-molecular-weight AN/AAT copolymer were less prominent than those of the solution containing high-molecular-weight AN/AAT copolymer.

In AN/AAT copolymer solutions, two opposite effects of the thermodynamic quality of solvent on apparent viscosity can be expected. On the one hand, some shrinkage of molecular coils would reduce viscosity. On the other hand, reduction of solvent power led to an increase in the polymer–polymer interactions, promotes aggregation and generally destabilizes the solution.[13] Increasing of the rotor speed continuously reduced the polymer–polymer interactions, which led to a decrease in the degree of association of the high-molecular-weight chains. Entanglement networks of the high-molecular-weight chains were destroyed. The high-molecular-weight chains partially uncoiled and orient themselves to the flow direction. Slippage of the high-molecular-weight chains occurred easily, and viscosity showed a trend of decreasing.

Effect of temperature on apparent viscosity of copolymer solutions

The solution containing poly(AN/AAT)2 copolymer was used to study the influence of temperature on the apparent viscosity of AN/AAT copolymer solutions by varying temperature from 30°C to 50°C at a constant rotor speed of 12 rpm. Table II illustrates the effects of temperature on the apparent viscosity of AN/AAT copolymer solutions while keeping the concentration of AN/AAT copolymer in the solutions constant at 10 wt %. With an increase in temperature, the apparent viscosity of the AN/AAT copolymer solutions showed a trend of decreasing. The higher the temperature, the more prominent was the solvent power of DMF. The rates of disentanglement and slippage of the entanglement network were faster. Flow of the high-molecular-weight chains occurred easily.

Determination of apparent flow-activation energy of solutions

According to the results summarized in Table II, the apparent flow-activation energy of poly(AN/AAT)2

copolymer solutions with a AN/AAT copolymer concentration of 10 wt % was calculated. Figure 2 shows a logarithmic plot of η versus T^{-1}. The apparent flow-activation energy of solutions estimated from the slope was 24.9 kJ/mol.

Effect of molecular weight of AN/AAT copolymer on the apparent flow-activation energy

The effect of the molecular weight of the AN/AAT copolymer on the apparent flow-activation energy of solutions was studied by varying AN/AAT copolymer concentration at a constant rotor speed of 12 rpm. Table III shows the effect of the molecular weight of AN/AAT copolymer on the apparent flow-activation energy of solutions while keeping the concentration of AN/AAT copolymer in the solutions constant at 10 wt %. It is evident from Table III that the changes in the apparent flow-activation energy of the solutions become less prominent along with the changes in the molecular weight of the AN/AAT copolymer, with the apparent flow-activation energy of the solutions independent of AN/AAT copolymer molecular weight, which is in agreement with the literature.[14] It was shown that the flow of the high-molecular-weight AN/AAT copolymer was accord with the character of the chain segment motion.

Effect of AN/AAT copolymer concentration on apparent flow-activation energy

For our initial experiment, the influence of AN/AAT copolymer concentration on the apparent flow-activation energy of AN/AAT copolymer solutions was discussed by varying poly(AN/AAT)2 copolymer content from 8 to 16 wt % at a constant rotor speed of 12 rpm. Figure 3 shows a plot of the apparent
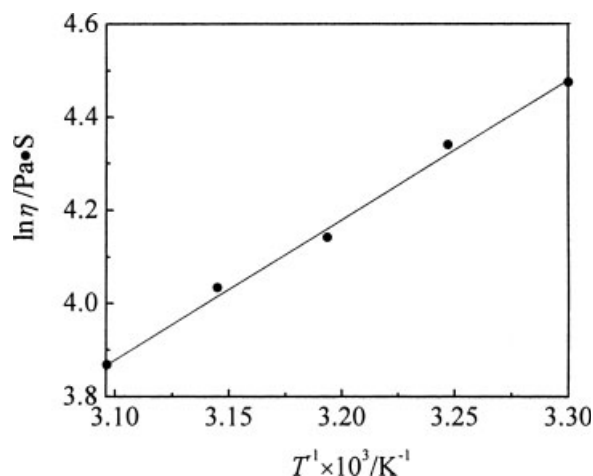

Figure 2 Dependence of apparent viscosity of poly(AN/AAT)2 solutions on temperature.

TABLE III
Effect of Molecular Weight of AN/AAT Copolymer on Apparent
Flow-Activation Energy of Solutions

Sample code	poly (AN/AAT)1	poly (AN/AAT)2	poly (AN/AAT)3	poly (AN/AAT)4
M_w ($\times 10^4$)	8.69	11.9	35.6	44.9
E_η (kJ/mol)	25.7	24.9	25.6	25.2

flow-activation energy of the copolymer solutions as a function of AN/AAT copolymer content in DMF. It is evident from Figure 3 that the apparent flow-activation energy of AN/AAT copolymer solutions increased continuously along with the increase in AN/AAT copolymer concentration. With an increase in AN/AAT copolymer concentration, it became difficult for the high-molecular-weight chains to flow, and the apparent flow-activation energy of AN/AAT copolymer solutions showed a trend of increasing.

Effect of alkali salts on rheological behavior of copolymer solutions

The effects of alkali salts on the apparent viscosity of poly(AN/AAT)2 copolymer solutions was studied by varying the concentration of alkali salts from 0 to 0.03 mol/L at a constant rotor speed of 12 rpm with the mixture maintained at 35°C and the concentration of poly(AN/AAT)2 copolymer in kept at 10 wt %. Figure 4 shows the changes in viscosity with the addition of KCl and NaCl. The apparent viscosity of copolymer solutions decreased continuously as the concentrations of KCl and NaCl increased up to 0.015 mol/L, and then apparent viscosity increased. The changes in viscosity of the solutions containing KCl were less prominent than those of the solutions containing NaCl.

According to a previous study,[15] the factors that affect the viscosity of copolymer solutions at a con-

stant shear rate can be divided into two groups. in the first group is the extent of high-molecular-weight entanglements, and in the second group is the free volume of high-molecular-weight polymers. Alkali salts were disassociated into ions by solvation effects when added to DMF solvent. Intermolecular interaction was reduced by the ions, which led to a decrease in the degree of association of high-molecular-weight polymers. Disentanglement and slippage of the entanglement crosslink began to occur. With an increase in the alkali salt concentration, the rate of disentanglement and slippage was faster than that of entanglement. The high-molecular-weight chains began to orient toward the flow direction, and when alkali salt concentration is above 0.015 mol/L, flow became more difficult, and the viscosity of the copolymer solutions showed a trend of increasing.

To study the effect of alkali salts on the apparent flow-activation energy of AN/AAT copolymer solutions, the alkali salt concentration was kept at 0.015 mol/L with a constant rotor speed of 12 rpm and a concentration of poly(AN/AAT)2 copolymer of 10 wt %. Table IV illustrates the effect of alkali salts on the apparent flow-activation energy of the poly (AN/AAT)2 copolymer solutions. The apparent flow- activation energy of the AN/AAT copolymer solutions shows an obvious trend of decreasing with the addition of alkali salts, and the changes in the solution containing NaCl were more prominent than those in the solution containing KCl.
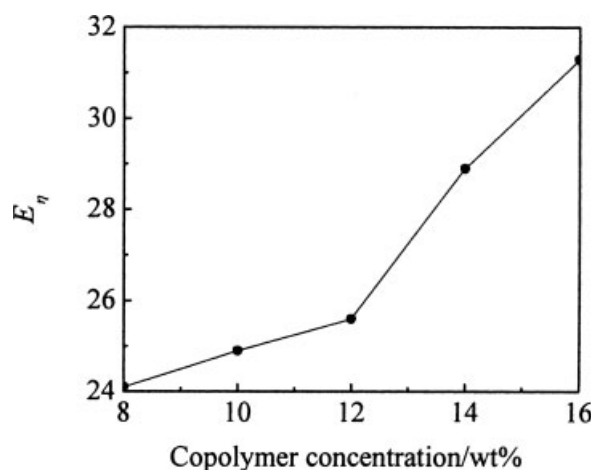

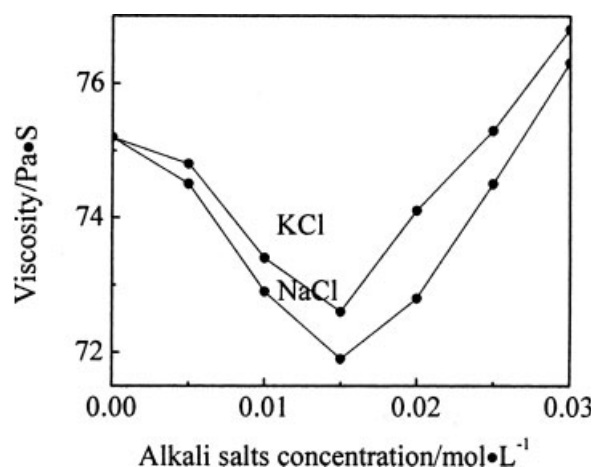**Figure 3** Effect of poly(AN/AAT)2 concentration on the apparent flow-activation energy of solutions.

Figure 4 Effect of alkali salts on viscosity of poly(AN/AAT)2 solutions.

TABLE IV
Effect of Alkali Salts on Apparent Flow-Activation
Energy of Poly(AN/AAT)2 Solutions

Additive	Without salt	NaCl	KCl
E_η (kJ/mol)	24.9	22.1	23.2

CONCLUSIONS

A laboratory study of viscosity behavior of dimethyl formamide solutions of acrylonitrile/ammonium acrylate copolymer has shown that the apparent viscosity of AN/AAT copolymer solutions decreased prominently as the rotor speed increased to 12 rpm. The changes in viscosity of the solutions became less prominent as the rotor speed increased beyond 12 rpm, which was in accord with a Newtonian flow character. The changes in the apparent flow-activation energy of solutions, as calculated by the Arrhenius equation, became less prominent along with the changes in the molecular weight of the AN/AAT copolymer. The apparent flow-activation energy of AN/AAT copolymer solutions increased continuously with an increase in the AN/AAT copolymer concentration. The apparent viscosity of copolymer solutions quickly decreased with the addition of KCl and NaCl. When the concentration of alkali salts exceeded 0.015 mol/L, the viscosity showed a trend of increasing. The apparent flow-activation energy of an/AAT copolymer solutions showed an obvious trend of decreasing with the addition of alkali salts, and the changes in the apparent flow-activation energy of the solution containing NaCl were more prominent than those of the solutions containing KCl. Such rheological behavior of DMF solutions of AN/AAT copolymers can be used to adjust the spinning process and improve the mechanical properties of AN precursors.

References

1. Gargallo, L.; Games, C. L.; Radic, D. Eur Polym J 1984, 20, 483.
2. James, C. M. Acrylic Fiber Technology and Application; Marcel Dekker: New York, 1995.
3. Richard, D.; Winters. U.S. Pat. 4,279,612 (1981).
4. Menachem, L.; Hilda, G.; Yechiel, N. J Macromol Sci Chem 1988, A25, 1367.
5. Chen, H.; Wang, C. G.; Liang, Y.; Cai, H. S. J Appl Polym Sci 2003, 89, 3492.
6. Chen, H.; Wang, C. G.; Liang, Y.; Cai, H. S. Chin J Chem Eng 2003, 11, 166.
7. Chen, H.; Zhang, W. X.; Wang, C. G.; Cai, H. S. Chin Polym Mater Sci Eng 2003, 19, 79.
8. Bajaj, P.; Paliwal, D. K.; Gupta, A. K. J Appl Polym Sci 1993, 49, 823.
9. Kashyap, A. K.; Kalpagam, V. J Polym Sci 1979, 17, 225.
10. Dong, J. Z.; Zhao, Y. M.; Chen, X. Y. Process of Synthetic Fiber; China Textile Press: Beijing, 1996.
11. Lan, L. W. Polymer Physics; Northwestern Polytechnical University Press: Xian, China, 1989.
12. Roychen, J.; Surekha, D.; Animesh, K. R. Polym Int 1991, 26, 89.
13. Mukesh, K. J.; Abhiraman, A. S. J Mater Sci 1987, 22, 278.
14. He, M. J.; Chen, W. X.; Dong, X. X. High Polymer Physics; Fudan University Press: Shanghai, 2000.
15. Bajaj, P.; Paliwal, D. K.; Gupta, A. K. J Appl Polym Sci 1998, 67, 1647.