Korean J. of Chem. Eng., **13**(6), 554-558 (1996)

APPARENT ELONGATIONAL VISCOSITY OF DILUTE POLYMER SOLUTIONS

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(Received 25 September 1995 • accepted 19 August 1996)

Abstract – Apparent elongational viscosity studies were made on dilute solutions of high molecular weight polymers using a fiber spinning apparatus designed for low shear viscosity liquids with substantial elongational effects. The experimental method involved the flow of solutions of polyacrylamide and poly(ethylene oxide) from a tube into an evacuated vessel. Experimental results showed that the apparent elongational viscosity obtained from the jet shape increased linearly with the stretch rate.

Key words: *Elongational Viscosity, Shear Viscosity, Poly(ethylene oxide), Polyacrylamide, Polymer Solution*

INTRODUCTION

High molecular weight polymers that reduce the friction in a pipeline are used in the oil industry to increase the capacity of crude oil pipelines. Molecules that are effective in drag reduction have molecular weights above 10^5. These molecules can elongate and interact with other molecules in high strain rate region of flow. It is generally agreed that only a few parts per million of polymer additives can markedly increase the elongational viscosity of solvent. Such a large elongational viscosity would alter the flow process.

An important limitation in obtaining elongational viscosity is that steady state in elongational flows may be reached only at low stretch rates and at long times of stretching. It is common to use the apparent elongational viscosity that is the instantaneous ratio of stress to stretch rate. Further, the apparent elongational viscosity represents a convenient parameter for comparative purposes in practice [Baid and Metzner, 1977].

The common elongational viscometer techniques for polymer solutions are tubeless siphon [Astarita and Nicodemo, 1970], fiber spinning method [Chang and Denn, 1979], converging flow method [Metzner, 1970], opposing nozzles [Fuller et al., 1987], and triple jet techniques [Oliver and Bragg, 1974]. In the fiber spinning viscometer the fluid is extruded from a die and collected on a take up drum. The stretching rate is controlled by the rotational speed. The diameter profile of the threadline is usually measured from photographs. The tensile stress along the thread line could be evaluated from an overall momentum balance equation at steady state [White, 1981] as

$$F(l)=F(x)+F_{air}+F_{surface}-F_{grav}+F_{inert} \tag{1}$$

The individual terms in Eq. (1) are expressed as

$$F(x)=\sigma_{11}\pi r^2(x) \tag{2}$$

$$F_{air}=2\pi\int_x^l 0.68\left(\frac{2\rho_a u r}{\eta_a}\right)^{-0.8}\cdot\frac{\rho_a u^2}{2}\cdot r\partial x \tag{3}$$

$$F_{surface}=2\pi\delta\left[\frac{r(x)}{\sqrt{1+\dot{r}(x)^2}}-\frac{r(l)}{\sqrt{1+\dot{r}(l)^2}}\right] \tag{4}$$

$$F_{grav}=\int_x^l \rho g\pi r^2\partial x \tag{5}$$

$$F_{inert}=\rho Q[U(l)-U(x)] \tag{6}$$

The pressure drop technique [Sridhar and Gupta, 1985, 1988] provides better sensitivity in measuring tensile stress at the spinneret exit. The spinneret is replaced by two capillaries, and the fluid emerging from the upper capillary is stretched by vacuum. The tensile stress due to the stretching at the upper capillary exit is given as

$$\sigma_{11}=P_0-P_1 \tag{7}$$

For a constant volume flow rate, assuming a flat velocity profile, the local velocity is given by

$$U=\frac{Q}{\pi R^2} \tag{8}$$

The elongational viscosity is defined as the ratio of the normal stress difference to the stretch rate

$$\eta_E=\frac{\sigma_{11}-\sigma_{22}}{\dot{\varepsilon}} \tag{9}$$

The normal stress difference [Baid and Metzner, 1977] within uniaxial extension is given as

$$\sigma_{11}-\sigma_{22}=\sigma_{11}+\frac{\delta}{R} \tag{10}$$

The stretch rates which are defined as the velocity gradient in the flow direction are obtained by the subsequent differentiation of the radius profile

$$\dot{\varepsilon}=\frac{\partial U}{\partial x_1}=-\left(\frac{2Q}{\pi R^3}\right)\left(\frac{\partial R}{\partial x_1}\right) \tag{11}$$

Some studies have been made on polymer solutions for the

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elongational behavior. Vissmann and Bewersdorff [1990] made experiments on the influence of preshearing on the elongational behavior of dilute polymer solutions. The extensional flow fields were obtained by a modified rotational viscometer. In this technique they achieved the measurement of the elongational viscosity at concentrations as low as in drag reduction applications. This study showed that shear thinning in polymer solutions depends on the concentration and the molecular weight. The studies on the alignment angle which is defined as the angle between the positive shear rate direction and the major axis of the macromolecule by Cottrell [1969] reveal that the alignment angle in the region of the maximum increase in elongational viscosity is much smaller than the region where elongational viscosity starts to increase. This indicates that an orientation in the shear flow is responsible for the increase of the elongational viscosity. Moore and Pearson's [1975] tests on polyacrylamide solution showed that the elongational viscosities of long chain polymer solutions are greater by several orders of magnitude than the corresponding shear viscosities. The uniaxial extension flow fields in poly(ethylene oxide), polyacrylamide, and polystyrene solutions were produced by opposed jet, and molecular chain extension was detected by the birefringence appearance by Odell et al. [1988]. Odell designated critical strain rates according to the shape of birefringence. This critical point shows strong dependence on the concentration.

The purpose of this study is to examine the trend of apparent elongational viscosity of dilute polymer solution and determine which of external forces influencing tensile stress along the threadline would be important factor in evaluating elongational viscosity.

EXPERIMENT

Two polymers, poly(ethylene oxide) (PEO), and polyacrylamide (PAM) were chosen. PEO was Polyox WSR-301 of which weight average molecular weight is 4×10^6, manufactured by Union Carbide. PAM was Separan AP 273 of which weight average molecular weight is 1×10^7, manufactured by Dow Chemical. The concentrations of test solutions were in the range 500 to 3000 ppm for PEO and 50 to 100 ppm for PAM.

The fiber spinning apparatus used for the measurement of elongational viscosity is shown in Fig. 1. It is similar to that employed by Sridhar and Gupta [1985, 1988]. The fiber spinning apparatus consists of a solution head tank, a feed line with a needle valve, a plexiglass main chamber, vacuum system, and a manometer. For cleaning purpose the top of the plexiglass chamber is sealed with a threaded cap which is connected to a 10° inclined manometer to measure the pressure drop. Four liters of test solution placed in the head tank by means of a funnel for each run. Solutions were supplied to the slot in the top wall of the main chamber by gravity from a head tank and left through the upper nozzle. The thread length and the vertical alignment were adjusted by moving the lower nozzle. The flow rate was controlled by a needle valve at the entrance of the chamber. The chamber was filled with the test solution to a certain level. The vacumm pump was then started and the liquid leaving from the upper nozzle was stretched and sucked into the lower nozzle. The pressure drop in the chamber was taken as the tensile stress at the upper nozzle exit according to Eq. (7) with a sensitivity of 0.25 Pa. The flow rate was determined by measuring the time to collect a given volume of liquid in a graduated cylinder. All experiments were carried out at ambient temperature of 20°C. Still photographs of the thread were taken for all runs. An aperture of f8 and a shutter speed 1/60 sec, a macro zoom lens, and lighting were used with Tmax 400 film. 1 ppm of Rhodamine B dye was added in the solution to improve the visualization. Measurements of diameters along the threadline were obtained from negatives projected onto a white wall comparing the outside diameters of the nozzle images with their known outside diameters.

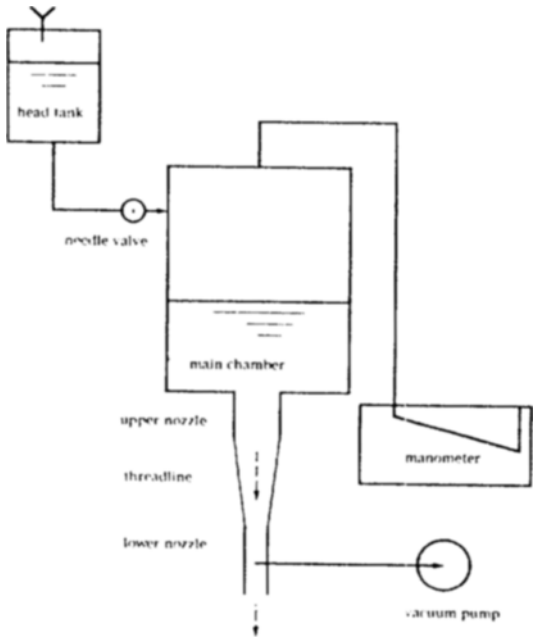

Fig. 1. Schematic diagram of fiber spinning apparatus.

The velocity profiles were computed from the radius profile using Eq. (8). The stretch rates along the threadline were computed from the volume flow rate and the diameter profile using Eq. (11). The tensile stress along the threadline was obtained from the momentum balance around the upper nozzle using Eq. (1). The elongational viscosity was calculated using Eq. (9) and Eq. (10).

RESULTS AND DISCUSSION

The basic data for elongational viscosity are the measured volume flow rate, thread shape, and tensile stress. The thread radius as a function of distance is measured from photographs. A large magnification is required for accurate measurement since the diameter is less than 1.5 mm. A direct measurement of the thread diameter is not usually possible. It is common to use a curve fitting method to smooth the diameter data. The curve fitting equations for diameter-distance data have been introduced by several researchers [Baid and Metzner, 1977; MacSporran, 1981; Moore and Pearson, 1975; Mewis and Cleyn, 1982; Spearot and Metzner, 1972; Hudson et al., 1974]. The

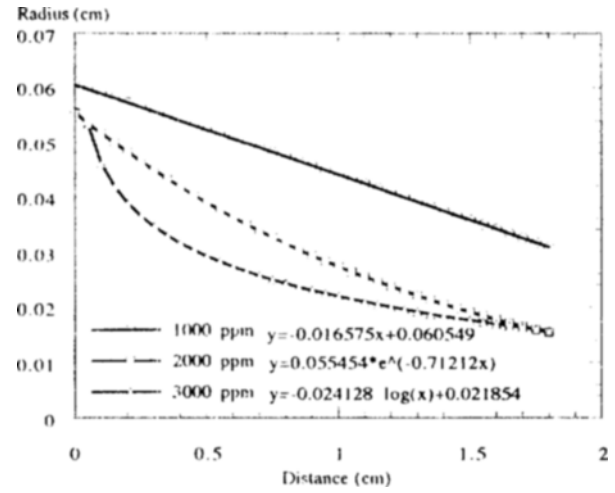

Fig. 2. Radius profile of PEO solution as a function of concentration. Tube ID: 1000 & 2000 ppm 1.194 mm, 3000 ppm 1.372 mm. The lines represent the calculated values.

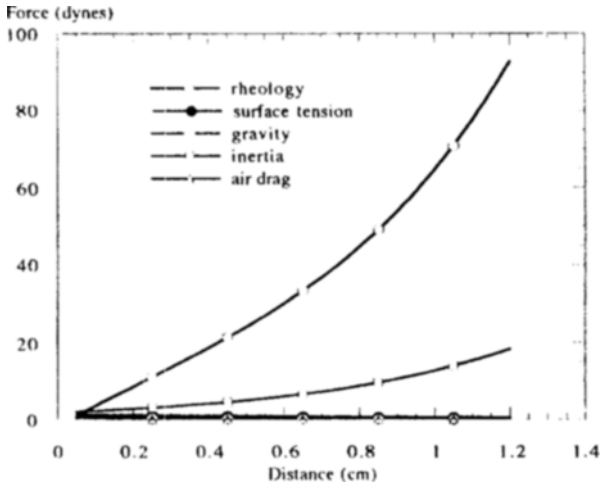

Fig. 3. Contributions to tensile stress in 50 ppm PAM solution for a 1.2 cm thread. Tube ID 1.194 mm, flow rate 0.51 cc/sec. The lines represent the calculated values referring to Eq. (1).

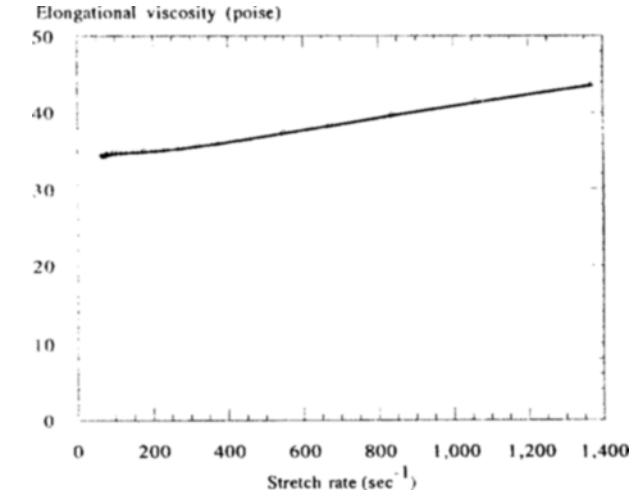

Fig. 4. Elongational viscosity of 500 ppm PEO solution for a 0.8 cm thread. Tube ID 1.067 mm, flow rate 0.29 cc/sec. The line connects the calculated points.

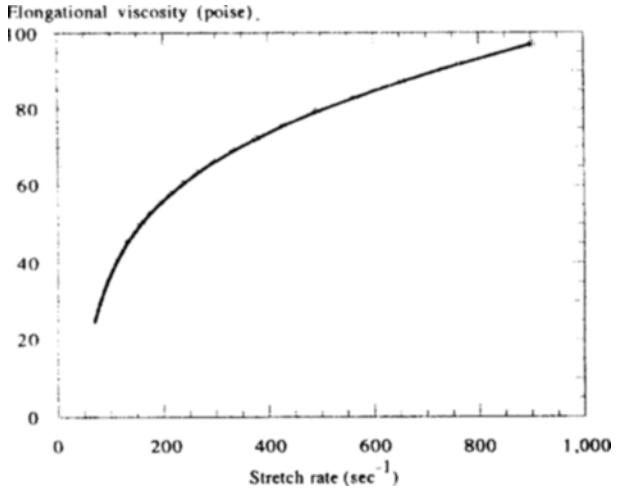

Fig. 5. Elongational viscosity of 1000 ppm PEO solution for a 1.2 cm thread. Tube ID 1.194 mm, flow rate 0.72 cc/sec. The line connects the calculated points.

stretch rates are obtained by differentiation of the radius profile of the threadline. The selection of a proper regression expression is a key factor for the elongational viscosity study. For example, when a polynomial equation is used, this expression gives a better fit of data with the highest R^2 value. However the oscillatory wave character leads to a random trend of elongational viscosity which is not a true behavior. Fig. 2 shows the radius profile of a PEO thread obtained by regression as a function of concentration. The R^2 values of regression were greater than 0.98. The radius at low concentration of PEO solution was found to become almost linearly dependent on axial distance. As concentration increases, the thread shape begins to change from linear to exponential and finally to logarithmic. This shape change indicates that PEO solution can be stretched more easily in high concentration.

Tensile stress at the tube exit was obtained from the pressure drop measurement. The tensile stress along the threadline was evaluated from Eq. (1). Contributions of viscoelastic drag, inertia, air drag, gravity, and surface tension to tensile stress have been compared in Fig. 3 using 50 ppm PAM solution. Viscoelastic drag is significant and shows a marked increase with the thread length. Inertia becomes important at the lower part of thread. Gravity, surface tension, and air drag forces on the thread were found to be small and almost negligible.

The apparent elongational viscosity which is a function of stretch rate was calculated from Eq. (9). Three different upper nozzles of 1.067 mm, 1.194 mm, and 1.372 mm with inside diameters were used for 500 ppm, 1000 ppm, and 3000 ppm PEO respectively. The nozzles used for PAM solution had an inside diameter of 1.194 mm. The inside diameter of lower nozzle was 0.686 mm. The results for apparent elongational viscosity at different concentrations of PEO solution are seen in Fig. 4 through 6. In Fig. 7, the apparent elongational viscosity of PAM

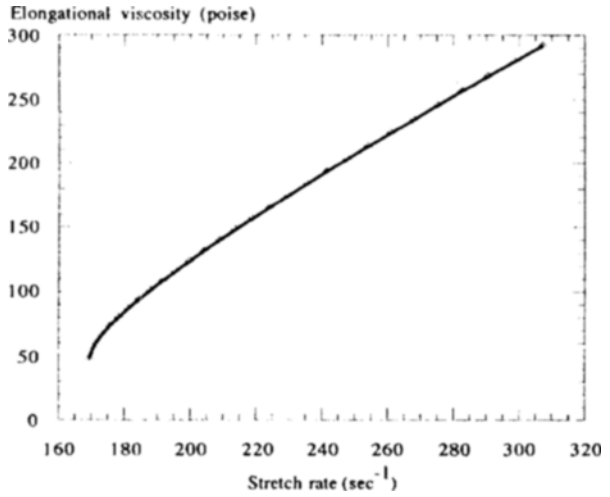

Fig. 6. Elongational viscosity of 3000 ppm PEO solution for a 1.8 cm thread. Tube ID 1.372 mm, flow rate 0.31 cc/sec. The line connects the calculated points.

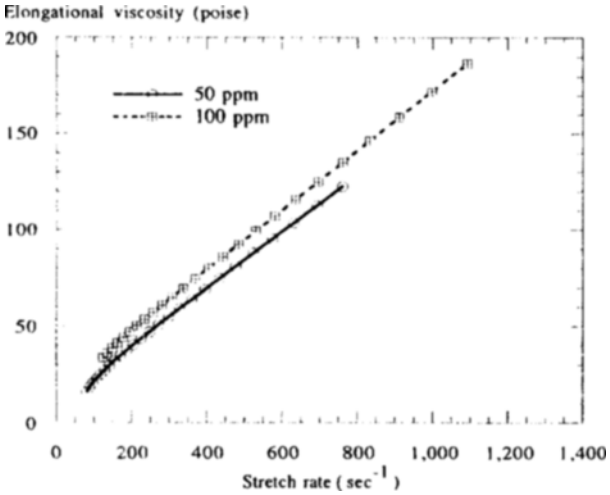

Fig. 7. Elongational viscosity of PAM as a function of concentration for a 1.2 cm thread. Tube ID 1.194 mm, 50 ppm 0.51 cc/sec, 100 ppm 0.27 cc/sec. The lines connect the calculated points.

solution as a function of concentration is plotted. Though the figures show results for two different polymeric solutions, the behavior of the elongational viscosity is similar. The maximum elongational viscosity varies with concentration. The higher the concentration of solution, the larger the elongational viscosity. In most cases, the elongational viscosity has a linear increase as a function of stretch rate. There is a nonlinear portion at the beginning of elongational viscosity, but this changes to linear shape. Several points could be noted for the explanation of the nonlinear increase at the beginning. Elongational viscosity for the regions near the nozzle exit is expected to be in error because it is assumed that in developing the momentum balance, the velocity has a flat profile. The flat velocity profile is known to start at a point which is about two nozzle diameters away from nozzle exit for a low speed jet [Adachi, 1987]. Another source of error is due to the past history of deformation. The flow near the nozzle exit is expected to be a fully developed Poiseulle flow which continues until it changes to pure elongational flow at a certain point downstream. The onset point in elongational viscosity could not be seen in the figures. It is clear that the deformation of the polymer solution occurs and the solution experiences a tensile stress before it leaves tube exit when the polymer solution undergoes uniaxial extension.

CONCLUSIONS

Apparent elongational viscosity was measured using a fiber spinning apparatus for comparison. The apparent viscosity of PEO and PAM solutions increased linearly with stretch rate. These results are similar to the well known results of polymer melts. Random trends of elongational viscosity of polymer solutions based on work of Chow et al. [1988], may be due to the selection of different regression expression for liquid thread shape. Viscoelastic drag and inertia were major contributors to the tensile stress along the threadline of polymer solutions.

NOMENCLATURE

$F(l)$: viscoelastic drag force at axial distance l [dyne]
$F(x)$: viscoelastic drag force at axial distance x [dyne]
F_{air} : air drag force [dyne]
F_{grav} : gravity force [dyne]
F_{inert} : inertia force [dyne]
$F_{surface}$: surface tension force [dyne]
g : acceleration of gravity [cm·sec^{-2}]
P_0 : pressure in main chamber without stretching [P_a]
P_1 : pressure in main chamber with stretching [P_a]
Q : volume flow rate [cm^3·sec^{-1}]
R : nozzle inner radius [cm]
r : thread radius [cm]
$\dot{r}$: radius gradient in the axial direction [-]
U : local velocity [cm·sec^{-1}]
η : shear viscosity [poise]
η_a : shear viscosity of air [poise]
η_E : elongational viscosity [poise]
ρ : density [g·cm^{-3}]
ρ_a : density of air [g·cm^{-3}]
σ_{11} : normal stress in the axial direction on a face normal to axial axis [dyne·cm^{-2}]
σ_{22} : normal stress in the radial direction on a face normal to radial axis [dyne·cm^{-2}]
δ : surface tension coefficient [dyne·cm^{-1}]
ε : stretch rate [sec^{-1}]

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