Elongational Stress of the Flow of Polymer Solutions*

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This review describes methods and techniques developed to date for measuring elongational stresses produced in elongational flows. Experimental results are presented and it is shown that in many cases the strain exerted on a fluid element is important for the stress in elongational flow fields of dilute and nondilute polymer solutions. In several cases, however, it is demonstrated that the elongational stress is correlated with the elongational rate and agrees with the prediction of the FENE dumbbells model of the second-order type.

Key Words : Viscoelastic Fluid, Elongational Flow, Elongational Stress, Rheometry, Constitutive Equation, Measurement

1. Introduction

Fluid flows are generally divided into two types: shear flow and elongational flow. Shear flow has been well analyzed and understood as metric flow for determining the viscosity and relaxation time of fluids. Elongational flow has not been thoroughly studied because of various experimental constraints and uncertainties, although it is substantially related to many practical flows such as the converging and inlet flow into an aperture, the flow in a packed bed, the flow near the wall in a turbulent flow, the flow in coating processes, and the squeezing flow.

The purpose of this paper is to present a short review of the method and technique developed so far for measuring elongational stresses, along with the experimental result and discussion concerning the elastic property of liquids tested.

Techniques developed for measuring elongational stress or elongational viscosity seem to be divided into three groups: The first one is a method utilizing the spinnability of a liquid column (liquid column spinning

method). The second one makes use of pressure differentials between the upstream and downstream of a contraction of an orifice or converging channel (pressure differential method) and the third one utilizes the reaction or thrust of jets flowing out of a small aperture (jet thrust or jet reaction method). Even by these techniques, the elongational stress is not directly measured and certain relationships are required to assess the stress from measured quantities. However, these relationships are omitted here due to limited space. See original papers for them.

2. Liquid Column Spinning Method

With this method, a liquid column flowing out of a tube, for example, is pulled or spun by sucking or taking up as shown in Fig. 1⁽¹⁾⁻⁽⁴⁾. Both the diameter of the liquid column and the pulling force are measured. Similar methods are the tubeless syphon^{(1),(5)-(8)} and liquid stretching using a falling cylinder^{(9),(10)}. Figure 2 shows an example of this method, where the elongational stress is plotted against the axial distance of the column of liquid⁽³⁾. Solid lines in the figure are predictions using the PTT model, but the values at the zero axial distance are given beforehand. As expected, this method is useful only for spinnable liquids or melts and the elongational rate attained is low.

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Fig. 1 Method of liquid column spinning

Fig. 2 Elongational stress ($\tau_{11} - \tau_{22}$) plotted against the axial distance for the liquid column spinning. The solid lines are predictions of the PTT model, but the values at the zero axial distance are fitted to the experimental data beforehand⁽³⁾

3. Pressure Differential Method

It is well known that pressure differentials between the upstream and downstream of the flow through a small hole differ between polymer solutions and Newtonian fluids. Naturally the idea was conceived that this phenomenon would be useful in estimating elongational stress and some attempts have been made so far^{(8),(11)–(15)}. The scheme of this method is given in Fig. 3. A small orifice or a converging nozzle is set up in a channel and pressure differentials are measured between upstream and downstream positions. Elongational stress is assessed with the measured pressure differentials. Pressure differentials are quantities easy to measure and therefore we do not need a sophisticated apparatus in this method, which is a merit of this method. However, the pressure differentials are frequently less than 1 mm head in water for small elongational stresses. Additionally they are sensitive to flow conditions: Once vortices occur in the measuring region, the

Fig. 3 Pressure differential method

Fig. 4 Elongational stress ($\tau_{11} - \tau_{22}$) vs. elongational rate ($\dot{\epsilon}$) obtained by the pressure differential method using a converging channel⁽¹⁴⁾. Radii of the converging channel are 8.92 mm, 7.09 mm, and 5.69 mm at the taps 2, 3, and 4, respectively

pressure differentials increase greatly because of the extra energy dissipation caused by complexity of the flow. These are surely demerits of this method. Figure 4 gives an example of the elongational stress obtained by James and others who used a converging nozzle designed to produce a constant rate of elongation in the core flow except the boundary layer flow near the nozzle wall⁽¹⁴⁾. We see that the elongational stress is not correlated with the elongational rate. This may be due to the effect of strain to which macromolecules are subjected at each pressure tap. We will discuss this in a later section.

4. Jet Thrust and Jet Reaction Methods

Thrust or reaction of jets issuing from an elongational flow field seems to be superior to pressure differentials in measuring the elongational stress, because the jet thrust is directly related to the integrated amount of tensile stress, but the pressure differential is a differential and indirect one, and it is difficult to measure its small value exactly, as mentioned in section 3. Thrust or reaction of jets is

measured as shown in Fig. 5. With the jet thrust method, Metzner and Metzner⁽¹⁶⁾, Oliver and Bragg⁽¹⁷⁾, and Hasegawa and others⁽¹⁸⁾⁻⁽²⁰⁾ used small orifices, while Oliver and Ashton⁽²¹⁾ used a nozzle producing constant elongational rates as James⁽¹⁴⁾ did for the pressure differential method. Figure 6 shows the result obtained by Oliver and Ashton⁽²¹⁾. We see that the elongational stress is not correlated with the strain rate. Hasegawa and co-workers⁽¹⁸⁾⁻⁽²⁰⁾ measured the reaction of the jet, instead of the thrust, issuing from small orifices for very dilute polymer solutions of ppm order. In their experiment a condition was chosen so that no vortex was generated in the upstream region of the orifice, because, once vortices occur, the flow field becomes too complicated to determine the elongational rate. They assumed a radial uniformly converging flow for a measuring flow field, actually measured the velocity along the center line of the flow field upstream of the orifices, and confirmed that water and 100 ppm PEO solution have nearly the same center velocity distribution as the radial converging flow⁽²²⁾. Figures 7, 8, and 9 give the elongational stress plotted against the elongational rate for PEO 10 ppm, PEO 50 ppm and Separan 5 ppm solutions in water. We see that for PEO 10 ppm and

Fig. 5 Jet thrust and jet reaction methods

Fig. 6 Elongational stress ($\tau_{11} - \tau_{22}$) vs. elongational rate (ϵ) obtained by the jet thrust method⁽¹⁷⁾

Separan 5 ppm the elongational stress is not correlated with the elongational rate over most of the orifice diameters used, but for almost all data of PEO 50 ppm and for a part of the data of PEO 10 ppm ranging

Fig. 7 Elongational stress ($\tau_{11} - \tau_{22}$) vs. elongational rate (ϵ) obtained by the jet reaction method⁽²²⁾ for PEO 10 ppm solution in water. Solid and broken lines show predictions by FENE dumbbells model

Fig. 8 PEO 50 ppm solution in water. See the caption of Fig. 7

Fig. 9 Elongational stress ($\tau_{11} - \tau_{22}$) vs. elongational rate (ϵ) obtained by the jet reaction method⁽²²⁾ for Separan 5 ppm in water

above the elongational rate of 10^4 sec^{-1} , a correlation between elongational rate and elongational stress exists. For other dilute PEO solutions the same trend is seen⁽²²⁾.

5. Opposing Jet Apparatus

One of the devices recently marketed is an opposing jet apparatus⁽²³⁾⁻⁽²⁶⁾. This is a type of jet reaction method: It utilizes the force necessary to suck test liquids into a channel through a small hole. As illustrated in Fig. 10, fluid is drawn into opposing tube inlets to create a stagnation flow around the mid-plane. One inlet is stationary and the other is part of a balance arm to measure the force exerted by the entering fluid. This force, divided by the tube area, is taken to be the tensile stress at the inlet. The elongational rate is approximated by the entry velocity divided by the distance from the mid-point to the tube entrance. The opposing jet device has been commercialized by Rheometrics Inc.

6. Correlation of the Elongational Stress Data with the Mean Velocity

As shown above, the elongational stress obtained with various experiments is not a function of the elongational rate except for in a few cases of PEO solutions. However, it is shown that the same data are, in many cases, correlated with the mean velocity at the location of the measuring point. Figure 11 gives

Fig. 10 Opposing jets apparatus

Fig. 11 Elongational stress ($\tau_{11} - \tau_{22}$) of Fig. 2 replotted against the square of the local velocity (V^2) of the liquid column

Fig. 12 Elongational stress ($\tau_{11} - \tau_{22}$) of Fig. 4 replotted against the local velocity (V) of the converging channel

the same data that are given in Fig. 2. They are now replotted against the local velocity squared of the liquid column and we see a correlation. Next the experimental result obtained by the pressure differential method, which is shown in Fig. 4, is given again in Fig. 12 as a function of the local mean

Fig. 13 Elongational stress ($\tau_{11} - \tau_{22}$) of Fig. 6 replotted against the nozzle exit velocity (V)

velocity in the nozzle, and a correlation is seen. This kind of correlation in the pressure differential method is seen also with another, different polymer solution called M_1 , which is mentioned in a later section, but is not presented here. The data of Fig. 6 obtained by the jet thrust method, are given against the mean velocities at the exit of each nozzle in Fig. 13, and a good correlation is seen again. Furthermore the data of PEO 10 ppm and Separan 5 ppm obtained by the jet reaction method (Figs. 7 and 9) are plotted versus the velocity at the orifice, as shown in Figs. 14 and 15. We see that, although the data are rather scattered, some correlation exists between the two. The same correlation between elongational stress and velocity is seen for the data by Metzner and Metzner⁽¹⁶⁾.

Table 1 shows relationships between elongational stress and velocity for various solutions [dilute (Hasegawa), nondilute (Chan, Oliver, James, Metzner) and with different methods liquid column spinning (Chan), pressure differential of constant elongational channel (James), jet thrust of orifice (Metzner), jet thrust of constant elongational rate nozzle (Oliver), jet reaction of orifice (Hasegawa)]. In most of the above cases, the gradient of the elongational stress vs. velocity in log-log plot is close to 2.0. Then for simplicity we put the correlation experimentally obtained as

$$\tau_{11} - \tau_{22} \propto V^2. \quad (1)$$

When this relation is made dimensionless using a reference velocity V_0 , we have

$$(\tau_{11} - \tau_{22}) / (\rho V_0^2) = K (V/V_0)^2. \quad (2)$$

Here ρ is the fluid density. V_0 is not a definite

Fig. 14 Elongational stress ($\tau_{11} - \tau_{22}$) of Fig. 7 replotted against the orifice mean velocity (V)

Fig. 15 Elongational stress ($\tau_{11} - \tau_{22}$) of Fig. 9 replotted against the orifice mean velocity (V)

value, but we may take, for example, the onset velocity of deformation of entangled macromolecules for it.

7. Discussion

7.1 Elastic property of the fluid

It is interesting that Eq. (2) holds true under various conditions of elongational flows. Then a question arises as to what information can be deduced

Table 1

Method	Researchers	Solution	Elongational stress
Liquid column spinning	Chan et al. ⁽³⁾	50ppm Separan AP273 solution in water	$2.2\rho V^{1.57}$
Pressure differential	James et al. ⁽¹⁴⁾	4.1% solution of polyethylmethacrylate in dipropylene glycol monomethyl ether	$0.5\rho V^2$
	James et al. ⁽¹⁵⁾	M1 fluid; a solution of PIB in polybutene and kerosene, with viscosity of 3 Pa s at 20 °C	24 °C: $(7.1 \sim 13.3)\rho V^{2.2}$ 40 °C: $1.0\rho V^2$
Jet thrust	Oliver and Ashton ⁽¹⁸⁾	3.5% polymer in Iranian light oil	$0.05\rho V^{2.2}$
	Metzner and Metzner ⁽¹⁶⁾	Separan AP 30 in water	0.5% : $1.28\rho V^{1.61}$ 0.083% : $0.79\rho V^{1.64}$
Jet reaction	Hasegawa and Nakamura ⁽²²⁾	PEO and Separan solution less than 20 ppm	$(0.1 \sim 0.5)\rho V^2$
		PEO solutions larger than 50 ppm	$\propto (\text{elongational rate})^{2.0}$

Fig. 16 Strain of a fluid element

from it. Consider a fluid element subjected to elongational strain, as shown schematically in Fig. 16. At a reference position X^i , we take dS_0 for the length of the element, A_0 for the cross-sectional area, and V_0 for the velocity. Similarly at a position x^i the length of the element is dS , the cross-sectional area of the element A , and the velocity V . The coordinate system is taken to be the orthogonal Cartesian coordinate system. Then $dS^2 - dS_0^2$ represents the strain given by the following relation.

$$dS^2 - dS_0^2 = 2E_{KL}dX^K dX^L \quad (3)$$

where

$$2E_{KL} = g_{kl}(x) \frac{\partial x^k}{\partial X^K} \frac{\partial x^l}{\partial X^L} - G_{KL}(X) \quad (4)$$

is a strain tensor of the Lagrange type. When the direction 1 is taken to be the flow direction, the flow becomes one-dimensional and G_{KL} and g_{kl} are Kronecker delta, and furthermore $dX^1 = dS_0$, $dx^1 = dS$. Therefore we have the following relation.

$$2E_{11} = (dS/dS_0)^2 - 1 \quad (5)$$

From the constancy of the element volume we have

$$A_0 dS_0 = A dS. \quad (6)$$

Also the equation of continuity gives

$$A_0 V_0 = A V. \quad (7)$$

Then we have the following equation from the above relations.

$$2E_{11} = (V/V_0)^2 - 1 \quad (8)$$

Furthermore, in the case that V/V_0 is much larger than unity, we obtain

$$2E_{11} = (V/V_0)^2 \quad (9)$$

and from Eqs. (2) and (9) we have

$$(\tau_{11} - \tau_{22})/(\rho V_0^2) = K \cdot 2E_{11}. \quad (10)$$

That is, $(\tau_{11} - \tau_{22})/(\rho V_0^2)$ is proportional not to the elongational rate but to the strain of the element. This means the elastic property of the fluid.

7.2 Prediction of the FENE dumbbells model

As shown in Figs. 7 and 8, the elongational stress for PEO solutions is correlated with the elongational rate over some range: the ranges above 10^4 sec^{-1} for 10 ppm and above 10^3 sec^{-1} for 50 ppm. These data are now compared with the FENE dumbbells model described by Bird et al.⁽²⁷⁾ The FENE dumbbells model developed in a series of γ and ω and truncated by the second order is expressed as

$$\begin{aligned} \tau = & c[\eta]_0 \eta_s \gamma \\ & - \frac{1}{2} \frac{b+5}{b+7} \frac{c([\eta]_0 \eta_s)^2 M}{RT} ((\omega \cdot \gamma - \gamma \cdot \omega) - 2\gamma^2). \end{aligned} \quad (11)$$

In this equation b is a constant, c is the concentration of the solution, $[\eta]_0$ is the intrinsic viscosity

evaluated at the zero shear rate, R is the gas constant, T is the absolute temperature, τ is the stress tensor due to the existence of polymer, ω is the vorticity tensor and γ is the rate of strain tensor. The constants in the equation are all determined from the viscosity measurement and manufacturer's specifications. Calculated values by this model are shown in Figs. 7 and 8 as solid lines. We see that both the experimental and the predicted values agree well. Also a good agreement for the data of other concentrations of PEO 18 solution is obtained but it is omitted here. A study is being conducted in the author's laboratory on applicability of this model to other kinds of polymers.

8. Concluding Remarks

As stated above, there are various methods and techniques for measurement of elongational stress. Which is the best or most suitable for a given liquid? The answer is vague and may depend on the properties of the liquid: If the liquid is viscous and elastic enough, the spinning method may be proper, and if the liquid is a dilute solution, then the jet thrust or jet reaction method may be good. The pressure differential method is probably useful to nondilute and nonconcentrated solutions, that is, intermediate solutions. But in general the problem is open to question. Concerning this, it is of value to mention the M 1 project carried out several years ago. In the project a single fluid called M 1 (0.244% polyisobutylene in a mixed solvent consisting of 7% kerosene in polybutene) was chosen as a test liquid. This test liquid was prepared at Monash University in Australia and dispatched to researchers who were interested in elongational flows and had the facilities for measuring the elongational stress of this liquid. The experimental results were gathered and discussions conducted. This procedure was written up in a special issue of *Journal of Non-Newtonian Fluid Mechanics*, 35(1990)⁽²⁸⁾. In that issue, we find, to our regret, that the results of the participants were too diverse to deduce which method or technique is good or reliable. In this project the solid like property described in the present review was reported^{(9),(15)} but different behavior was also mentioned⁽²⁹⁾. It is not easy to measure elongational stress at the present stage, but at the same time more efforts are expected to be made to find and develop means of gauging it, because it is considered to play an important role in many actual fluid flows in laboratories and industries.

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