RELAXATION TIME OF POLYMER SOLUTIONS FROM ROD-CLIMBING HEIGHT

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Abstract — When the polymer solution is sheared from the boundary, the induced normal stresses are perpendicular to the planes of shear. The free-surface of the liquid is then deformed in the direction of the rod axis and it gives the rod-climbing height. From this rod-climbing experiment, the relaxation time of a polymer solution can be analyzed.

In this paper, the result of rod-climbing constant for the second-order fluid obtained by previous investigators is being correlated with the rheological properties of the polymer solution and then the relaxation time is calculated. Being compared with other experimental methods, it is found that the relaxation time from this method is rather simple to obtain.

INTRODUCTION

It is widely known that the Newtonian fluid near the rotating rod is pushed outward by a centrifugal force, and a dip near the center of the liquid surface forms. This is typical of the flow near the rotating shaft of a stirrer. On the other hand, the opposite phenomenon is observed in a polymeric liquid; the polymeric liquid climbs up the rod. The streamlines are closed circles and the extra tension along the lines strangulates the fluid and forces it inwards against the centrifugal force and upwards against the gravitational force. This phenomenon was first described by Garner and Nissan [1].

However, Weissenberg [2] was the first to explain this effect from the normal stress concept of the polymer solution, thus it is called the "rod-climbing" or "Weissenberg effect". He showed that the simple notation of an extra tension along the streamline could be used to obtain qualitative explanation of a large number of experiments. The experimental arrangement was such that the liquid was sheared in a gap between an outer vessel rotated with an angular velocity, and an inner member which was held against rotation and either rigidly fixed in position or free to move up and down the axis of rotation.

Assuming that the velocity is independent of the coordinate along the axis of the cylinder, the free surface remains relatively horizontal and the two

material functions of the Reiner-Rivlin theory are replaced by constants, Serrin [3] achieved the same result as Weissenberg did. In addition, for a general simple fluid Coleman and coworkers [4] computed the value of the normal stress from the Couette flow field in an infinite cylinder. The overthrust of the normal stress on the fictitious plane of constant pressure is the basis for the approximate computation of the direction of climbing. However, they did not consider gravity and surface tension.

Despite the difficulty of calculating the free surface profile from the given rheological equation of state, Joseph et al. [5, 6] and Beavers and Joseph [7, 8] were able to calculate the free surface profile using the second-order fluid model. From the shape of the free surface, Joseph and Fosdick [5] determined the value of the climbing constant. Either the method of slopes or the method of profile fitting, can be used to determine the rod-climbing constant. In the method of slopes, the height rise as a function of rotation speed, is measured and a slope is read off.

In this paper, the result of rod-climbing experiment which is combined with the coefficients of a second-order fluid model, is then correlated with the first and second normal stress difference coefficients. In addition, from the correlation of the first normal stress difference coefficient and the relaxation time of a polymer solution, the relaxation time is finally obtained from the rod-climbing constant.

THEORY

Assuming that the air above the free surface cannot exert tangential forces, and that the difference between the normal stress on the liquid side and the air pressure on the air side of the free surface is balanced by surface tension, Joseph and Fosdick [5] calculated the free surface by the domain perturbation method. In their theory, a boundary value problem in a given region of space was solved by mapping it onto a standard region of simple shape. The mapped problem was then expanded using a power series in the parameter which characterized the domain deformation. The perturbation problems arising in the expansion are solved successively in the standard region. The resulting series is then mapped back into the original domain.

The perturbation of the rest state is constructed as a series in powers of the rotation speed, ω. A neat ordering for each of the powers is also present. At zeroth order in ω, a flat surface with atmospheric pressure above and hydrostatic pressure below exists. At second-order in ω, an azimuthal field appears without a change of pressure. There is no deviation from the flat azimuthal velocity field, which induces a pressure change via central forces. The pressure change, in turn, produces the first deviation of the free surface from flatness.

The velocity is decomposed with axially symmetric velocity components (u, v, w) in cylindrical coordinates (r, θ, z) as follows:

$$u \equiv v(r, \ z)e_\theta + v$$

$$v \equiv u(r, \ z)e_r + w(r, \ z)e_z . \tag{1}$$

In addition, v may be found from a stream function $\Psi(r, \ z)$:

$$v = e_\theta \times \frac{1}{r} \nabla \Psi. \tag{2}$$

The extra stress τ plays an important role in the rod-climbing phenomena and is presented as follows:

$$\tau = \tau e_\theta e_\theta + te_\theta + e_\theta t + \pi \tag{3}$$

where t is a vector in a plane perpendicular to e_θ and π is a symmetric tensor in this plane. τ is also represented by the complete nth order approximation formula and i th order of τ is defined in terms of the Rivlin-Erickson tensors [7].

Using these equations, Joseph and Fosdick [5] obtained the following dynamic equation

$$-\frac{1}{r} \frac{\partial \Phi}{\partial \theta} + \nabla \cdot t + \frac{2}{r}t_r = \rho(\nabla v \cdot v - \frac{uv}{r}) . \tag{4}$$

Here $\Phi \equiv p + \rho gz$ and t_r is the physical component of t.

The first order solution for simple fluids is exactly the same as that for the Newtonian fluid at first order. Considering the surface tension, the two-parameter expansion procedure is adopted and then the second order solution is obtained as follows [6]

$$h(a; \ \omega, \ \varepsilon) \simeq h_s(a, \ \varepsilon)$$

$$+ \frac{4\pi^2 a}{\sigma(s)^{1/2}} \left[\frac{4(3\alpha_1 + 2\alpha_2)}{4 + \kappa} - \frac{\rho a^2}{2 - \kappa} \right] \frac{\omega^2}{2} \tag{5}$$

where h_s is static rise due to wetting, σ is the surface tension, a is the radius of the rod, ρ is the density of the fluid, ω is the rotational speed of the rod, and $\kappa = a(s)^{1/2}$ and $s = \rho g/\sigma$ where g is the gravitational acceleration.

From the rod-climbing experiment, the observed values of h vary linearly with ω^2. The slope of this line can be obtained and the theoretical values of this may also be derived from eq. (5) as follows;

$$\frac{dh}{d\omega^2} \Big|_{\omega \to 0} = -\frac{2\pi^2 a}{\sigma(s)^{1/2}} \left[\frac{4(3\alpha_1 + 2\alpha_2)}{4 + \kappa} - \frac{\rho a^2}{2 + \kappa} \right]. \tag{6}$$

In addition, the climbing constant β is defined as

$$\beta = 3\alpha_1 + 2\alpha_2 . \tag{7}$$

From eq. (6), β is calculated with the known values of σ and $\frac{dh}{d\omega^2} \Big|_{\omega \to 0}$:

$$\beta = \frac{4 + \kappa}{4} \left[\frac{\sigma\sqrt{s}}{2\pi^2 a} \frac{dh}{d\omega^2} \Big|_{\omega \to 0} + \frac{\rho a^2}{2 + \kappa} \right]. \tag{8}$$

To study the rod-climbing in the second-order fluid, we need to correlate eq. (8) with the coefficients of the second-order fluid model. The retarded-motion expansion is attempted to generalize the Newtonian constitutive equation in a systematic way by expanding the stress tensor in a Taylor series about the Newtonian fluid. The fundamental kinematic tensors $\gamma_{(1)}, \gamma_{(2)}, \cdots \gamma_{(n)}$, are called as the first, second, $\cdots$, nth rate of strain tensors.

The first of these is defined to be identical to the rate of strain tensor and the remaining are defined through a recurrence relation as follows [9]:

$$\gamma_{(1)} \equiv \dot{\gamma}$$

$$\gamma_{(n+1)} = \frac{D}{Dt} \gamma_{(n)} - [(\nabla v)^T \cdot \gamma_{(n)} + \gamma_{(n)} \cdot (\nabla v)^T] \tag{9}$$

where $\gamma(n+1)$ is the nth convected derivative of the shear tensor $\gamma_{(1)}$. To construct a constitutive equation

that describes small deviation from Newtonian behavior, we assume that the fluid is incompressible and that the stress tensor is symmetric and can be expressed as a polynomial in the rate of strain tensors $\gamma_{(n)}$. Then the retarded-motion expansion can be applied in this system, given here through terms of third order:

$$\underset{\approx}{\tau} = - \; \underline{[b_0\gamma_{(1)} + b_1\gamma_{(2)} + b_2(\gamma_{(1)} \cdot \gamma_{(1)}) + b_3\gamma_{(3)}}$$
$$+ b_4(\gamma_{(1)} \cdot \gamma_{(2)} + \gamma_{(2)} \cdot \gamma_{(1)}) + \cdots\cdots]. \tag{10}$$

Here b_0, b_1, b_2, etc. are material parameters. If we only take the first-order term, eq. (10) gives the constitutive equation for the incompressible Newtonian fluid, and b_0 is the viscosity. The dashed underlined terms are called as second-order fluid model. Then the viscometric functions for the second-order fluid are as follows [9]:

$$\eta = b_0$$
$$\Psi_1 = -2b_1$$
$$\Psi_2 = b_2. \tag{11}$$

Here Ψ_1 is the first normal stress difference coefficient, Ψ_2 is the second normal stress difference coefficient and η is the solution viscosity.

In addition, the second-order fluid is also usually given in terms of Rivlin-Erickson tensors [4],

$$\underset{\approx}{\tau} = -[a_0\underset{\approx}{A_1} + a_1\underset{\approx}{A_2} + a_2\underset{\approx}{A_1} \cdot \underset{\approx}{A_1}] \tag{12}$$

where $\underset{\approx}{A_1}$ and $\underset{\approx}{A_2}$ are Rivlin-Erickson tensors.
The coefficients of eqs. (10) and (12) are interrelated by

$$b_0 = a_0$$
$$b_1 = a_1$$
$$b_2 = a_2 + 2a_1. \tag{13}$$

Therefore we finally obtain the following correlation from eqs. (11) and (12).

$$a_1 = -\Psi_1/2$$
$$a_2 = \Psi_2 + \Psi_1. \tag{14}$$

The rod-climbing constant β is then correlated with the coefficients of the second-order fluid molel:

$$\beta = 3a_1 + 2a_2 = -3\Psi_1/2 + 2\Psi_2 + 2\Psi_1 = \Psi_1/2 + 2\Psi_2. \tag{15}$$

For the steady shear flow, the second-order fluid model becomes to the Criminale-Erickson-Filbey (CEF)

constitutive equation [10] as follows:

$$\underset{\approx}{\tau} = -\eta\underset{\approx}{\dot{\gamma}} - \left(\frac{1}{2}\,\Psi_1 + \Psi_2\right)(\underset{\approx}{\dot{\gamma}} \cdot \underset{\approx}{\dot{\gamma}}) + \frac{1}{2}\,\Psi_1\,\frac{\mathscr{D}\underset{\approx}{\dot{\gamma}}}{\mathscr{D}t} \tag{16}$$

where $\dfrac{\mathscr{D}}{\mathscr{D}t}$ is the Jaumann derivative.

In addition, the Zaremba-Fromm-Dewitt(ZFD) equation is derived from a single Maxwell element analogy [11]:

$$\underset{\approx}{\tau} + \lambda\,\frac{\mathscr{D}\underset{\approx}{\tau}}{\mathscr{D}t} = -\eta\underset{\approx}{\dot{\gamma}} \tag{17}$$

where $\lambda = \dfrac{\eta}{G}$ is the relaxation time which implies the ratio between fluid-like characteristics and solid-like characteristics.

The retarded motion expansion of eq. (17) gives

$$\underset{\approx}{\tau} = -\left(1 + \lambda\,\frac{\mathscr{D}}{\mathscr{D}t}\right)^{-1}\eta\underset{\approx}{\dot{\gamma}}$$
$$= -\eta\underset{\approx}{\dot{\gamma}} + \lambda\,\frac{\mathscr{D}(\eta\underset{\approx}{\dot{\gamma}})}{\mathscr{D}t} + \cdots\cdots. \tag{18}$$

Comparing eqs. (16) and (18), the relaxation time (λ) is expressed in terms of the first normal stress difference coefficient (Ψ_1) and viscosity (η) as follows:

$$\lambda = \frac{\Psi_1}{2\eta}. \tag{19}$$

Therefore we obtain the viscosity and the first normal stress difference coefficient of the second-order fluid model:

$$\eta(\dot{\gamma}) = \eta_0, \; \Psi_1 = 2\eta_0\lambda. \tag{20}$$

This corresponds with the fact that for a second-order fluid model the shear stress is proportional to the shear rate and the primary normal stress difference is proportional to the square of the shear rate [12].

For many polymeric systems, it is well known that Ψ_2 is negative and has an absolute value much smaller than Ψ_1. For simplicity we choose $\Psi_2/\Psi_1 \simeq 0$ [9], so eq. (15) becomes

$$\beta = 0.5\,\Psi_1. \tag{21}$$

Eq. (21) gives the correlation between the rod-climbing constant and the first normal stress difference coefficient.

RESULTS AND DISCUSSION

The relaxation time of a polymer solution is then calculated from eqs. (20) and (21) as

$$\lambda = \frac{\beta}{\eta} \ . \tag{22}$$

This equation shows that the relaxation time is proportional to the rod-climbing constant and is inversely proportional to the solution viscosity. Therefore, from eqs. (8) and (22), the relaxation time is finally obtained from the rod-climbing experiment as follows:

$$\lambda = \frac{4+\kappa}{4\eta} \left[\frac{\sigma\sqrt{s}}{2\pi^2 a} \left(\frac{dh}{d\omega^2} \right)_{\omega\to 0} + \frac{\rho a^2}{2+\kappa} \right]. \tag{23}$$

This is the first attempt to correlate the relaxation time with the rod-climbing experiment for the second-order fluid. With the informations of a polymer solution such as density, surface tension and solution viscosity, we can obtain the experimental relaxation time by simply measuring the free-surface from eq. (23).

For the rod-climbing experiment, Joseph and Fosdick [5] showed that the second-order fluid model agrees well with experimental results for STP solution which consists mainly of a polyisobutylene polymer dissolved in petroleum oil. On the other hand, Joseph et al. [6] showed that the free surface rises only if $r^2 < 4\beta/\rho$ when ω is small. This relation provides the criteria of selecting the rod size and explains why it is better to use small diameter rods in rod-climbing experiments. In addition, comparing Doi and Edwards model with Curtiss and Bird model, Hassager [13] argued that the Doi-Edwards model will always "rod-dipping", whereas the Curtiss-Bird model capable of predicting the experimentally observed rod-climbing when an additional parameter $\varepsilon > 1/8$, provided the radius is so small that inertial effects do not dominate.

The relaxation times from this rod-climbing experiment can be compared with those from the creep recovery experiments using a rotational rheometer [14]. The recoverable strain after cessation of steady state flow at shear stress (τ_s), is being measured and the relaxation time is calculated using $\lambda = R^{(s)}\eta$. Here $R^{(s)}$ is the limiting value of the recoverable compliance for large t.

From the molecular theory, it is also available to obtain the relaxation time of a polymer solution. By generalizing the effective medium theory of the hydrodynamics of a polymer solution, Muthukumar and Freed [15] derived the concentration dependent relaxation times. The relaxation times of all the Rouse mode were all lengthened as a function of the concentration of the polymer solutions.

This present analysis is valid only for low shear rate. However, the rod-climbing experiment is a rather simple method to obtain the relaxation time of the polymer solution comparing with other rheological methods. The experimental study on this subject is being currently investigated. The relaxation times from both the rod-climbing experiment and the molecular theory will be compared in the future work.

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NOMENCLATURE

$\underset{\sim}{A}$, : Rivlin-Erickson tensor
$b_0, b_1, b_2, b_3, \cdots$: material parameters
e_r, e_θ, e_z : r, θ, z-component unit vector
g : gravity constant
h : rod-climbing height
h_s : static rise
r, θ, z : cylindrical coordinates
$R^{(s)}$: limiting value of the recoverable compliance
u, v, w : axially symmetric velocity vectors
u, v, w : axially symmetric velocity components
s : $\rho g/\sigma$
t_r : physical component of $\underset{\sim}{t}$
$\underset{\sim}{t}$: vector in a plane perpendicular to e_θ

Greek Letters

$\alpha_0, \alpha_1, \alpha_2, \alpha_3$: nth order fluid constants
β : rod-climbing constant
∇ : plane gradient operator
ρ : fluid density
$\dot{\gamma}$: rate of strain tensor
η : solution viscosity
λ : relaxation time
$\underset{\sim}{\tau}$: deviatoric stress tensor
$\underset{\sim}{\tau}_s$: shear stress
σ : surface tension
$\underset{\sim}{\omega}$: voticity tensor
ω : rotation rate
Ψ_1 : first normal stress difference coefficient
Ψ_2 : second normal stress difference coefficient
κ : $a(s)^{1/2}$
Φ : $p + \rho gz$
$\underset{\sim}{\pi}$: symmetric tensor in eq. (3)
$\dfrac{D}{Dt}$: Stokes derivative
$\dfrac{\mathscr{D}}{\mathscr{D}t}$: Jaumann derivative

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