Optical Rheology of a Polydimethylsiloxane Fluid in Jeffrey-Hamel Type Flow

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***Abstract*— *The rheo-optical behavior of a viscoelastic polydimethylsiloxane (PDMS) fluid was examined at room temperature for various pressure drops (flow rates) across a Jeffrey Hamel type converging wedge flow cell. The strain-rates were computed from local velocity measurements using laser Doppler anemometry (LDA), and the planar extensional flow behavior of the polymer melt was studied via birefringence measurements along the centerline of the flow cell. The linear relation between the stress and polarizability tensors were confirmed over a range of strain rates that extended well into the non-Newtonian region. The first normal stress difference (FNSD) was calculated from the local velocity measurements using a two-term Goddard-Miller model with a single Maxwell-type relaxation time constant of 0.0174 s computed from Rouse model and a zero-shear viscosity of 300 Pa.s. A linear stress-optical coefficient of 1.41 x 10^{-10} Pa^{-1} was obtained for PDMS in planar extensional flow at room temperature from the flow birefringence measurements and the first normal stress difference (FNSD) computed using the Goddard-Miller model. This compares well with values for PDMS in the range of 0.909 – 1.84 x 10^{-10} Pa^{-1} at room temperature as reported by various researchers.*

Keywords*— *Polydimethylsiloxane, Flow Birefringence, Jeffrey-Hamel Flow, Stress-Optical Coefficient, Goddard-Miller Model.

I. INTRODUCTION

Polymer macromolecules exhibit isotropic behavior when they are completely randomly distributed. However, flow deformation causes orientation of the macromolecules leading to anisotropy in the transport properties like birefringence [1-3].

Anisotropy to transmission of light by an optical medium produces birefringence, or differences in refractive indices in orthogonal directions. According to Flory [4], the degree of anisotropy in refractive index (birefringence) for a chain network is represented as

$$\Delta N = (2\pi/9)\,(\nu/V)\,[(\bar{n}^2 + 2)^2/\bar{n}\,]\,(\bar{\alpha}_{xx} - \bar{\alpha}_{yy}) \tag{1}$$

Where ν/V represents the number of segments per unit volume (a segment is the portion of a macromolecular chain between two adjacent entanglement points), $\bar{n}$ is the refractive index of the isotropic non-ordered material, and **(**$\bar{\alpha}_{xx} - \bar{\alpha}_{yy}$**)** is the difference in the averaged polarizabilities of the chain along the x and y axes.

In the case of flexible polymer solutions and melts, the net optical anisotropy caused by flow can be obtained by measuring differences in refractive indices in the direction of the principal stresses. When the direction of propagation of the electric field vector of a polarized light beam coincides with the direction of one of the principal stresses of an optically anisotropic macromolecular fluid flowing through a transparent channel, the difference in birefringence in the other two directions is related to the difference in the corresponding principal stresses via the stress-optical law. According to this law, in a wide range of conditions involving not too large stresses, there is a linear relation between the components of the refractive index (polarizability) and stress tensors given by

$$\Delta N = C\,\Delta\sigma \tag{2}$$

where C is a material constant known as the stress-optical coefficient, ΔN is the difference in main refractive indices, and Δσ is the corresponding difference in the two principal stresses. The sign and magnitude of the stress-optical coefficient depends on the chemical structure of the polymer, which is governed by the polarizability of the bonds between the atoms of the polymer molecule and the direction of the bonds with respect to the polymer backbone. Since the deviatoric components of the stress and polarizability tensors are linearly related, the orientation of the principal axes will coincide with that of the optical axes. According to the theory of rubber photoelasticity [4] for a network of freely jointed Gaussian chain, the stress-optical coefficient is given by

$$C = (2\pi/45kT)\,[(\bar{n}^2 + 2)^2/\bar{n}]\,(\alpha_1 - \alpha_2) \tag{3}$$

where $\bar{n}$ is the mean refractive index of the material, k is the Boltzmann constant, T is the absolute temperature, α_1 is the polarizability of the chain link parallel to the link, and $\alpha_2$is the polarizability of the chain link transverse to the link.

Extensive experimental work has been done on stress-optical laws ranging from solids concentrated polymer solutions [5-7]. Since the proportionality of stress and refractive index does not imply proportionality of the stress and strain rate, the stress-optical law holds good for polymer melts well into the non-Newtonian region of flow [8]. The only requirement is that both stress and the refractive index tensors are governed by the orientation function. This will be true as long as the flow does not create a change in the magnitude of the macromolecular chain end-to-end vector. Janeschitz-Kriegl [9] has shown experimentally that, for many polymers, the linearity of the stress-optical law is valid up to a shear stress of 10^4 Pa and tensile stress of 10^6 Pa.

Majority of the rheo-optical studies of polymeric systems done so far involved the mechanical measurements of stress and optical measurements of birefringence to evaluate the linear stress-optical coefficient [10-13]. In this paper we illustrate the use of optical techniques (laser Doppler anemometry) measure birefringence, compute stress and then evaluate the linear stress-optical coefficient of a polydimethylsiloxane (PDMS) melt at room temperature in planar extension along the centerline of a converging wedge flow cell.

1.1 Velocity Vector, Rate-of-Strain and Stress Tensors

Assuming the flow in the converging wedge cell is two-dimensional, the components of the velocity vector in circular coordinates (Figure 1) are

$$V_r = f(r, \theta) \qquad \text{and} \qquad V_\theta = V_z = 0 \tag{4}$$

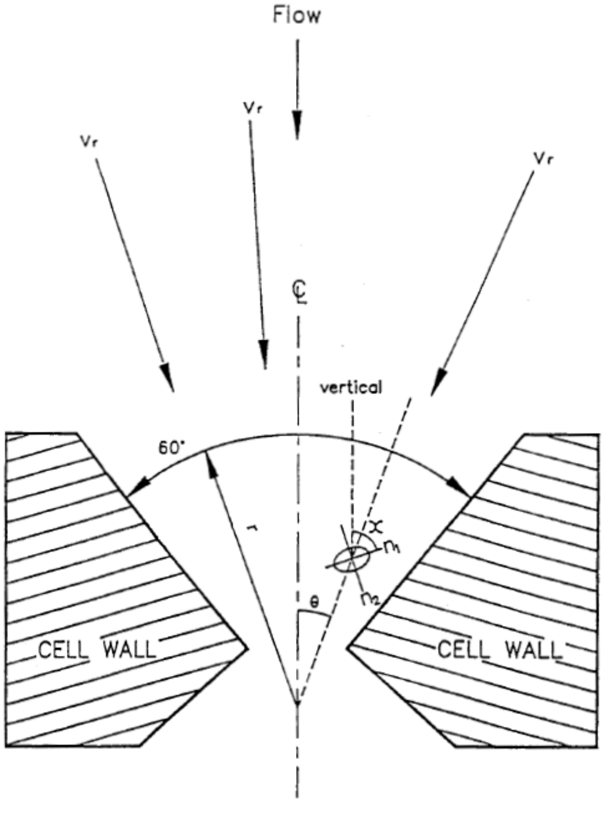

FIGURE 1. GEOMETRY OF THE TWO-DIMENSIONAL JEFFREY-HAMEL TYPE CONVERGING WEDGE FLOW CELL

Along the centerline where the flow is purely extensional, the component of velocity vector is

$$V_r = f(r) \tag{5}$$

The rate of strain tensor ($\underline{\underline{\dot{\gamma}}}$) along the centerline have the following components:

$$\underline{\underline{\dot{\gamma}}} = \begin{bmatrix} 2\partial V_r/\partial r & 0 & 0 \\ 0 & 2V_r/r & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{6}$$

Since there is no flow of the fluid in the direction of propagation of light (z-direction), the stress tensor ($\underline{\underline{\tau}}$) along the centerline have the following components:

$$\underline{\underline{\tau}} = \begin{bmatrix} \tau_{rr} & 0 & 0 \\ 0 & \tau_{\theta\theta} & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{7}$$

1.2 Equation of Continuity

The equation of continuity in cylindrical coordinate system for steady-state flow of an incompressible fluid in a converging two-dimensional flow channel (where $\partial V_\theta/r\partial\theta$ is negligible) is given by

$$\partial(rV_r)/\partial r = 0 \qquad \text{or} \qquad rV_r = \text{constant} \tag{8}$$

1.3 Linear Stress-Optical Law Equations

For two-dimensional converging wedge flows, Adams et al. [10] gave the following forms of the linear stress-optical law:

$$\tau_{r\theta} = [\Delta N (\sin 2\chi \cos 2\theta - \cos 2\chi \sin 2\theta)/2C] = [\Delta N \sin (2\chi - 2\theta)]/2C \tag{9}$$

$$\begin{aligned} \tau_{rr} - \tau_{\theta\theta} &= [\Delta N (\cos 2\chi \cos 2\theta + \sin 2\chi \sin 2\theta)/C] \\ &= [\Delta N \cos (2\chi - 2\theta)]/C \end{aligned} \tag{10}$$

Where χ is the angle between the principal molecular orientation axis and the cell centerline, and θ is the angular coordinate of the intersection of the two split monochromatic light beams at the point of measurement (Figure 1).

Here ΔN is the birefringence of the material and given by the equation

$$\Delta N = R\,\lambda/d \tag{11}$$

where d is the thickness of the birefringent material, λ is the wavelength of the monochromatic light used, and R is the relative retardation of the two plane-polarized components of the monochromatic light emerging from the birefringent material.

Along the centerline of the converging wedge cell where the flow is purely extensional, both χ and θ are zero. Therefore, the linear stress optical relation in the reduces to

$$\tau_{rr} - \tau_{\theta\theta} = \Delta N/C \tag{12}$$

1.4 Goddard-Miller Model

The Goddard-Miller model [14] is a quasilinear corotational constitutive equation obtained by using only the first term in the Goddard memory-integral expansion [15]. This model, which can also be obtained as a result of applying the Boltzmann Superposition principle to a viscoelastic model in a cororating frame of reference, has been used successfully to describe the rheologolical behavior of PDMS [16-17]. In an integral form, the Goddard-Miller model is written as

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t} G(t-t')\underline{\underline{\dot{\Gamma}}}'dt' \tag{13}$$

where G(t – t')is the relaxation modulus and $\underline{\underline{\dot{\Gamma}}}'$ is the corotating rate-of-deformation tensor.

The corotating rate-of-deformation tensor ($\overset{\bullet}{\underline{\underline{\Gamma}}}{}'$) is represented by the Taylor series expansion about t' as

$$\overset{\bullet}{\underline{\underline{\Gamma}}}{}' = \underline{\underline{\gamma}}(t) - [(t - t')\, D\underline{\underline{\gamma}}(t)/Dt] + ½\, [(t - t')^2\, D^2\underline{\underline{\gamma}}(t)/Dt^2] - \tag{14}$$

where D/Dt is the corotational time derivative or Jaumann derivative.

The Jaumann derivative tells how the components of a tensor change with time as seen by an observer moving with the fluid and rotating with it. For a second-order tensor, the Jaumann derivative is defined as

$$D(\,)/Dt = \partial(\,)/\partial t + V.\nabla(\,) + [\,\underline{\underline{\omega}}.(\,) - (\,).\underline{\underline{\omega}}\,] \tag{15}$$

where $\underline{\underline{\omega}}$ is the vorticity tensor which corrects for the rotary motion of the fluid.

The rate-of-deformation tensor ($\overset{\bullet}{\underline{\underline{\gamma}}}$) and vorticity tensor ($\underline{\underline{\omega}}$) are given by

$$\overset{\bullet}{\underline{\underline{\gamma}}} = \nabla V + (\nabla V)^t \tag{16}$$

$$\underline{\underline{\omega}} = \nabla V - (\nabla V)^t \tag{17}$$

Along the centerline of the converging wedge cell, the flow is purely planar extensional and hence, the vorticity tensor ($\underline{\underline{\omega}}$) is zero.

For this study, a single Maxwell-type relaxation modulus is used and given by the equation

$$G(t - t') = (\eta_o/\lambda_o)\, e^{-(t - t')/\lambda_o} \tag{18}$$

where η_0 is a characteristic viscosity like zero-shear viscosity and λ_0 is a characteristic time constant.

Substituting the rate-of-strain tensor and using only the first two terms of the Taylor series expansion for the corotating rate-of-deformation tensor ($\overset{\bullet}{\underline{\underline{\Gamma}}}{}'$) yields the following terms for the stress tensor of the Goddard-Miller model for purely extensional flow along the centerline of the two-dimensional converging wedge cell:

$$\tau_{rr} = -\,2\,\eta_o\,\{(\partial V_r/\partial r) - \lambda_o\,[V_r\,(\partial^2 V_r/\partial r^2)]\} \tag{19}$$

$$\tau_{\theta\theta} = -\,2\,\eta_o\,\{(V_r/r) - \lambda_o\,[(V_r/r)\,(\partial V_r/\partial r - V_r/r)]\} \tag{20}$$

Therefore, the first normal stress difference ($\tau_{rr} - \tau_{\theta\theta}$) according to the truncated Goddard-Miller model is given by

$$\tau_{rr} - \tau_{\theta\theta} = -\,2\,\eta_o\,\{[(\partial V_r/\partial r) - (V_r/r)] - \lambda_o\,V_r\,[(\partial^2 V_r/\partial r^2) - (1/r)(\partial V_r/\partial r) + V_r/r^2]\} \tag{21}$$

II. EXPERIMENTAL

2.1 Flow Cell Geometry

The schematic of the 60° converging wedge flow cell used for this study is shown in Figure 1. The width of the flow cell is 5.00 cm and it is capable of withstanding a pressure of 1000 kPa. Two such cells were used for the study, one for velocity measurements and another for flow birefringence measurements with modified windows in order to minimize the contribution to the measured birefringence.

2.2 Polydimethylsiloxane (PDMS) Fluid Properties

Linear PDMS fluids and melts are ideally suited for flow birefringence studies because of their thermal, physical and chemical stability. They have relatively low surface tension (19-21 x 10^{-3} Nm^{-1}), thus minimizing the problem of formulation and entrainment of bubbles that poses a tremendous practical difficulty in optical measurements. PDMS exits in the liquid or molten state at room temperature, thus eliminating the need to maintain high temperatures that often hinders optical measurements. PDMS fluids are highly transparent and the polymer chain monomer unit has relatively small refractive index anisotropy. The experimental polymer used for this study was a linear amorphous Dow Corning Type 200 polydimethylsiloxane fluid. The polymer was analyzed using a conventional gel permeation chromatograph (GPC) at 30^{o}C with toluene as the solvent, and the following properties were obtained:

Number-Average Molecular Weight (M_n) = 6.79 X 10^4

Weight-Average Molecular Weight (M_w) = 2.327 X 10^5

z-Average Molecular Weight (M_Z) = 3.459 X 10^5

Polydispersity Ratios: $M_w/M_n = 3.43$

$M_z/M_n = 4.95$

The steady-state rheometric characterization of PDMS in simple shear was performed using a Weissenberg Rheogoniometer, and the results shown in Figure 2. The zero-shear viscosity was found to be 300 Pa.s.

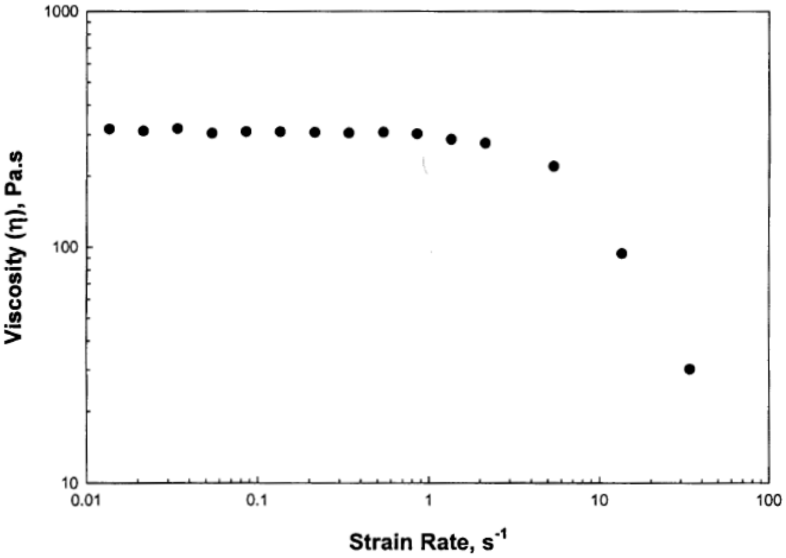

FIGURE 2. STEADY-STATE SIMPLE SHEAR VISCOSITY OF PDMS AS A FUNCTION OF SHEAR RATE USING A WEISSENBERG RHEOGONIOMETER.

2.3 Laser Doppler Anemometry (LDA)

The local velocities along the centerline of the unmodified converging wedge flow cell were measured using a monochromatic laser Doppler anemometry (LDA) in differential Doppler or fringe mode with forward scattering. A monochromatic helium-neon laser beam (wavelength = 0.6328μ, diameter = 600μ) is split into two separate beams and then converges in a small reference volume in the flowing polymer located at the mid-point between the two windows of converging cell. As a result, a diffraction pattern is set up and the motion of the polymer macromolecules moving through this reference volume scatters light. This scattered light produces a Doppler frequency proportional to the velocity of the polymer.

2.4 Orientation Angle and Flow Birefringence

The local flow birefringence of the modified converging wedge flow cell was measured by adding a quartz compensator to the set off cross-polarizers (a half-wave plate and an analyzer). The cross-polarizers were used to measure the orientation angle, which is the angle between the principal molecular orientation axis and the cell centerline. The linearly vertical polarized beam from the monochromatic He-Ne laser traverses the along the width of the flow cell and the transmitted beam is then analyzed to obtain the net molecular orientation. For planar extensional flow along the centerline of the cell, the orientation angle should be zero because the principal molecular orientation axis and the cell centerline coincide. The quartz compensator, placed between the converging flow cell and the analyzer, produces an exact canceling retardation by compensating the phase difference of the polarized monochromatic light introduced by the polymer flowing through the cell.

III. RESULTS AND DISCUSSION

3.1 Linearity of the Stress-Optical Law

When a macromolecular polymer fluid is stretched, there is a decrease in entropy associated with the orientation of the network chains. Stresses and orientation are also caused by the phenomena of macromolecular chain stretching. So it does not come as a surprise that, as a first approximation, a simple proportionality exits between the stress (entropic) and birefringence (orientation). In the limits of small macroscopic deformation, the root mean square (RMS) of the end-to-end distance of a Gaussian chain is rather small compared to the length of the stretched chain. As the strain/stress increases, both orientation and birefringence of the macromolecular chain increases till it approaches a saturation point. In fact, entropy change accompanying a complete alignment of chain segments must be - ∞. From this qualitative discussion one can hypothesize that the ratio of measured birefringence to the corresponding stress difference should deviate in a downward direction from the value of the constant stress-optical coefficient (C). This has been found in polymer melts subjected to very high tensile stresses [18]. However, in an overwhelming majority of experiments [8,11] that are relevant to practical situations in polymer processing, stresses appear to be too small for deviation from the linear stress-optical law.

For the stress-optical law to be linear there are two limits to its validity; (a) an upper limit for the stress and (b) a time scale of the deformation process must be large enough to allow for establishment of internal thermodynamic equilibrium.

The assumption has always been made that the time scales for the establishment of internal equilibrium are due to rapid vibrational modes between backbone molecules. These are very short compared to the macroscopically observable time scales of the bulk motion. As a consequence, the latter time scale must be solely due to the relatively low rates of change of the locations of the entanglements. For this study, we assumed that the internal thermodynamic equilibrium was established very quickly.

The upper bound in the stress can be determined from measurements in pure extensional flow because, generally, stresses in extension are many times higher than stresses in shear. For this study, the flow birefringence measurements were made between any two radial positions along the centerline and related to the first normal stress difference (FNSD) by the following equation:

$$(\tau_{rr} - \tau_{\theta\theta})_{r=r1} - (\tau_{rr} - \tau_{\theta\theta})_{r=r2} = [(\Delta N)_{r=r1} - (\Delta N)_{r=r2}]/C \tag{22}$$

Therefore, a plot of the difference in normal stresses versus the difference in flow birefringence between the two radial positions along the centerline should yield a straight line in the linear stress-optical region. Figure 3 shows such a plot between r = 1.1 cm and r = 2.1 cm, and it indicates a linear nature of the stress-optical law for PDMS up to a pressure drop of 689 kPa (100 psi) across the converging flow cell. Although this is a necessary condition to confirm the linearity of the stress-optical law, it is not a sufficient condition. The slight zero-offset evident in Figure 3 is probably caused by an optical window effect, and it is extremely difficult to eliminate for PDMS because of the very low intrinsic anisotropy of the fluid.

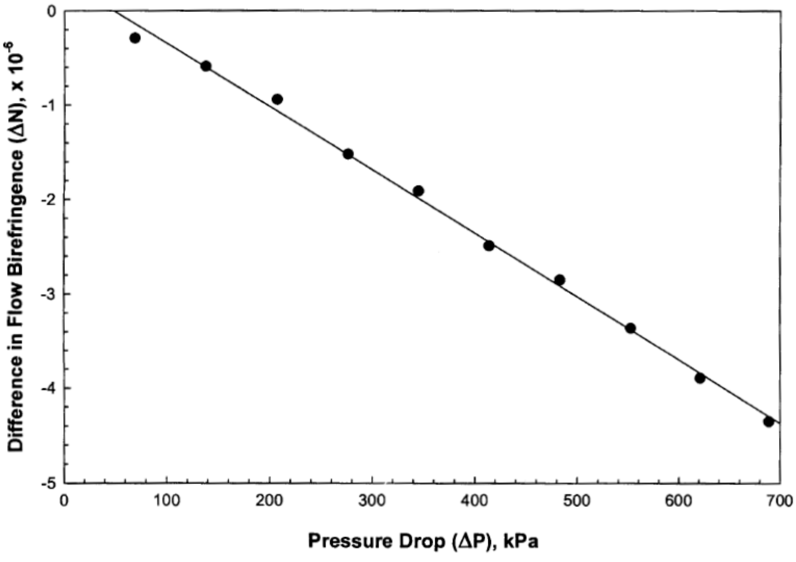

FIGURE 3. DIFFERENCE IN CENTERLINE BIREFRINGENCE (BETWEEN r = 1.1 cm AND r = 2.1 cm) AS A FUNCTION OF PRESSURE DROP ACROSS THE FLOW CELL.

In order to confirm the sufficient condition for the linearity of stress-optical law for PDMS up to a pressure drop of 689 kPa, the equation of momentum along the centerline of the converging flow cell has to be examined. The r-directed momentum balance equation along the centerline is given by

$$\rho\, rV_r\, \partial V_r/\partial r = (\tau_{rr} - \tau_{\theta\theta}) - r\,[\partial(p + \tau_{rr})/\partial r] \tag{23}$$

Using the mean value theorem, we can write the above equation for any radial position (r) as

$$R\, r\, V_r \Delta V_r/\Delta r = \left(\overline{\tau_{rr} - \tau_{\theta\theta}}\right) - (r\,[\Delta\pi/\Delta\rho]) \tag{24}$$

where $\pi = \pi + \tau_{\rho\rho}$.

For the stress-optical law to be linear, the average value of normal stress difference from the entrance to the exit of the flow cell $\left(\overline{\tau_{rr} - \tau_{\theta\theta}}\right)$ must retain a constant proportionality with the overall pressure drop across the flow cell. Therefore,

$$\frac{\int_{r_{in}}^{r_{out}} \Delta N dr}{\left[r_{out} - r_{in}\right]} = \overline{\Delta N} = \left(\overline{\tau_{rr} - \tau_{\theta\theta}}\right) \tag{25}$$

Thus using the measured birefringence (ΔN) versus r data along the centerline from entrance to exit at different pressure drops, the average birefringence (ΔN) can be evaluated. This was done by extrapolating the centerline flow birefringence (ΔN) data measured between r = 1.1 to 2.1 cm to the entrance and the exit using equation 25 as shown in Figure 4. A straight line plot of ΔN vs ΔP was obtained along the centerline, clearly indicating that the linear stress-optical law is valid up to a pressure drop of 689 kPa across the flow cell.

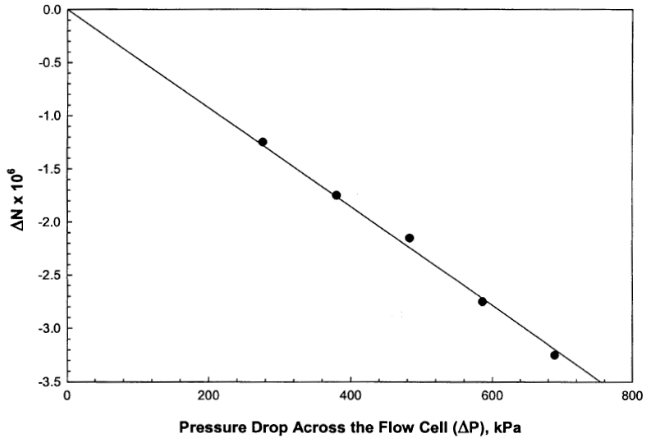

FIGURE 4. AVERAGE CENTERLINE BIREFRINGENCE AS A FUNCTION OF PRESSURE DROPS ACROSS THE FLOW CELL.

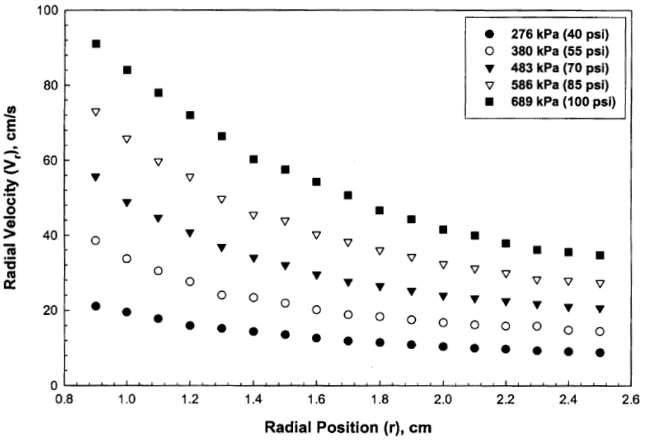

FIGURE 5. CENTERLINE RADIAL VELOCITY AS A FUNCTION OF RADIAL POSITION FOR VARIOUS PRESSURE DROPS ACROSS THE FLOW CELL.

3.2 Velocity and Extensional Rates

The local velocities (V_r) as a function of radial position (r = 0.9 to 2.5 cm) along the centerline of the unmodified converging flow cell for different pressure drops were obtained using LDA and shown in Figure 5. The planar extensional rates ($\partial V_r/\partial r$) were obtained by differentiating the local velocity data. It can be seen that as the radial position increases, both local velocity and the extensional rate decrease.

3.3 Equation of Continuity

As mentioned earlier, the equation of continuity for steady-state flow of PDMS in the converging two-dimensional flow channel (where $\partial V_\theta/r\partial\theta$ is negligible) is given by rV_r = constant. Figure 6 shows a plot of the equation of continuity (rV_r) as a function of the centerline radial position (r) for different pressure drops across the flow cell. It can be seen that the value of rV_r is nearly constant and it is proportional to the pressure drop, thereby indicating the two-dimensional nature of the flow through the converging wedge cell.

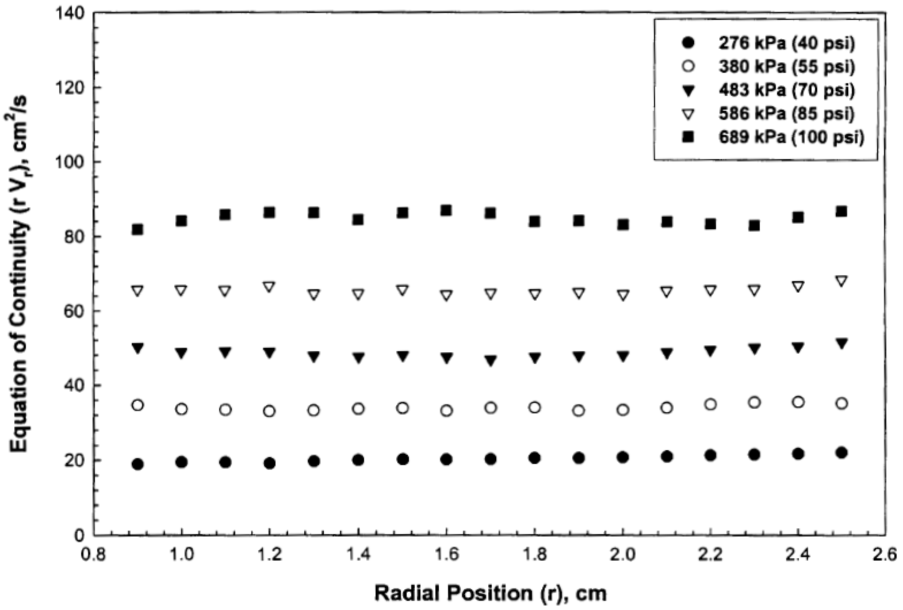

FIGURE 6. EQUATION OF CONTINUITY AS A FUNCTION OF THE CENTERLINE RADIAL POSITION FOR VARIOUS PRESSURE DROPS ACROSS THE FLOW CELL.

3.4 First Normal Stress Difference (FNSD)

The first normal stress difference ($\tau_{rr} - \tau_{\theta\theta}$) can be computed from the truncated Goddard-Miller model using equation 21given by

$$\tau_{rr} - \tau_{\theta\theta} = - 2\, \eta_o \{[(\partial V_r/\partial r) - (V_r/r)] - \lambda_o V_r [(\partial^2 V_r/\partial r^2) - (1/r)(\partial V_r/\partial r) + V_r/r^2]\} \quad (27)$$

Thus, we require the local velocity (V_r), extension rate ($\partial V_r/\partial r$) and its derivative ($\partial^2 V_r/\partial r^2$), zero-shear viscosity (η_0) and characteristic time constant (λ_0) in order to evaluate the first normal stress difference ($\tau_{rr} - \tau_{\theta\theta}$) at different radial position along the centerline of the converging flow cell for various pressure drops.

The single Maxwell-type time constant (λ_0) was obtained from the Rouse model [19] for polymer melts. According to the Rouse model for a polymer melt with large number of molecules in the spring-bead molecular structure, the relaxation time (λ_0) is given by

$$\lambda_0 = (6/\pi^2)\, [(\eta_0\, M)/(\rho\, R\, T)] \quad (28)$$

where M is the molecular weight, ρ is the density, R is the Universal gas constant, and T is the temperature. For the PDMS used in this study at room temperature (T = 25 °C), the relation time using equation 27 gives

$$\lambda_0 = (6/\pi^2)\, [(\eta_0 M)/(\rho P T)] = (6/\pi^2)\, [(300 \text{ x } 232.7)/(987 \text{ x } 82.057 \text{ x } 10^{-6} \text{ x } 1.01325 \text{ x } 10^5 \text{ x } 298)] = 0.0174 \text{ s}$$

The first normal stress difference in planar extensional flow along the cell centerline for this study was computed using λ_0= 0.0174s and η_0 = 300 Pa.s, and listed in Table 1.

TABLE 1
FIRST NORMAL STRESS DIFFERENCE ($\tau_{rr} - \tau_{\theta\theta}$) COMPUTED USING THE TWO-TERM GODDARD-MILLER MODEL ALONG THE CENTERLINE OF THE JEFFREY-HAMEL TYPE CONVERGING WEDGE FLOW CELL

Pressure	r = 2.1 cm	r = 1.9 cm	r = 1.7 cm	r = 1.5 cm	r = 1.3 cm	r = 1.1 cm
Drop (ΔP) in kPa	($\tau_{rr} - \tau_{\theta\theta}$) in kPa	($\tau_{rr} - \tau_{\theta\theta}$) in kPa	($\tau_{rr} - \tau_{\theta\theta}$) in kPa	($\tau_{rr} - \tau_{\theta\theta}$) in kPa	($\tau_{rr} - \tau_{\theta\theta}$) in kPa	($\tau_{rr} - \tau_{\theta\theta}$) in kPa
276	- 6.35	- 6.53	- 8.66	- 10.63	- 13.29	- 14.94
380		- 10.05	- 11.76		- 17.25	- 21.09
483	- 12.36	- 13.06	- 14.76	- 20.29	- 21.64	- 28.10
586		- 27.96	- 32. 11		- 38.02	- 42.13
689	- 18.42	- 26.17	- 31.10	- 35.28	- 45.56	- 53.50

3.5 Linear Stress-Optical Coefficient

The room-temperature linear stress-optical coefficient (C) for PDMS in planar extensional flow at various pressure drops (flow rates) can be obtained from equation 12 using the measured birefringence along the cell centerline and the first normal stress difference (FNSD) calculated from the two-term Goddard-Miller model (equation 27) with a single Maxwell-type relaxation time constant of 0.0174 s and a zero-shear viscosity of 300 Pa.s. Thus, a plot of ΔN vs $(\tau_{rr} - \tau_{\theta\theta})$ should give a straight line passing through the origin with the slope equal to the linear stress-optical coefficient (C). Figure 7 shows such a plot for pressure drops of 276, 380, 483, 586, and 689 kPa across the converging wedge flow cell. A linear stress-optical coefficient of 1.41 x 10^{-10} Pa^{-1} was obtained for PDMS at room temperature. This compares well with values of 1.35 x 10^{-10} Pa^{-1} by Wales [11], 0.909 x 10^{-10} Pa^{-1} by Liberman et al. [12], 1.56-1.84 x 10^{-10} Pa^{-1} by Galante and Frattini [13]for a low and a high molecular weight PDMS, and 1.44 x 10^{-10} Pa^{-1} by Subramanian et al. [20].The positive sign of the stress-optical coefficient confirms that the polarizability of the backbone of PDMS chain is indeed highest in the chain direction.

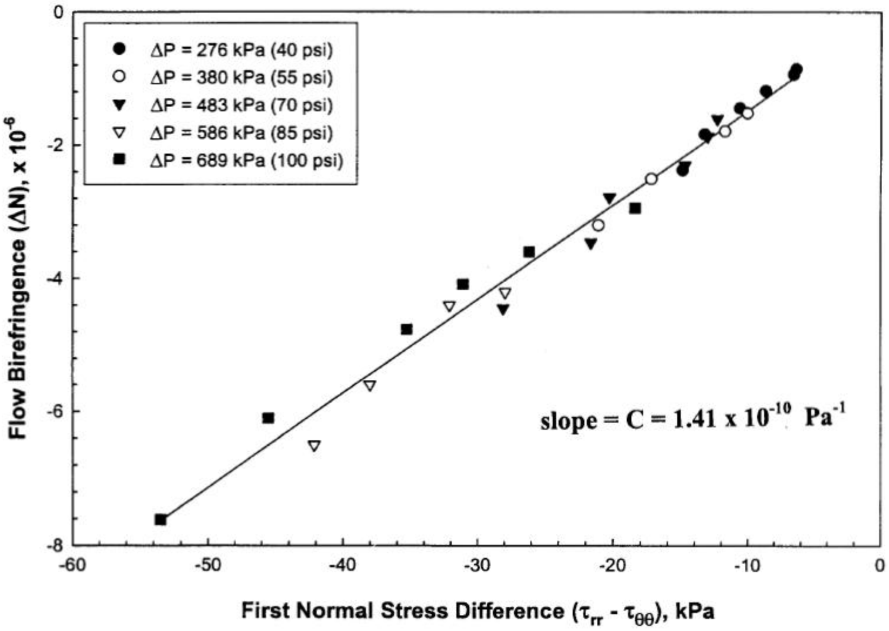

FIGURE 7. MEASURED FLOW BIREFRINGENCE VS. COMPUTED FIRST NORMAL STRESS DIFFERENCE (USING THE TWO-TERM GODDARD-MILLER MODEL) IN PLANAR EXTENSIONAL FLOW ALONG THE CELL CENTERLINE FOR VARIOUS PRESSURE DROPS ACROSS THE FLOW CELL.

IV. CONCLUSION

We have shown that the linear stress-optical coefficients of an amorphous polymer melt or fluid can be estimated from flow-induced birefringence and laser Doppler anemometry measurements. Unlike many previous studies that measured stresses mechanically, the stresses can be evaluated by choosing an appropriate constitutive equation that best describes the rheological behavior of the polymer. The strain-rates can be computed from local velocity measurements using laser Doppler anemometry. The linear relation between the stress and polarizability tensors, which generally valid over a range of strain rates that extended well into the non-Newtonian region, can then be used to obtain the stress-optical coefficient.

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