Rheol Acta 35:297–302 (1996)

ORIGINAL CONTRIBUTION

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Stress tensor measurement using birefringence in oblique transmission

Received: 24 October 1995
Accepted: 18 April 1996

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Abstract A method for measuring the stress tensor of liquids obeying the stress-optical rule is presented. In particular, the procedure makes it possible to determine the shear stress, and the first and second normal stress differences for rheometric flows. This technique is an extension of the procedure recently described by Burghardt and coworkers (Brown et al., 1995) wherein light is sent obliquely through a sample sheared between transparent plates. However, in the present development, the light is transmitted in the plane containing the velocity gradient and neutral directions, thereby reducing the necessary optical measurements by one. A polystyrene-tricresyl phosphate (TCP) solution is used as the test sample. The first and second normal stress differences in steady shear flow measured by this method show good agreement with the mechanical results measured by Madga et al. (1993) using a modified cone and plate rheometer. The transient behavior of the first and second normal stress differences following the start-up of shear flow is also presented.

Key words Birefringence – stress tensor – rotational rheometer – first normal stress difference – second normal stress difference

Introduction

Optical measurement of the stress tensor using the stress-optical rule offers several advantages. These include the possibility of spatially resolved measurements (Rajagopalan et al., 1992; Galante and Frattini, 1993), fast response times (Zebrowski, 1985), and accurate normal stress difference determinations (Brown et al., 1995). The latter capability is particularly valuable since measurements of the second normal stress difference, N_2, can be obtained. The conventional, mechanical methods used to obtain the material function can be difficult to perform.

The majority of data reported for N_2 rely on the measurement of a pressure distribution in a modified cone and plate rheometer (Magda et al., 1993). However, these mechanical techniques have the disadvantage of only being applicable to steady state flows. Alternatively, the use of birefringence measurements can accommodate time-dependent flows, such as oscillatory shear (Kornfield et al., 1991) and step strains (Brown et al., 1995).

In this paper, we present a method for measuring the complete stress tensor using light transmitted through the sample at an oblique angle. This is an extension of the strategy employed by Burghardt and coworkers (Brown et al., 1995), but reduces the number of required optical measurements from three to two. Data are offered on a semi-dilute solution of polystyrene in tricresyl phosphate (TCP), which compare favorably to data acquired by mechanical means by Magda and coworkers (1993). Both steady state and transient shear flow data are reported.

Stress-optical rule

The optical measurement of stress relies on the validity of the "stress-optical rule". This relationship states that the deviatoric parts of the stress and refractive index tensors are simply proportional to one another. In other words,

$$n_{ij} = C\sigma_{ij} \ , \tag{1}$$

where C is the stress-optic coefficient and is found to be independent of molecular weight, polydispersity, and, in the case of solutions, is independent of polymer concentration over a wide range of compositions. This rule can be written in the following component forms,

$$\sigma_{12} = \frac{1}{2C}\Delta n_{12}\sin 2\chi \ , \tag{2}$$

$$N_1 = \frac{1}{C}\Delta n_{12}\cos 2\chi \ , \tag{3}$$

$$N_2 = \frac{1}{C}\Delta n_{23} = \frac{1}{C}\Delta n_{13} - \frac{1}{C}\Delta n_{12}\cos 2\chi \ , \tag{4}$$

where Δn_{ij} is the birefringence in the (i,j) plane. Here the shear flow is taken as $u_i = \dot{\gamma} x_2 \delta_{i1}$ where $\dot{\gamma}$ is the shear rate. The angle χ measures the orientation of the principal values of the stress and refractive index tensors in the (1, 2) plane (the plane of the flow). It is evident that measurement of the angle χ and the birefringences Δn_{12} and Δn_{13} is sufficient to determine the shear stress, σ_{12}, the first normal stress difference, N_1, and the second normal stress difference, N_2.

In general, birefringence is measured in the plane normal to the propagation direction of the light, since this plane will contain the electric vector. Therefore, using a Couette cell, with light propagating along the 3 axis, the shear stress and first normal stress difference can be determined. Using polarization modulation techniques, this can be accomplished with a single experiment, since it is possible to simultaneously measure Δn_{12} and χ in a Couette cell. In principle, the second normal stress difference could be determined by sending light along the 1 axis, but this is normally impractical. Sending light along the 2 axis in a parallel plate flow cell, on the other hand, allows measurement of the "third normal stress difference", $N_3 = N_1 + N_2 = \frac{1}{C}\Delta n_{13}$. Certainly, the stress tensor can be recovered by combining measurements with light sent along the 3 axis with measurements performed using light sent along the 2 axis. However, for highly birefringent materials, such as polymer melts, it can be difficult to make measurements with light sent along the 3 axis since the optical path length is normally quite large when this geometry is used.

Measurement of optical properties

Optical train

The optical train is shown in Fig. 1 and is described in detail in Fuller (1995). The light source is a He-Ne laser with a wavelength of 632.8 nm. Prior to passage through the sample, the light is modulated in its polarization by passing through a polarizer, a photoelastic modulator, and a quarter wave plate. These elements have respective orientations of 0°, 45°, and 0°. This combination produces linearly polarized light that oscillates in its orientation by a frequency of 50 kHz and at an amplitude prescribed by the photoelastic modulator. The light is then transmitted through the sample, which is held between two quartz disks that form a parallel plate flow cell. After passing through a circular polarizer located after the flow cell, the light intensity is measured using a photodiode. This intensity has the following Fourier expansion

$$I = I_{DC} + I_\omega \sin(\omega t) + I_{2\omega}\cos(2\omega t) + \ldots , \tag{5}$$

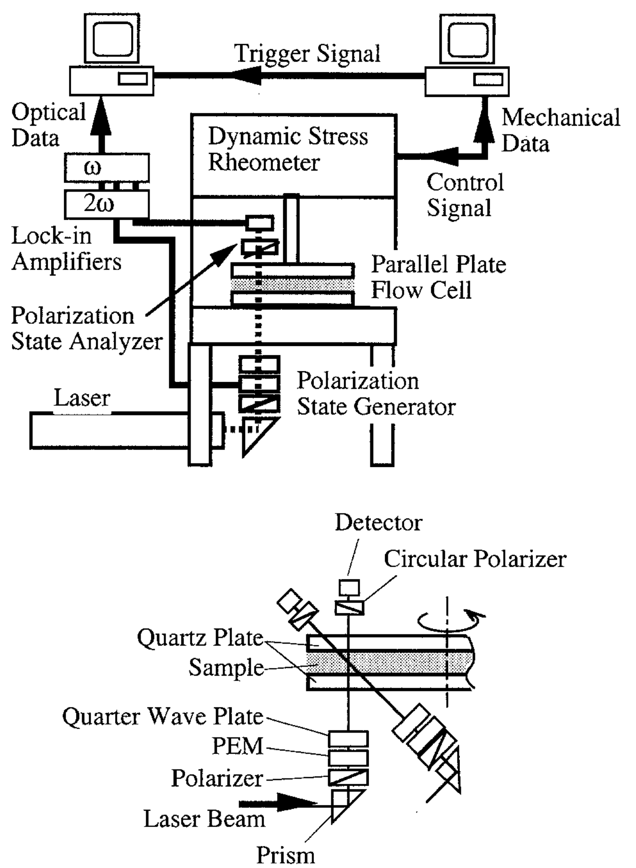

Fig. 1 Schematic diagram of the combined mechanical rheometer and optical train

where I_{DC} is the DC component of the light intensity. The amplitudes of the first and second harmonic, I_ω and $I_{2\omega}$, are measured by two lock-in amplifiers and are

$$I_\omega = I_{DC} R_\omega = -2 I_{DC} J_1 \cos\alpha \sin\delta \ , \tag{6}$$

$$I_{2\omega} = I_{DC} R_{2\omega} = 2 I_{DC} J_2 \sin\alpha \sin\delta \ , \tag{7}$$

for a sample with zero dichroism. The parameters J_1 and J_2 are calibration constants. The angle α defines the orientation of the principal axes of the refractive index tensor in the plane orthogonal to the axis of light propagation and, in general, will be different from χ. Likewise, the retardation, $\delta = 2\pi \Delta n d/\lambda$, is related to the birefringence, Δn, in that same plane. Here d is the optical path length and λ is the wavelength. The unknown δ and α are calculated directly from knowledge of the measured ratio functions R_ω and $R_{2\omega}$ defined in Eqs. (6) and (7).

Oblique angle measurement

The birefringences, Δn_{12} and Δn_{32}, in the (1, 2) and (3, 2) planes are required to calculate N_1 and N_2 using Eqs. (2) to (4). In the present development, a parallel plate flow cell is used with the light transmitted at an oblique angle and contained within the (2, 3) plane as shown in Fig. 2. The propagation axis is oriented at an angle θ relative to the 3 axis. Two separate experiments are then conducted: one where $0 < \theta < \pi/2$, and one where $\theta = \pi/2$. Using an analysis procedure discussed in Fuller (1995), the desired birefringences and orientation angle are calculated as

$$\Delta n_{12} = -\frac{\Delta n \cos 2\alpha}{\cos\theta \sin 2\chi} \ , \tag{8}$$

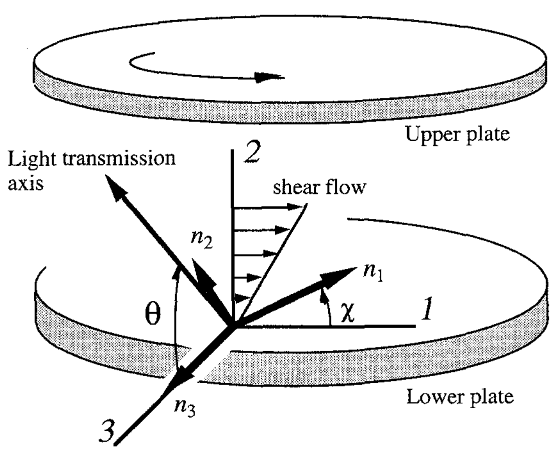

Fig. 2 Coordinate system of the parallel plate flow cell

$$\Delta n_{32} = \Delta n_{12} \cos^2\chi - \Delta n_{\pi/2} \ , \tag{9}$$

$$\tan 2\chi = \frac{\Delta n \cos 2\alpha \cos\theta}{\Delta n \sin 2\alpha - \Delta n_{\pi/2} \sin^2\theta} \ , \tag{10}$$

where $\Delta n_{\pi/2}$ denotes the birefringence measured by setting $\theta = \pi/2$. Once these values are available, the shear and normal stress differences can be calculated. If the sample has the property that $N_2 \approx 0$, the above equations reduce to

$$\Delta n_{12} = \frac{\Delta n}{1 - \cos^2\theta \sin^2\chi} \ , \tag{11}$$

$$\tan\chi = \frac{1 + \tan\alpha}{(1 - \tan\alpha)\cos\theta} \ , \tag{12}$$

and only a single measurement at a single value of θ is required.

The method of performing oblique angle measurements of birefringence in the (2, 3) plane can be contrasted against the procedure followed by Burghardt and coworkers (Brown et al., 1995). In their method, the propagation axis of the light is contained within the (1, 3) plane. When this occurs, the angle α is always either 0° or 90° by symmetry and insufficient information is acquired to determine the components of the refractive index tensor in just two measurements and a total of three must be made.

Experimental apparatus and materials

Experimental arrangement

Figure 1 shows a schematic diagram of the experimental apparatus. A dynamic stress-controlled rheometer (Rheometrics DSR) was used as the platform supporting the flow cell and allowed for the simultaneous measurement of optical and mechanical responses. The incident optics were located below the parallel flow cell of the rheometer and the receiving optics and detector were mounted above. The optical train was mounted onto a rotatable frame that allowed the propagation axis of the laser beam to pivot about an axis of rotation that was parallel to the center plane of the sample contained within the parallel plate flow cell. The plate diameter was 38.1 mm and the upper plate rotated to induce shear. All measurements were made with an oblique angle of $\theta = 48°$ measured in air. The transmission point of the light was chosen to be as close to the outer edge of the top plate as possible to minimize the variation of the shear rate along the light beam passing through the sample.

To compare optical measurements of Δn_{12} and χ measured using oblique light transmission with measurements using the more conventional Couette flow cell geometry, a Rheometrics Optical Analyzer (ROA) was used.

Materials

The sample was a 6 wt% solution of polystyrene in tricresyl phosphate. The molecular weight was 2 million and the distribution was characterized by $M_w/M_N = 1.1$. The experiments were carried out at room temperature, 20 °C.

Results and discussion

Steady shear flow

In Figs. 3 and 4 we compare measurements of Δn_{12} and χ measured using the parallel flow cell and oblique light transmission with measurements obtained using a Couette cell with light propagating along the vorticity axis (the 3 axis). As seen in these figures, the oblique axis transmission technique is capable of reproducing both optical properties over the shear rate range investigated. In Figs. 5 and 6, the normal stress differences N_1 and N_2 measured using oblique angle transmission are compared against mechanical data obtained by Magda and coworkers using a modified cone-and-plate rheometer. Also shown in Fig. 5 are the results of calculating N_1 from a single oblique angle measurement by assuming $N_2 = 0$, and these results are surprisingly accurate.

The comparison of N_2 measurements in Fig. 6, and in Fig. 7 where the ratio N_2/N_1 is plotted, show that the oblique angle technique with two measurements is capable of an acceptable degree of accuracy. Our results

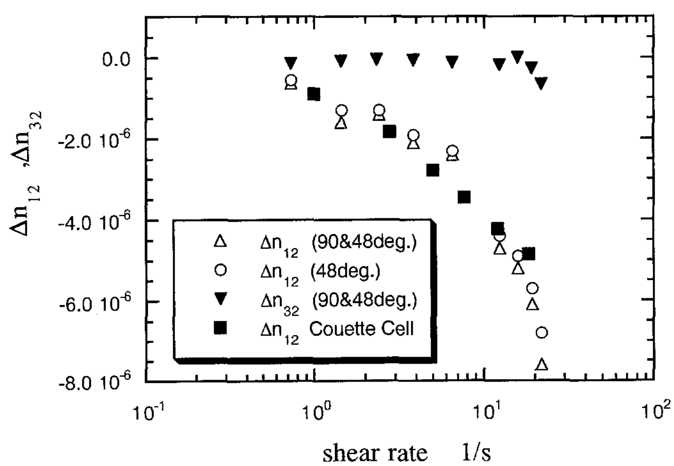

Fig. 3 Steady state birefringence as a function of shear rate: comparison of oblique angle transmission in parallel plate flow and Couette flow measurements with light transmitted along the vorticity axis

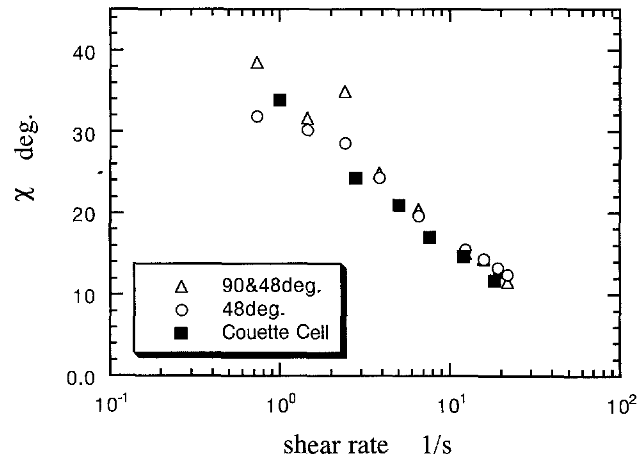

Fig. 4 Steady state orientation angle as a function of shear rate: comparison of oblique angle transmission in parallel plate flow and Couette flow measurements with light transmitted along the vorticity axis

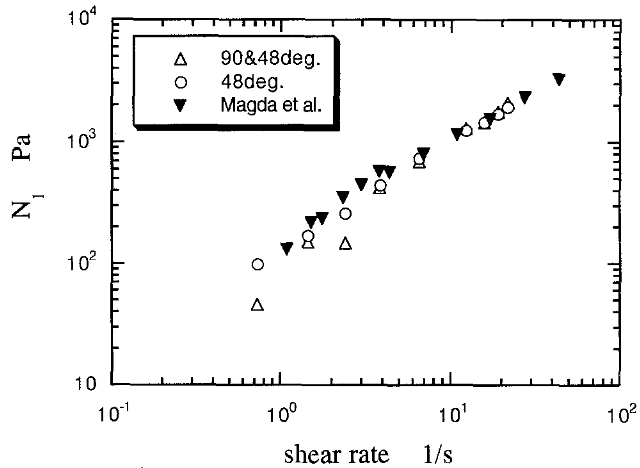

Fig. 5 First normal stress difference as a function of shear rate. Open triangles: data taken using oblique angle transmission with $\theta = 48°$ and $\theta = 90°$. Open circles: data taken using oblique angle transmission with $\theta = 48°$ and assuming $N_2 = 0$. Filled triangles: mechanical measurements taken by Magda and coworkers

are slightly larger than those found by Magda and coworkers, but the difference is acceptable given the basic difficulties in acquiring accurate measurements of N_2.

Transient shear flow

The mechanical methods of measuring the second normal stress difference can only be used for steady state flow. Optical measurements, on the other hand, have the capability to capture transient responses of the material property. Recently, Burghardt and coworkers (Brown et al., 1995) have used the three oblique transmission measurement technique and a sliding plate shear cell to obtain

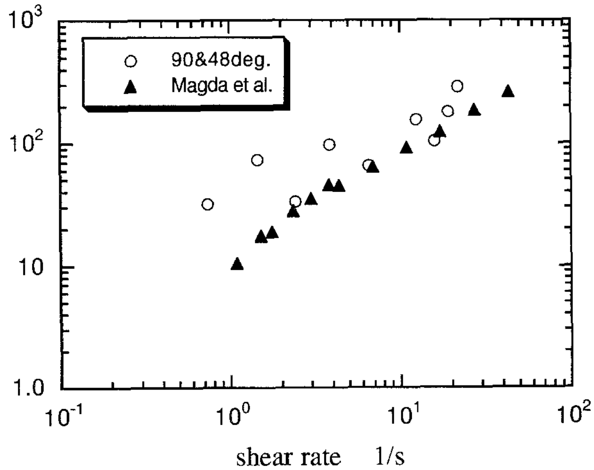

Fig. 6 Second normal stress difference as a function of shear rate. Open circles: data taken using oblique angle transmission with $\theta = 48°$ and $\theta = 90°$. Filled triangles: mechanical measurements taken by Magda and coworkers

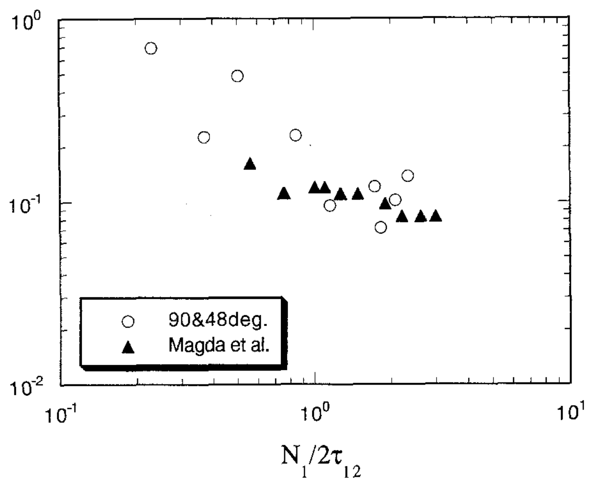

Fig. 7 The ratio $-N_2/N_1$ as a function of the ratio $N_1/2\tau_{12}$. Open circles: data taken using oblique angle transmission with $\theta = 48°$ and $\theta = 90°$. Filled triangles: mechanical measurements taken by Magda and coworkers

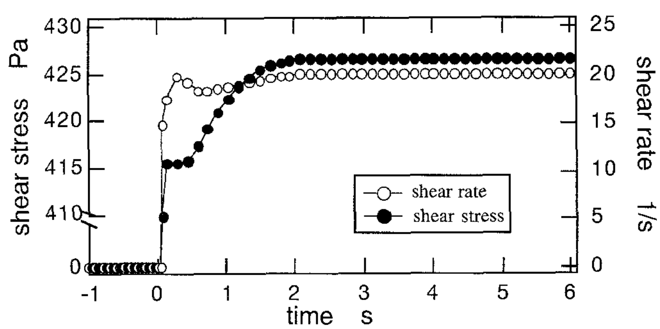

Fig. 8 Shear stress (filled circles) and shear rate (open circles) as functions of time following the start up of flow

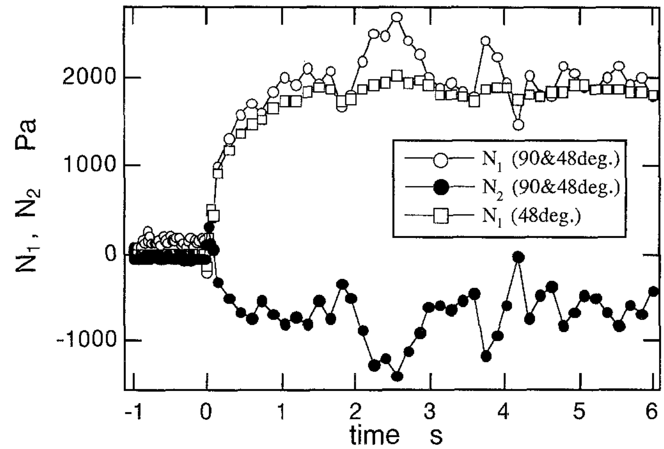

Fig. 9 Normal stress differences as a function of time following the start up of flow. Open circles: first normal stress determined using oblique angle transmission with $\theta = 48°$ and $\theta = 90°$. Open squares: first normal stress determined using oblique angle transmission with $\theta = 48°$ and assuming $N_2 = 0$. Filled circles: second normal stress determined using oblique angle transmission with $\theta = 48°$ and $\theta = 90°$

the response of concentrated polymer solutions to step strains. In the present development, the use of a rotating parallel plate device (which is not possible when the strategy used by Burghardt and coworkers is used) allows the inception of shear flow to be studied. In Figs. 8 and 9, $N_1(t)$ and $N_2(t)$ are plotted following the application of a shear stress of 425 Pa at time zero. At this level of stress, the evolution of both normal stress differences is found to be monotonic in time. Noise is apparent in the data and its source is most likely the fact that two separate experimental runs were necessary to acquire the necessary information at $\theta = 90°$ and $\theta = 48°$ since only one optical train was available. Ideally, it would be preferable to have two optical trains at two separate values of θ to minimize the introduction of random error in the measurement associated with the necessity of carrying out two separate experimental runs that are assumed to be dynamically identical. Noise of a similar magnitude is also evident in the data reported by Brown et al. (1995) using the triple oblique angle method.

Conclusions

The method of birefringence measurements using oblique angle transmission in the (2, 3) plane was demonstrated to lead to acquisition of the full stress tensor with only two separate optical measurements. Comparison against data obtained using a more conventional geometry with a Couette cell and mechanical measurements of the normal stress differences led to the conclusion that this procedure is capable of accurately determining the shear

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stress and both the first and normal stress difference. Since this method can be applied to rotational flow cells such as parallel plates and cone and plates, highly birefringent materials such as melts and liquid crystals could be conveniently examined. In addition, transient flow measurements are easily accommodated.

Acknowledgment The authors thank Prof. J. Magda for making rheological measurements on N_1 and N_2 available for comparison.

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