The multipass rheometer

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Synopsis

This article describes the technical performance and initial results for a new, two-piston, "multipass rheometer." Fluid is contained within a capillary by two servo-hydraulically controlled pistons. Both steady flow and oscillatory data can be obtained from the device with mean pressure as an independent adjustable variable. Steady and oscillatory data are presented for a silicone oil and a viscoelastic solution and certain data are compared with results obtained from a Rheometrics RDS-II mechanical spectrometer or with literature data. The results show that the multipass rheometer is capable of extending the experimental ranges of many conventional rheometers, particularly in terms of pressure control, high shear rates, and multiple, successive flow measurements. ©1995 Society of Rheology.

I. INTRODUCTION

The most widely used rheometers at present are either rotational or piston driven devices. Rotational rheometers, pioneered by the Weissenberg type and extended by companies such as Rheometrics, Bohlin, and Carrimed, offer a wide range of rheological test options [see, for example, Brownsey (1988)]. Most measurements are carried out using a parallel plate or cone and plate geometry and both time-dependent linear viscoelastic data together with nonlinear steady shear measurements can be obtained for well-defined rheometric deformations. The capillary rheometer [see, for example, France (1988)] tends to be used for "single shot" steady flows. One major difference between the two types of rheometers is that the rotational rheometers contain a free surface, whereas in a capillary rheometer the material is fully contained with no free surfaces.

In this article we describe the full technical performance of a new rheometer that can carry out experiments that are usually accessed either by using existing rotational rheometers or by using capillary-type machines. The new "multipass rheometer" allows a wide range of rheometric deformations to be imposed on the fluid and also allows independent mean pressure variation. Measurements on the pressure dependence of viscosity of a Newtonian fluid will be presented and compared with studies from the literature. Low-pressure data for a viscoelastic fluid will be compared with data obtained by ourselves and other workers using existing rheometer types.

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II. THE MULTIPASS RHEOMETER

The principle of the multipass rheometer (MPR) was recently described by Mackley et al. (1994a) but no experimental data were presented in that paper. The device consists of a "test section" that is positioned between two servo-hydraulically driven pistons as shown in Fig. 1. The configuration is not new as Westover (1961) also used a double piston arrangement to measure the pressure dependence of viscosity for polyethylene melts and Kadijk and Van den Brule (1994) recently reported on a two-piston machine which they used to obtain the pressure dependence of the flow curves of a range of polymer melts. An alternative, single-piston device capable of imposing high hydrostatic pressures on the fluid was presented by Galvin et al. (1981) to measure the pressure dependence of the viscosity of lubricating oils. The "Vilastic" capillary rheometer, based on an instrument developed by Thurston (1972, 1987) and commercialized by Bohlin, employs a vibrating diaphragm in order to oscillate a fluid within a capillary [Bohlin Instruments (1994)].

Our machine consists of two servo-hydraulically driven pistons which can be moved separately or together. The principle behind the machine is simple. An appropriate test section is chosen, which for rheological measurements would normally be a capillary. Fluid is introduced into the rheometer and then one piston is advanced until the desired mean fluid hydrostatic pressure is reached. For the current machine, this ranges from

FIG. 1. Schematic diagram of the multipass rheometer with full instrument on left-hand side (total height from table top ~75 cm) and center section on right-hand side (height from base ~15 cm). (A) linear displacement transducers, (B) servo-actuators, (C) accumulators, (D) inlet/bleed valves, (E) top piston, (F) center section (see close-up), (G) thermocouples, (H) safety screen, (I) frame, (J) table top, (K) pistons, (L) pressure transducers, (M) flanges incorporating o-rings, (N) cooling/heating jackets, (O) capillary, (P) thermocouples, (Q) ball valves, (R) base, (S) inlet/outlet.
atmospheric pressure to ~ 210 bar (21 MPa). When the hydrostatic pressure is set, the two pistons are then synchronously driven such that their separation remains constant. A wide range of input signals can be used but in this article we report on two. In the “multipass steady” mode the pistons advance at constant velocity for a given time, yielding steady shear data. The piston position is then held constant for a set dwell time and then the piston motion is reversed. In this way a multitude of successive steady flow measurements can be made on the same test fluid. Alternatively, a time periodic oscillation can be applied where both the amplitude and frequency of oscillation can be varied. Pressure transducers on either side of the capillary enable time-dependent differential pressure measurements to be made from which rheological parameters can be determined.

The technical specification of the MPR is given in Tables I and II. High precision servo-hydraulics, comprising controller, valve, and actuator, control the displacement of the pistons and their positions are monitored by linear displacement transducers. The MPR is under computer control. By presenting the appropriate output signals to the servo

**TABLE I. Equipment specification.**

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacture of MPR</td>
<td>Eland Test Plant, St John’s Road, Hampton Wick, Kingston upon Thames, KT1 4AN, England</td>
</tr>
<tr>
<td>Servo valves</td>
<td>electrohydraulic servo valve, Moog, type E760</td>
</tr>
<tr>
<td>Servo controller</td>
<td>analog servo controller, Kelsey Instruments, type K600</td>
</tr>
<tr>
<td>Piston seals</td>
<td>spring-loaded PTFE, Glydring</td>
</tr>
<tr>
<td>Displacement transducers</td>
<td>variable resistive vector transducer, Penny and Giles</td>
</tr>
<tr>
<td>Pressure transducers</td>
<td>strain-gauge transducers, Entran, EPX series</td>
</tr>
<tr>
<td>Interface board</td>
<td>12 bit, National Instruments, type MO16L9</td>
</tr>
<tr>
<td>Programming</td>
<td>graphical, National Instruments, Labview</td>
</tr>
</tbody>
</table>

**TABLE II. Technical specification and performance.**

<table>
<thead>
<tr>
<th>Feature</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barrel material</td>
<td>stainless steel</td>
</tr>
<tr>
<td>Barrel/piston diameter</td>
<td>12 mm</td>
</tr>
<tr>
<td>Mean set hydrostatic pressure</td>
<td>1–210 bar (0.1–21 MPa)</td>
</tr>
<tr>
<td>Piston velocity</td>
<td>0.05–300 mm/s</td>
</tr>
<tr>
<td>Wall shear rate</td>
<td>0.1–600 s⁻¹ (8.0 mm capillary)</td>
</tr>
<tr>
<td></td>
<td>50–3×10⁷ s⁻¹ (1.0 mm capillary)</td>
</tr>
<tr>
<td>Wall strain</td>
<td>10–1000% (8.0 mm capillary)</td>
</tr>
<tr>
<td></td>
<td>2000–5×10⁹% (1.0 mm capillary)</td>
</tr>
<tr>
<td>Viscosity range</td>
<td>10⁻²–2×10⁶ Pa s⁻¹</td>
</tr>
<tr>
<td>Maximum displacement</td>
<td>15 mm</td>
</tr>
<tr>
<td>Position resolution</td>
<td>order 10 μm</td>
</tr>
<tr>
<td>Frequency</td>
<td>0.01–200 Hz</td>
</tr>
<tr>
<td>Max. oscillatory amplitude</td>
<td>7.5 mm center to peak²</td>
</tr>
<tr>
<td>Temperature</td>
<td>−10–170 °C</td>
</tr>
<tr>
<td>Sample volume</td>
<td>10–20 ml</td>
</tr>
</tbody>
</table>

¹Depending on choice of capillary, pressure transducer, and deformation rate.
²For frequencies up to 7 Hz.
controller, both independent piston motion and synchronous movement is possible. Pressure, displacement, and temperature signals can be monitored and manipulated using our computer software.

Fluid loading normally consists of introducing the fluid through the lower inlet valve, with the top piston fully retracted, thus leaving the barrel open at the top. Fluid is then introduced until it reaches the top of the barrel, after which the top piston is advanced, ejecting excess fluid through the open top valve. Both valves are then closed, after which experiments can begin.

III. OPERATING MODES

The instrument can operate in a number of ways. To begin with, the pistons can be positioned independently from each other in order to pressurize the fluid prior to the experiment. Once the desired pressure is reached, the pistons' motions can be coupled by driving each piston from the same input reference signal, and operated in multipass steady or oscillatory motion.

A. Multipass steady mode

Fluid in the barrel can be driven in a steady mode and the pressure difference across a capillary measured. This process can be repeated any number of times, hence “multipass” rheometry. For a capillary of radius $a$ and length $L$, for a fixed flow rate $Q$, the wall strain rate $\dot{\gamma}_w$ for a Newtonian fluid with no-slip boundary conditions, is given by

$$\dot{\gamma}_w = \frac{4Q}{\pi a^3},$$

with the flow rate $Q$ equal to $\pi R^2 v_p$, with $v_p$ the piston velocity and $R$ the piston radius [see, e.g., Walters (1975) or Barnes et al. (1989)]. For non-Newtonian fluids, the wall shear rate calculated using Eq. (1) is underestimated for shear-thinning fluids. A Rabinowitsch correction deals with this effect [see for instance Brydson (1981) or Walters (1975)]. This provides a correction for the wall shear rate, depending on the deviation of the $Q$-$\Delta P$ curve, so

$$\dot{\gamma}_w = \frac{1}{\pi a^3} \left(3Q + \Delta P \frac{dQ}{d(\Delta P)}\right).$$

The wall shear stress $\tau_w$ is related to the pressure difference $\Delta P$ across the capillary as $\tau_w = a\Delta P/2L$ and is independent of the fluid's properties. The viscosity of the fluid can be calculated by simply dividing wall stress by wall strain rate. For a Newtonian fluid

$$\eta = \frac{a^4 \Delta P}{8LR^2 v_p}.$$  

The multipass steady mode is implemented by feeding a cycle of (a) dwell, (b) downward motion, (c) dwell, and (d) upward motion to the output channels. This cycle is then repeated (hardware controlled) until it is stopped by an interrupt signal.

B. Oscillatory mode

The fluid can also be driven harmonically, allowing the dynamic moduli of the fluid to be calculated from the phase angle $\delta$ between applied strain and measured shear stress. Analogous to the derivation given by Brydson (1981) the amplitude in wall shear stress is the following function of the amplitude $\Delta P_{\text{max}}$ of the differential pressure:
From the constitutive equation for a viscoelastic fluid of complex viscosity \( \eta^*(\tau = \eta^* \dot{\gamma}) \) we can derive the velocity profile \( u(r) \) in the tube:

\[
u(r) = \frac{\Delta P_{\text{max}}}{4L \eta^*} (a^2 - r^2).
\] (4)

The profile in oscillatory mode is therefore a parabolic profile as long as the given constitutive equation is valid, that is, as long as the measurements are taken in the linear viscoelastic regime and the flow is fully developed.

The maximum wall shear strain can be obtained by integrating Eq. (1):

\[
\gamma_w = 4V/\pi a^3.
\] (5)

with \( V \) the volume displacement arising from a center to peak stroke \( x_{\text{max}} \) of the piston \((V = \pi R^2 x_{\text{max}})\). The storage and loss moduli can be written as follows:

\[
G' = \frac{a^4 \Delta P_{\text{max}}}{8LR^2 x_{\text{max}}} \cos \delta \quad \text{and} \quad G'' = \frac{a^4 \Delta P_{\text{max}}}{8LR^2 x_{\text{max}}} \sin \delta.
\] (6a,b)

Equations (5) and (6a,b) are only valid as long as linear strains are not exceeded.

As was the case with the steady mode, the oscillatory mode employs a hardware-controlled continuous sine wave until this is stopped by an interrupt signal.

The phase difference between oscillatory strain and the resulting oscillatory stress (or in this case the oscillating piston positions and the resulting differential pressure) is calculated using a cross-correlation method. This method also gives the values of the applied and resulting amplitudes. The following integrals are evaluated for the applied piston positions \( x(t) \), where \( x(t) = x_0 \sin(\omega t + \phi) \), with \( \phi \) a phase angle due to the arbitrary point in time at which we start the data acquisition.

\[
I_1 = \int_0^{2\pi} x(t) \sin \omega t \, dt \quad \text{and} \quad I_2 = \int_0^{2\pi} x(t) \cos \omega t \, dt.
\] (7a,b)

Likewise, integrals \( I_3 \) and \( I_4 \) are evaluated for the differential pressure \( P(t) \) \([P(t) = P_0 \sin(\omega t + \phi_p)]\), in which \( \phi_p \) arises from the phase angle \( \delta \) and the arbitrary point in time at which data acquisition is started:

\[
I_3 = \int_0^{2\pi} P(t) \sin \omega t \, dt \quad \text{and} \quad I_4 = \int_0^{2\pi} P(t) \cos \omega t \, dt.
\] (7c,d)

The amplitudes of applied and resulting signals \((x_0 \text{ and } P_0, \text{ respectively})\) are

\[
x_0 = \frac{1}{\pi} \sqrt{I_1^2 + I_2^2} \quad \text{and} \quad P_0 = \frac{1}{\pi} \sqrt{I_3^2 + I_4^2},
\] (8a,b)

and the phase angle between the two signals is

\[
\delta = \phi - \phi_p = \arctan \frac{I_2}{I_1} - \arctan \frac{I_4}{I_3}.
\] (8c)

These relations may be easily checked by solving the integrals [Eqs. (7a)–(7d)] analytically.
IV. INERTIA EFFECTS

For the high flow rates, especially when using a 1-mm-diam capillary, we need to ascertain that laminar flow is still present in the capillary. The Reynolds number Re gives a rough guide as to whether laminar flow or turbulence prevails; for tube flow, \( \text{Re} = \frac{2 \pi a \rho v}{\eta} \) with \( v \) the mean fluid velocity in the capillary, \( \rho \) the density of the fluid, and \( a \) the capillary radius. The critical Reynolds number is of order 1000 [Brodkey and Hershey (1988)] and at higher values, flow becomes turbulent.

In the oscillatory mode we need to consider the oscillatory Reynolds number \( \text{Re}_o \): \( \text{Re}_o = \frac{2 \pi a \rho \omega x_0}{\eta} \), with \( \omega \) the frequency in rad/s and \( x_0 \) the oscillation amplitude.

In 1960, Thurston presented some calculations describing the flow profiles of a viscoelastic fluid oscillating in a tube. He proved that depending on the value of a dimensionless number \( Y = \frac{\rho v}{\eta} \) and the degree of elasticity of the fluid, the velocity profile is no longer parabolic, but becomes more complicated, invalidating our equations with which we evaluate the viscoelastic moduli. He showed, however, that for values of \( Y < 2 \), there are no deviations.

V. VISCOUS HEATING

In some cases, the shear rates at the wall of the capillary can be very large and the effect of viscous heating needs to be considered. The work \( W_f \) exerted on the sample per unit time equals \( W_f = F V_c - \Delta P A_c V_c \) with the surface area \( A_c \) equal to the area of the capillary and \( \Delta P \) the measured pressure difference. The average velocity of the material within the capillary \( V_c \) is equal to the piston velocity increased by a factor equal to the ratio of piston to capillary areas: \( V_c = \frac{\rho v}{R^2/a^2} \). The energy per unit time required to heat up the sample equals \( W_T = \dot{m} c_p \Delta T \), where \( c_p \) is the heat capacity of the sample, \( \Delta T \) the temperature rise, and \( \dot{m} \) is the mass transported per unit time (\( \dot{m} = \rho \pi R^2 v_p \)). Thus the average adiabatic temperature rise that can be expected from viscous heating can be calculated by equating \( W_f \) to \( W_T \): \( \Delta T_{\text{max}} = \Delta P/c_{p} \). Typical values are \( c_{p} = 2 \text{ J/g K} \) and \( \rho = 10^5 \text{ g/m}^3 \). These values lead to an expected temperature rise of 1 °C for every 20 bar (2 MPa) differential pressure.

VI. ENTRY EFFECTS

Using a capillary geometry to measure rheometric quantities introduces errors because of the contribution of the extensional deformation at the entry of the capillary to the shear deformation inside the capillary itself. Often, a Bagley correction is carried out using a range of capillary lengths, leading to the quantification of the extensional contribution in an apparent capillary length increase [see, e.g., Barnes et al. (1989) or Walters (1975)]. With the limited number of capillary lengths currently available with our instrument, a Bagley correction has not been carried out.

VII. MATERIALS AND METHODS

Three fluids were investigated with the multipass rheometer: A Newtonian silicone oil from Ambersil Ltd., with a viscosity at room temperature of order 1 Pa s. Two viscoelastic fluids were chosen. The first was a standard fluid A-100, consisting of 5 wt. % polyisobutylene (Exxon Chemical Ltd.) in decalin (decahydronaphthalene) [see, for example, Liang and Mackley (1994)]. For the linear viscoelastic measurements we have prepared a second solution of polyisobutylene in decalin: 20 wt. % polyisobutylene (PIB) (Dow Chemical, The Netherlands).
In this article, we have focused on the application of the instrument as a rheometer. We have used three capillaries of length (mm)/diameter (mm) of 40/1.0, 10/1.0, and of 40/8.0.

Both steady and oscillatory measurements have been carried out and comparisons made using a strain-controlled Rheometrics RDS-II mechanical spectrometer fitted with a 0.01 N m force rebalance transducer (for the A-100 fluid) or with a 0.2 N m force rebalance transducer (for 20% PIB in decalin). In all cases a cone and plate geometry was used of diameter 25 mm. A Rheometrics DSR, stress-controlled dynamic rheometer was used for the silicone oil, also fitted with a 25-mm diam cone and plate geometry.

VIII. RESULTS
A. Silicone oil in steady shear

The oil was injected into the barrel using a syringe. Initially, the oil remained unpressurized. The temperature was maintained at 30 °C in the 1.0 mm capillary and 350 bar pressure transducers were chosen. In the multipass steady mode the pistons perform a continuous cycle of moving up together, resting, moving down, and resting. Operating the instrument in this mode, the positions of the pistons, as well as the pressure response of the pressure transducers were monitored. The result can be seen in Fig. 2(a) where the piston speed is 20 mm/s. This corresponds to a wall shear rate of 20 000 s⁻¹. During the
FIG. 3. Multipass steady measurements on silicone oil at 30 °C, capillary diameter 1.0 mm, piston displacement 6 mm, pressurized to 50 bar. 350 bar pressure transducer; differential pressure vs piston speed using: a long capillary (40 mm) (●), a short capillary (10 mm) (○). Error bars give indication of error only at higher piston speeds; lines: initial slopes.

periods of rest, zero pressures are recorded. During the upward motion of the piston, the lower pressure transducer registers a positive pressure and during the downward motion, the upper transducer responds in the same way [Fig. 2(a)]. The differential pressure is shown in Fig. 2(b) giving an indication of the quality of the data and its reproducibility for each pass.

In Fig. 3 the result is shown of the pressure difference, averaged in multipass steady mode, for a range of piston speeds for both a long (L = 40 mm) and a short capillary (L = 10 mm), both of 1.0 mm diameter. The sample was pressurized to 50 bar. In this figure the chosen piston speeds lead to wall shear rates between 1000 and 100 000 s⁻¹. It is seen that the relation between pressure difference and piston speed is initially linear, as expected for Newtonian fluids. The viscosity calculated from the slopes of the graphs are 0.94 ± 0.05 Pa s for the L = 40 mm capillary and 0.95 ± 0.05 Pa s for the L = 10 mm capillary which is a good correspondence and it can be concluded that entry effects do not appear to play a major role in this case. As will be seen later, the viscosity of this particular fluid depends on the applied pressure and for atmospheric pressure the viscosity at 50 bar needs to be reduced by 8%, leading to η = 0.87 ± 0.05 Pa s for both capillaries, and this compares well with values obtained with the DSR rheometer (0.91 ± 0.01 Pa s at 30 °C).

At piston speeds of 15 mm/s, corresponding to 15 000 s⁻¹ and greater, the observed pressure response becomes nonlinear. The flow in the capillary is still laminar as the Reynolds's number is only 6 for the 40 mm/s piston speed. The observed nonlinearity could be due to shear thinning, shear heating, or other effects. Calculating the maximum temperature rise from the work exerted on the sample and assuming a heat capacity of 2 J/g K leads to an expected temperature increase of approximately 2.5 °C for ΔP = 47 bar recorded for a piston speed of 40 mm/s. At 40 mm/s the viscosity has decreased by a factor corresponding to about an 8 °C temperature rise. Although, compared to the Newtonian viscosity, this measured viscosity decrease thus seems to be greater than that calculated for shear heating, because of the multipass nature of the measurements, the sample may be further heated due to successive passages. From Fig. 3 it is therefore difficult to assess the relative importance of shear heating and shear thinning. It is plausible that shear thinning contributes to the effect: Dyson et al. (1965) found silicone oil to display non-Newtonian behavior, even under relatively mild conditions of shear rate and
The Eyring theory of liquids [see Tabor (1991)] predicts nonlinearity of stress-strain rate curves under the influence of high hydrostatic pressures and high deformation rates. It is not likely that the nonlinearity measured in this article is attributable to this as we are still operating under relatively mild conditions of pressures and shear rates.

The dependence of the viscosity on the mean fluid pressure at a temperature of 30 °C has been measured. At a piston velocity of 10 mm/s, corresponding to ~10 000 s⁻¹ [where the stress–strain relationship for the fluid is still linear (see Fig. 3)] the viscosity was measured at fluid pressures between 1 and 220 bar (0.1 and 22 MPa). It can be seen in Fig. 4 that pressurization from 1 to 220 bar causes a viscosity enhancement of ~40%. This compares well with literature values. The pressure dependence of viscosity can be given by the Barus equation: \( \eta_P = \eta_0 e^{\beta P} \) (with \( \eta_P \) the viscosity at pressure \( P \), \( \eta_0 \) the viscosity at atmospheric pressure). The coefficient \( \beta \) obtained from Fig. 5 is \( (1.6 \pm 0.2) \times 10^{-8} \text{ Pa}^{-1} \). Barnes et al. (1989) and Wilson (1985) give \( \beta = 1-2 \times 10^{-8} \text{ Pa}^{-1} \) for a typical mineral oil, Dyson et al. (1965) gives \( \beta = 1.81 \times 10^{-8} \text{ Pa}^{-1} \) for a silicone fluid.

At a piston speed of 10 mm/s (wall shear rate ~10 000 s⁻¹), a temperature scan was carried out. The temperature dependence of the viscosity found with the multipass rheometer was compared with a conventional rheometer. A stress-controlled Rheometrics DSR rheometer was used, allowing accurate temperature sweeps. The result is given in Fig. 5. It can be seen that there is a reasonably good agreement between the two instruments. Mild contributions from shear heating or shear thinning in the MPR (shear rates 10 000 s⁻¹) may have lead to the MPR measurements lying about 5% below the DSR values.

**B. Silicone oil in oscillatory mode**

A further test concerned the oscillatory mode of the rheometer. Again, the 1.0-mm-diam capillary was used. The temperature was 30 °C and initially, the fluid remained unpressurized. A graph of piston positions and differential pressure is given in Fig. 6, where it can be seen that the response to the sinusoidal deformation is sinusoidal with a phase difference of 90°.

Using the cross-correlation method to calculate phase angle and pressure amplitudes, we have plotted the pressure response as a function of piston frequency and amplitude. The results are given in Fig. 7 for a few frequencies between 0.1 and 1 Hz. The temperature was 30 °C and the applied mean pressure 50 bar. It is immediately clear that the
response is nonlinear except for the lowest frequency of 0.1 Hz. From the initial slopes, however, a viscosity can be calculated and compared to Rheometrics data. For 0.1, 0.25, 0.5, and 1 Hz, the calculated viscosities are 1.08±0.05, 1.04±0.05, 1.03±0.05, and 1.0±0.1 Pa·s for a set pressure of 50 bar. Recalculated to atmospheric pressure (reduce by 8%, see Fig. 4), these values are 0.99±0.05, 0.95±0.05, 0.94±0.05, and 0.9±0.1 Pa·s which compare well with the DSR data: 0.91±0.01 Pa·s at 30 °C.

The nonlinear response at higher frequencies and strains may be due to a number of factors. First, the nonlinear response may be due to viscous heating which is significant for pressures we typically register in Fig. 7. Due to the multipass nature of the oscillatory mode, the effect may be enhanced (as discussed for Fig. 3). Second, some entrapped air pockets may act as compressive springs, introducing apparent viscoelasticity in the sample. This possibility is supported by the measured decrease of the phase angle as amplitudes become larger. Only at 0.1 Hz is this effect fully absent for the amplitude range we have investigated. From a calculation of the oscillatory Reynold’s number, we may safely conclude that the material displays laminar flow for all data points shown in

![Graph showing temperature vs viscosity for silicone oil](image)

**FIG. 5.** Multipass steady experiments on silicone oil, capillary diameter 1.0 mm, length 40 mm, piston displacement 6 mm, piston speed 10 mm/s, no prior pressurization, 35 bar pressure transducer. Apparent viscosity vs temperature for MPR (○) and DSR (●).

![Graph showing oscillatory behavior](image)

**FIG. 6.** MPR oscillatory experiments on silicone oil at 30 °C, capillary diameter 1.0 mm, length 40 mm, piston amplitude 5 mm, 350 bar pressure transducer. Piston position and differential pressure at $\omega = 1$ Hz, no prior pressurization.
Fig. 7. The inertia effects described by Thurston (1960) do not play a role as \( Y \) does not exceed order 0.05 for these data, still very much lower than the critical value of 2.

The dependence of the measured pressure difference on the static pressure was also investigated in oscillatory mode. The same dependence of viscosity on pressure was found as we obtained in steady shear. The phase angle does not vary significantly with pressure.

To test the repeatability of the experiments, some oscillatory experiments were carried out (amplitude sweeps at two different frequencies), the instrument was then dismantled, reassembled, and the experiment was repeated. It transpires that the repeatability is very good, with only 2% difference between the experiments.

C. A-100 fluid in steady shear

The standard viscoelastic fluid A-100 is a polyisobutylene dissolved in decalin. The rheological characterization of this material has recently been published by Liang and Mackley (1994).

The fluid was injected into the rheometer and tested at 30 °C at a mean applied pressure of 20 bar. The 1.0-mm-diam capillary was used, leading to very high shear rates. In Fig. 8 it can be seen that the apparent viscosity at a shear rate of 50 000 s\(^{-1}\) equals 40 mPa s. Moreover, it can be seen that the trend, presented by the RDS-II data at shear rates between 0.1 and 200 s\(^{-1}\), continues to shear rates of the order of 10\(^5\) s\(^{-1}\).

As pressure differences in this experiment are very small, shear heating effects may be ruled out. Entry effects, however, may become more important now that we are dealing with a viscoelastic material.

D. 20% PIB/Decalin in small-strain oscillatory shear

For these experiments, the capillary of length 40 mm and diameter 8.0 mm was used. The device was held at a temperature of 25 °C. A pressure transducer of maximum range of 15 bar (1.5 MPa) was used.

The linear viscoelastic behavior of this material was checked using the Rheometrics RDS-II. The linear viscoelastic region extends up to strains of approximately 100%. The behavior of the complex moduli \( G' \) and \( G'' \) follows a typical polymer pattern with \( G'' \) dominating at low frequencies and \( G' \) dominating at high frequencies. These measure-
FIG. 8. Multipass steady experiment on A-100 fluid at 30 °C, capillary 1.0 mm diameter, length 40 mm, pressurized to 20 bar, 350 bar pressure transducer. Viscosity vs wall shear rate. Inserted is the steady shear result as measured with the Rheometrics RDS-II rheometer.

ments can be seen in Fig. 9 (+ and X symbols) from which can be derived the spectrum of relaxation times [Mackley et al. (1994b)].

We then proceeded to reproduce these data with the multipass rheometer. The maximum linear strain of ~100% corresponds to a piston amplitude of 0.5 mm. Frequencies were chosen between 0.05 and 30 Hz, corresponding to 0.3 and 180 rad/s. It can be seen in Fig. 9 that there is a very good correspondence between the RDS-II data and the data obtained with the MPR. Because of limits of pressure resolution at the low-frequency end, no data could be achieved below 0.05 Hz (0.3 rad/s) where the measured pressure differences are below $2 \times 10^{-2}$ bar.

At frequencies above ~50 rad/s, deviation starts to occur between the RDS-II and the MPR. As pressure differences in this region begin to approach 1 bar, this may be caused by entrapped air, acting as a compressive spring. The inertial effect that Thurston (1960) describes does not play a role as values of $\gamma$ do not exceed 0.5 for the data points presented in Fig. 9.

FIG. 9. MPR oscillatory experiments on 20% PIB in Decalin at 25 °C, capillary diameter 8.0 mm, length 40 mm, no prior pressurization, 15 bar pressure transducer. $G'$ (triangles) and $G''$ (circles) vs frequency on two separate days (filled/open symbols), between 0.02 and 30 Hz. Inserted the results as measured with the Rheometrics RDS-II rheometer ($G': \times , G'':+$).
A dynamic strain sweep was also compared: measurement of $G'$ and $G''$ were carried out at 1 Hz, with piston amplitudes ranging from 0.2 to 5 mm. It can be concluded from Fig. 10 that the linear region seems to extend to slightly higher strains as measured with the MPR. This is also found for other frequencies (not shown) and may be due to the fact that for tube flow, at the strain indicated on the x axes of these figures, a considerable proportion of the material does not experience nonlinear strains, and the deviation from linearity may be less than experienced in a uniform strain cone and plate geometry. Moreover, Eqs. (6a), (6b) are strictly speaking only valid in the linear regime. The values of $G'$ and $G''$ at linear strains are reproduced, as already seen in the frequency sweep.

E. 20% PIB/Decalin in steady shear

The MPR was operated in its multipass steady mode and the steady shear behavior is shown in Fig. 11, where the wall shear stress is plotted versus shear rate. MPR measure-
FIG. 12. Multipass steady experiments on 20% PIB in Decalin at 25 °C, capillary diameter 8.0 mm, length 40 mm, piston displacement 4 mm, piston speed 20 mm/s, no prior pressurization, 15 bar pressure transducer. Piston position and differential pressure.

ments were carried out between piston speeds ranging between 1 and 200 mm/s. Below 1 mm/s, low-pressure resolution prohibits reliable data processing. A region of constant viscosity extends up to, $\sim 3 \text{ s}^{-1}$, after which shear thinning occurs. The Newtonian plateau corresponds very well with the data measured with the RDS-II. At shear rates above $10 \text{ s}^{-1}$, the results of RDS-II and MPR do no longer compare. It seems that, compared to the RDS-II, the viscosity as measured with the MPR decreases with increasing shear rate in a much smoother fashion, up to the maximum applied shear rate of 500 s$^{-1}$.

Recently it has been shown by Mackley et al. (1994b) that for many complex fluids, a comprehensive characterization based on a generalized Maxwell model (with a spectrum of relaxation times) and a Wagner-type damping function is satisfactory, certainly for polymer-based systems. The model involves measurement of $G'$ and $G''$ versus frequency (Fig. 9) leading to the spectrum of relaxation times, and measurement of step-strain curves, leading to a damping factor $k$. In this scheme of rheological characterization, the steady shear behavior may be calculated. Step-strain data for 20% PIB/Decalin (Fig. 13) lead to a value of $k$ of 0.23, typical for polymer systems. The calculated shear stress versus shear rate curve is also plotted in Fig. 11. The MPR follows the behavior predicted by the model much more closely. It shows that for this material, anomalous flow behavior found using a cone and plate geometry is not found using the MPR. The experimental data suggest no-slip boundary conditions at all shear rates in the MPR and the presence of apparent slip in the RDS-II at shear rates greater than $10 \text{ s}^{-1}$.

The anomalous behavior found with the RDS-II is consistent with a recent observation by Binding et al. (1994) who showed the existence of instabilities in rotary flow of a class of similar solutions (S1 fluids, which are solutions of PIB in a decalin/polybutene mixture). These instabilities have also been discussed in a review by Larson (1992).

The fact that the fluid we are dealing with is not Newtonian necessitates a Rabinowitsch correction. As the deviation of the $Q-\Delta P$ plot is known, this is easy to perform. In Fig. 9 it can be seen that this correction leads to an even better agreement between the MPR results and the prediction.

Close inspection of a multipass steady profile presented in Fig. 12 of a 2 mm piston motion at 20 mm/s shows that, instead of instantaneous pressure response after piston motion, the pressure relaxes back to zero in a finite time. This could indicate the fluid's stress-relaxation behavior in a step-strain experiment. The wall strain imposed in this
FIG. 13. Multi-pass steady experiments on 20% PIB in Decalin at 25 °C, capillary 8.0 mm diameter, length 40 mm, no prior pressurization, 15 bar pressure transducer. Relaxation moduli from pressure trace of Fig. 12 vs time (data points). Inserted the result as measured with the Rheometrics RDS-II rheometer for strains of 100%, 200%, 300%, 400%, and 500% (lines). The thick line corresponds to a strain of 400%.

experiment is ~ 400%. The pressure relaxation of all upward piston motions were re-calculated to wall shear stress relaxation and the relaxation modulus. The result is plotted in Fig. 13, together with the stress relaxation behavior measured with the RDS-II. The agreement is not perfect, but certainly of the right order of magnitude.

It should be noted that in Figs. 2(a) and 2(b) a "relaxation" is also seen for the silicone oil, but this is probably due to relaxation via some entrapped air pockets.

The result of the "stress relaxation" experiments serves as a corroboration of our overall result, which is that good agreement can be found between a conventional rheometer and the multipass rheometer.

IX. DISCUSSION AND CONCLUSION

This article has shown that the multipass rheometer is capable of matching both steady shear and oscillatory data obtained using standard rheometers. The MPR offers a number of potential advantages over existing machines and some of these features have been demonstrated here. The silicone oil data form an example where multiple successive steady shear measurements can be carried out on a small volume of fluid (~ 10 ml). In the case of silicone oil the material was stable and the rheology did not change with time. However, there are a number of fluids where continued shearing might result in a rheological change. The MPR offers the potential to evaluate these fluids in a fully constrained small volume. The additional feature of independent pressure control also opens up possibilities for a wide range of experiments.

The recent developments in servo control provide high precision displacement over a wide range of frequencies. The polyisobutylene results published here show that within a frequency range of 0.03–10 Hz, we are able to match existing rheometers in terms of linear viscoelastic measurements. In principle the upper range of frequencies that can be obtained using the servo system is 200 Hz and this also offers interesting possibilities for future measurements.

This article has demonstrated that the MPR can carry out experiments well outside the normal range of most other instruments. The high shear rate nonlinear behavior of the silicone oil is one example and the high shear rate steady shear data for the A-100 solution is another. Pressure dependence measurements reported here are consistent with
and extend other people’s findings. It has also been shown that the effect of slip in a cone–plate geometry may be overcome using the MPR.

At present the 10 μm spatial resolution of the displacement transducer and hence a possible pressure variation of up to 1 bar of the enclosed fluid limits our choice of pressure transducers. This in turn limits the apparatus to relatively high, steady shear rates while in the oscillatory mode the fluid’s moduli need to be relatively high in order to measure significant pressure differences in linear deformations. Currently the usefulness of the machine is restricted to high viscosity systems and the data presented here do demonstrate the potential of the current machine at high viscosities, high levels of viscoelasticity, and at high shear rates. The apparatus may well be suited to studying rheological changes during liquid–solid transitions.

We believe that this article has demonstrated the viability of the MPR as a rheometer that is capable of carrying out a broad set of rheological measurements under controlled conditions. In addition, the device is potentially very flexible in operation and a wide range of insert test sections can be visualized [see Mackley et al. (1994a)]. The device could in the future prove to be useful in the field of rheo-optics, mixing, and also reactions, where the independent control of pressure, temperature, and shear can all be important factors.

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