Rheometry for non-Newtonian fluids*

2.1 Introduction

The rheological characterisation of non-Newtonian fluids is widely acknowledged to be far from straightforward. In some non-Newtonian systems, such as concentrated suspensions, rheological measurements may be complicated by non-linear, dispersive, dissipative and thixotropic mechanical properties; and the rheometrical challenges posed by these features may be compounded by an apparent yield stress.

For non-Newtonian fluids, even the apparently simple determination of a shear rate versus shear stress relationship is problematical as the shear rate can only be determined directly if it is constant (or nearly so) throughout the measuring system employed. While very narrow shearing gap coaxial cylinder and cone-and-plate measuring geometries provide good approximations to this requirement, such systems are often of limited utility in the characterisation of non-Newtonian products such as suspensions, whose particulate/aggregate constituents preclude the use of narrow gaps. As most measuring geometries do not approximate to constant shear rate, various measurement strategies have been devised to overcome this limitation. The basic features of these rheometrical approaches, and of the main instrument types for their implementation, are considered below.

2.2 Capillary viscometers

Capillary viscometers are the most commonly used instruments for the measurement of viscosity due, in part, to their relative simplicity, low cost and (in the case of long capillaries) accuracy. However, when pressure drives a fluid through a pipe, the velocity is a maximum at the centre: the velocity gradient or shear rate $\dot{\gamma}$ are a maximum at the wall and zero in the centre of the flow. The flow is therefore non-homogeneous and capillary viscometers are restricted to measuring steady shear functions, i.e. steady shear stress–shear rate behaviour for time independent fluids [Macosko 1994]. Due to their inherent similarity to

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many process flows, which typically involve pipes, capillary viscometers are widely employed in process engineering applications and are often converted or adapted (with relative ease) to produce slit or annular flows.

### 2.2.1 Analysis of data and treatment of results

It is convenient to consider the case of an ideal capillary viscometer involving a fluid flowing slowly (laminar) and steadily through a long tube of radius $R$, at a constant temperature, and with a pressure drop $(-\Delta p)$, between its ends [Whorlow, 1992]. Then, for fully developed flow, the following relationship may be derived relating the shear stress at the wall of the tube, $\tau_w$, to the volume of liquid flowing per second through any cross-section, $Q$, and the shear stress $\tau$ (see equation (2.1)):

$$\frac{Q}{\pi R^3} = \frac{1}{\tau_w} \int_0^{\tau_w} \tau^2 f(\tau) \, d\tau$$

(2.1)

Here $\tau_w = (R/2)(-\Delta p/L)$ where $(-\Delta p/L)$ is the magnitude of the pressure drop per unit length of tube (the pressure gradient) and the shear stress $\tau$ at any radius $r$ is $(r/2)(-\Delta p/L)$. A graph of $Q/\pi R^3$ vs. $\tau_w$ gives a unique line, for a given material, for all values of $R$ and $(-\Delta p/L)$.

For a Newtonian fluid, with $\dot{\gamma} = f(\tau) = \tau/\mu_N$, equation (2.1) yields the Poiseuille equation,

$$Q = \frac{\pi R^4 (-\Delta p)}{8\mu_N L}$$

(2.2)

from which the viscosity $\mu_N$ can be calculated using a value of $Q$ obtained for a single value of $(-\Delta p/L)$, and the shear rate at the tube wall is $4Q/\pi R^3$ or $(8V/D)$. Turning to the most commonly-used model approximations to non-Newtonian flow behaviour, the following relationships are obtained for the power-law model (in the form $\mu = m\dot{\gamma}^{n-1}$), written at $r = R$:

$$\tau_w = \frac{R}{2} \left(\frac{-\Delta p}{L}\right) = m \left\{ \left(\frac{3n + 1}{4n} \frac{8V}{D}\right)^{\frac{1}{n}} \right\}$$

(2.3)

and, for the Bingham model (in the form $\dot{\gamma} = f(\tau) = (\tau - \tau_0^B)/\mu_B$) of we obtain,

$$\left(\frac{8V}{D}\right) = \frac{4}{\mu_B} \frac{\tau_w}{4} - \frac{\tau_0^B}{3} \left(1 - \frac{1}{4} \left(\frac{\tau_0^B}{\tau_w}\right)^{\frac{3}{2}}\right)$$

(2.4)

where $\mu_B$ is the ‘plastic viscosity’.

For flow curves of unknown form, equation (2.1) yields (after some manipulation, see Section 3.2.5):
Rheometry for non-Newtonian fluids

\[
f(\tau_w) = \left( \frac{8V}{D} \right) \left\{ \frac{3}{4} + \frac{d(\log 8V/D)}{4d(\log \tau_w)} \right\}
\]  

(2.5)

Various forms of this equation are used, a common form (often termed the Weissenberg–Rabinowitsch or Rabinowitsch–Mooney equation) being,

\[
\dot{\gamma}_w = \dot{\gamma}_{wN} \left( \frac{3n' + 1}{4n'} \right)
\]

(2.6)

where \( n' = d(\log \tau_w)/d(\log \dot{\gamma}_{wN}) \), \( \dot{\gamma}_w \) is the shear rate at the wall and \( \dot{\gamma}_{wN} = (8V/D) \) is a nominal shear rate obtained by using the formula appropriate to the Newtonian fluid.

For shear-thinning fluids, the apparent shear rate at the wall is less than the true shear rate, with the converse applying near the centre of the tube [Laun, 1983]. Thus at some radius, \( x^*R \), the true shear rate of a fluid of apparent viscosity \( \mu \) equals that of a Newtonian fluid of the same viscosity. The stress at this radius, \( x^*\tau_w \), is independent of fluid properties and thus the true viscosity at this radius equals the apparent viscosity at the wall and the viscosity calculated from the Poiseuille equation (equation (2.2)) is the true viscosity at a stress \( x^*\tau_w \). Laun [1983] reports that this ‘single point’ method for correcting viscosity is as accurate as the Weissenberg–Rabinowitsch method.

Serious errors may be incurred due to wall slip, e.g. in the case of concentrated dispersions where the layer of particles may be more dilute near the wall than in the bulk flow: the thin, dilute layer near the wall has a much lower viscosity, resulting in an apparent slippage of the bulk fluid along the wall.

The occurrence of this phenomenon may be tested by comparing the viscosity functions obtained using capillaries of similar length-to-radius ratios, \( L/R \), but of different radii. Any apparent wall slip may then be corrected for and the true viscosity of the fluid determined by extrapolating the results obtained to infinite pipe diameter. In the relation developed by Mooney [1931], apparent wall shear rates obtained for constant length-to-radius ratio are plotted against \( (L/R) \).

Departures from ideal flow near either end of the pipe (end effects) may be eliminated by considering the total pressure drop \( (-\Delta p)_t \), between two points beyond opposite ends of a uniform bore tube in terms of \( (-\Delta p/L) \), the pressure gradient in the central part of the tube of length \( L \) and an end correction, \( \varepsilon \). The latter may be very large for non-Newtonian fluids. Using tubes of different length, a plot of \( (-\Delta p)_t \) versus \( L \) yields the value of \( (-\Delta p/L) \) if the upper part of the plot is linear, and \( \varepsilon \) may be found by extrapolation to zero \( L \).

Note that in applying this procedure to polymer systems it is conventional to plot pressure against \( L/R \) to construct the so-called Bagley plot [Bagley 1957].

As the construction of the Bagley plot requires considerable experimental effort, in practice a single long \( (L/R \geq 60) \) capillary is usually deemed to provide accurate results on the assumption that all corrections may be safely ignored. This assumption is not always warranted and the reader is referred to
other texts (see ‘Further Reading’) for details concerning additional sources of error, which may require consideration of kinetic energy corrections, pressure dependence of viscosity, thixotropy, viscous heating, compressibility and, in the case of melts, sample fracture. A typical arrangement of a pressurised capillary viscometer is shown in Figure 2.1.

![Figure 2.1](image)

**Figure 2.1**  A pressurised capillary viscometer

**Example 2.1**

The following capillary viscometer data on a high pressure polyethylene melt at 190°C have been reported in the literature [A.P. Metzger and R.S. Brodkey, *J. Appl. Polymer Sci.*, 7 (1963) 399]. Obtain the true shear stress–shear rate data for this polymer. Assume the end effects to be negligible.

<table>
<thead>
<tr>
<th>(\frac{8V}{D}) (s(^{-1}))</th>
<th>(\tau_s) (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>22.4</td>
</tr>
<tr>
<td>20</td>
<td>31</td>
</tr>
<tr>
<td>50</td>
<td>43.5</td>
</tr>
<tr>
<td>100</td>
<td>57.7</td>
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<tr>
<td>200</td>
<td>75</td>
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<tr>
<td>400</td>
<td>97.3</td>
</tr>
<tr>
<td>600</td>
<td>111</td>
</tr>
<tr>
<td>1000</td>
<td>135.2</td>
</tr>
<tr>
<td>2000</td>
<td>164</td>
</tr>
</tbody>
</table>
Solution

From equation (2.5):

\[ f(\tau_w) = \dot{\gamma}_w = \left( \frac{3n' + 1}{4n'} \cdot \frac{8V}{D} \right) \]

and \( \tau_w = \frac{R}{2} \left( \frac{-\Delta p}{L} \right) \)

where \( \tau_w \) is the true shear stress at the wall irrespective of the type of fluid behaviour, whereas \((8V/D)\) is the corresponding shear rate at the wall only for Newtonian fluids. The factor \((3n' + 1)/4n'\) corrects the nominal wall shear rate \((8V/D)\) for the non-Newtonian fluid behaviour.

where \( n' = \frac{d \log \tau_w}{d \log (8V/D)} \)

![Figure 2.2 Rheological data of Example 2.1](image)

Thus, the given data is first plotted on log-log coordinates as shown in Figure 2.2 and the value of \( n' \) is evaluated at each point (value of \( 8V/D \)), as summarised in Table 2.1.
Table 2.1  Summary of Calculations

\[
\tau_w (\text{kPa}) \quad \left(\frac{8V}{D}\right) (\text{s}^{-1}) \quad n' = \frac{d \log \tau_w}{d \log (8V/D)} \quad \dot{\gamma}_w = \left(\frac{3n' + 1}{4n'}\right) \quad \left(\frac{8V}{D}\right) (\text{s}^{-1})
\]

<table>
<thead>
<tr>
<th>(\tau_w) (kPa)</th>
<th>(\left(\frac{8V}{D}\right)) (s(^{-1}))</th>
<th>(n')</th>
<th>(\dot{\gamma}_w)</th>
<th>(\left(\frac{8V}{D}\right)) (s(^{-1}))</th>
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</thead>
<tbody>
<tr>
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<td>0.50</td>
<td>12.5</td>
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</tr>
<tr>
<td>31</td>
<td>20</td>
<td>0.47</td>
<td>25.6</td>
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</tr>
<tr>
<td>43.5</td>
<td>50</td>
<td>0.43</td>
<td>66.6</td>
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<tr>
<td>57.7</td>
<td>100</td>
<td>0.42</td>
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</tr>
<tr>
<td>75</td>
<td>200</td>
<td>0.40</td>
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</tr>
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<td>0.31</td>
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</tr>
</tbody>
</table>

As can be seen, the value of the correction factor \((3n' + 1)/(4n')\) varies from 25\% to 55.6\%. Thus, the values of \((\tau_w, \dot{\gamma}_w)\) represent the true shear stress–shear rate data for this polymer melt which displays shear-thinning behaviour as can be seen from the values of \(n' < 1\).