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**DTI MATERIALS METROLOGY PROGRAMME 1996-1999  
PERFORMANCE OF ADHESIVE JOINTS**

**Project: PAJ1; Failure Criteria and their Application to Visco-  
Elastic/Visco-Plastic Materials  
Report No 1**

**REVIEW OF RHEOLOGICAL MEASUREMENT METHODS  
FOR VISCO-ELASTIC ADHESIVES**

**B C DUNCAN and A OLUSANYA**

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**ABSTRACT**

Design of processes involving the flow or spreading of adhesives often requires accurate characterisation of the adhesives rheology. There are many test methods for determining the rheology of fluids but many of them are unsuitable for rate-dependent, visco-elastic adhesives. In this report, a number of rheological measurement techniques have been reviewed. The most suitable methods for studying the flow properties of adhesives are those in which a wide range of shear rates are available, such as capillary and rotational rheometry. Oscillatory techniques enable more advanced study of the elastic and viscous nature of adhesives. Transient test methods, such as creep or stress relaxation, are only appropriate for situations where the flow rates are extremely slow or the adhesive is allowed to stand or spread without applied pressure.

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Approved on behalf of Managing Director, NPL, by Dr C Lea,  
Head of Centre for Materials Measurement and Technology

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**by B C Duncan and A Olusanya**

**1. INTRODUCTION**

Adhesives for structural joining applications are often used in the form of liquids or pastes that harden to form a bonded joint. The rheology of the adhesive controls its dispensing and spreading properties. Predictions of these are necessary in the design of manufacturing processes. Furthermore, the rate at which the mechanical properties develop during cure is needed to predict when a bonded component can be safely handled. There are many methods for studying the rheology of adhesives. Some of these are capable of following the development of properties from liquid to solid states. This review was carried out as part of Project 1 of the Performance of Adhesive Joints Programme. It is concerned with rheological measurement methods for materials which range from the fluid to the visco-elastic solid state.

As the theories of classical mechanics were developed, the distinctions were drawn between solids and liquids. Physical laws were formalised for their separate behaviours. Solids were assumed to obey Hookes Law and fluids obey Newtons Law of constant viscosity. A single viscosity coefficient is all that is required to define the behaviour of a non-compressible Newtonian fluid under any conditions of flow and stress. It is well known that this simplistic approach cannot describe the vast range of materials which are now in common usage.

Polymeric materials have visco-elastic properties showing characteristics of elastic solids and viscous liquids. Their rheological properties are non-Newtonian<sup>(1-3)</sup>. Most adhesives exhibit shear-rate dependent viscosities. These can be extended to describe the rheological properties of progressively stiffer materials, for example resins and modified rubbery materials such as polyurethanes.

In this report, methods for measuring rheological properties of adhesives are reviewed. There are many techniques available; selection of the appropriate technique depends on the properties of the material being tested and the type of data required. Full understanding of the rheology of rate-dependent materials cannot be obtained with single shear rate instruments.

## 2. MEASUREMENT METHODS

Walters<sup>(1)</sup> distinguishes two not necessarily unrelated objectives of rheological measurements:

Objective 1: is to determine the behaviour of non-Newtonian liquids in simple flow situations using suitable material functions. The purpose is to obtain correlations between molecular structure and material properties, and between material properties and behaviour in practical situations.

Objective 2: is to predict material behaviour in complex flow situations. This requires sophisticated mathematical treatments using data obtained from simple rheological experiments.

Viscosity and rheological measurements can be divided into three classes;

- (i) steady shear flow: for example, tube<sup>(4,6)</sup> and capillary<sup>(7)</sup> viscometry, falling ball viscometry<sup>(8, 9)</sup> and rotational rheometry<sup>(10, 11)</sup> techniques.
- (ii) Oscillatory testing: where the specimen is subjected to an oscillating force or deformation. Such tests can be performed using oscillatory rheometers<sup>(12)</sup> or dynamic mechanical testing<sup>(13)</sup> depending on the physical nature of the material.
- (iii) Transient condition testing: e.g., the variation of deformation with time after a change, usually sudden, of applied stress or the variation in stress after a deformation<sup>(14)</sup>. The magnitude of the deformation is dependent upon the visco-elastic properties of the test sample. These tests can be carried out on equipment used for steady shear flow.

The main methods employed for these three broad classes of rheological measurements will be discussed in the following sections. It must be remembered that the properties of adhesives are likely to be sensitive to rate and temperature. When selecting a rheological technique, consideration must be given to how rate and temperature are to be controlled/monitored.

## 3. SHEAR FLOW MEASUREMENT METHODS

### 3.1. TUBULAR AND SIMPLE CAPILLARY FLOW RHEOMETRY

#### 3.1.1 Theory

If a steady flow is assumed within a constant circular section, it is relatively straightforward to derive equations describing the velocity profile and pressure drop from the fundamental constitutive equations<sup>(1,2,3)</sup>. By measuring the pressure drop  $\Delta P$  as a function of the fluid volumetric flow rate,  $Q$ , it is possible to determine the fluid's behaviour in terms of an apparent viscosity.

Capillary rheometry is used to characterise a fluid's shear flow properties. It also allows an understanding of the way fluids flow in variable cross-section geometries. Fluid flow lies at the centre of all extrusion processes, whether batch or continuous. This includes, for example, the manufacture of plastic pipe and the dispensing of adhesives and other paste and fluid materials, blow

moulding for the production of polymeric films and injection moulding of complex shapes. Raw materials used in manufacture are becoming more complex in terms of their rheology and ever more complex shapes are being produced. Therefore, there is an increasing need to fully understand general flow in a tube and the specific case of capillary flow. It can be assumed that difficulties associated with capillary rheometry are mainly due to the end effects at the entry and exit points of the capillary. Corrections for these end effects and other sources of uncertainty are discussed in Appendix I.

The basic assumptions made are:

- 1) Velocity of the fluid at the capillary wall is zero.
- 2) There is laminar flow.
- 3) Hydrostatic pressure is uniform across any radial section of capillary.
- 4) Fluid flow does not change with respect to time.
- 5) Entrance and exit effects are assumed to be negligible.
- 6) The fluid is incompressible.

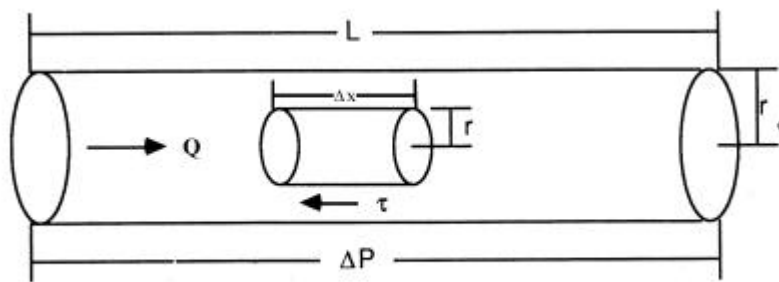


Figure 1: Forces on an element of fluid in tubular flow

Figure 1 shows the forces acting on an element of fluid in laminar, tubular flow. If the fluid is Newtonian then the constitutive relationship is given:

(Equation 1)

$$\tau = \eta \dot{\gamma}$$

where  $\tau$  is the shear stress,  $\eta$  is the Newtonian viscosity and  $\dot{\gamma}$  is the shear rate or velocity gradient of the fluid element.

The shear rate is given, for flow in a tube:

(Equation 2)

$$\dot{\gamma} = \frac{du}{dr} = - \frac{\Delta P}{2L\eta} r$$

Where  $u$  is the velocity at radius  $r$  and  $L$  is the length. Equation 2 shows that the shear rate is zero at the centre of the capillary increasing to a maximum at the wall. Thus, in capillary rheometry the shear rate and shear stresses are not uniform across the section being tested.

The pressure drop  $\Delta P$  can be expressed in terms of the volume flow rate  $Q$ , the capillary length  $L$  and radius  $r_0$ :

(Equation 3)

$$\Delta P = \frac{8hL}{\pi r_0^4} Q \quad \text{or} \quad Q = \frac{\pi r_0^4}{8h} \Delta P$$

A similar procedure can be used for other types of fluids. The constitutive equation for power law fluids is:

$$\tau = K (\dot{\gamma})^n$$

(Equation 4)

where  $K$  and  $n$  are constants. Where  $n = 1$ , this is the Newtonian fluid and  $K$  is the Newtonian viscosity,  $\eta$ .

For Bingham fluids, the constitutive equation is:

$$\tau = \tau_y + \eta \frac{du}{dr}$$

(Equation 5)

where  $\tau_y$  is the yield stress of the fluid. The yield stress implies that the fluid will not flow without the application of a minimum flow stress. In the case of an adhesive, a large yield stress would imply that the adhesive would not spread on its own.

Full derivations of the capillary flow equations from these constitutive equations are given in references 2 and 3.

### 3.1.2 Hydrostatic Head Viscometers

Figure 2 shows three types of hydrostatic head viscometers. These are the most popular and most used viscometers. These viscometers are used for general and high precision measurement of the viscosity of Newtonian fluids.

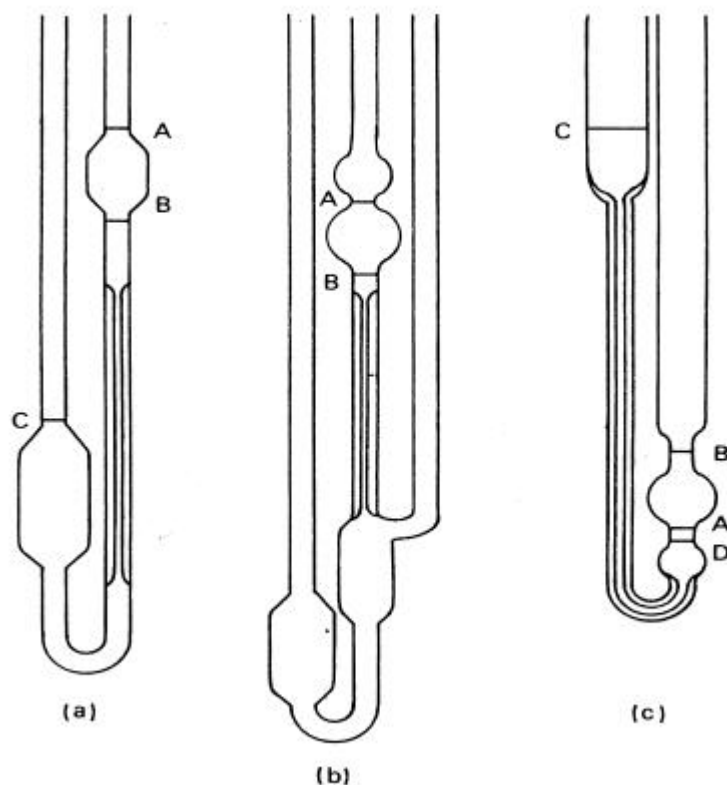


Figure 2: Three typical 'U' tube viscometers, a; Ostwald, b; Ubbelohde and c; reverse flow.

Each of these viscometers relies on measurement of the time for the fluid to fall or rise between marks A and B (which is proportional to the kinematic viscosity) to determine the flow rate,  $Q$ . The pressure drop,  $\Delta P$ , is calculated from the head of fluid. The use of tube viscometers such as these is covered in various standards documents<sup>(4-6)</sup>. These relatively cheap, easy to use viscometers are capable of high reproducibility and repeatability which is a major reason why they are used as secondary standards for the measurement of viscosity.

However, the pressure drops are low. Measurement of the rheology of thick, paste adhesives would be problematic, if not impossible, using such instruments. A further limitation of these types of viscometers is that they are not suitable for measuring the viscosity of non-Newtonian fluids. There are insufficient ranges of shear stress and shear rates available for the measurement of fluids exhibiting behaviour of this nature. For these reasons, hydrostatic head viscometers are unsuitable for the majority of adhesives.

### 3.1.3 Capillary Rheometers

A typical capillary rheometer<sup>(7)</sup> is shown in Figure 3. The type of capillary rheometer shown in Figure 3 uses a mechanical screw to apply the piston pressure. The speed of the piston can be varied thus allowing variable flow and shear rate tests. Internal transducers measure the pressure drop. The temperature of the fluid in the barrel is controlled using the oven. A variation on this instrument is the slit die rheometer where the cylindrical capillary is replaced by a thin rectangular slit. The method of analysis of the flow is similar to that for the capillary technique but the geometrical factors will differ.

This type of instrument is significantly more expensive than simple, non-mechanically driven instruments but benefits from having a wide range of shear rates available. The internal pressure transducers allow pressure measurement close to the capillary and the data can be logged to a chart recorder or PC. As part of the calibration routine for capillary rheometers, the dimensions of the capillary dies should be accurately measured, as indicated by the sensitivity of the measured pressure to the die diameter (equation 3).

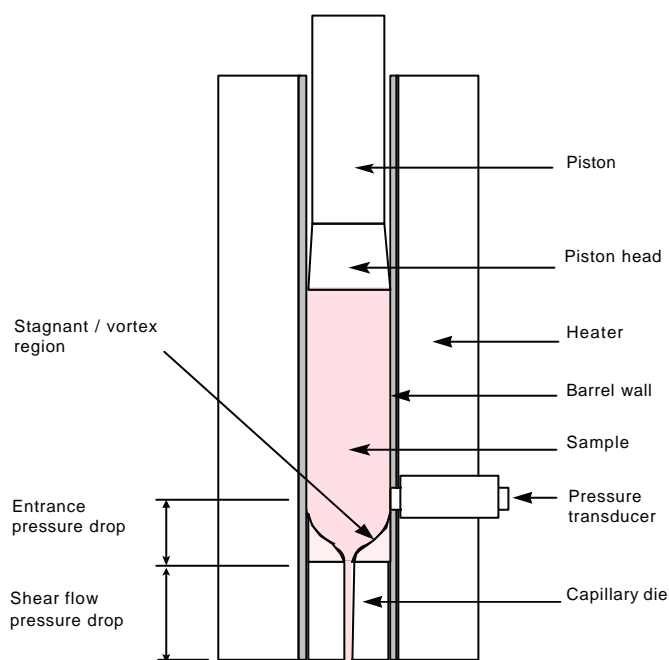


Figure 3: Capillary Rheometer

In less sophisticated types of capillary rheometer, masses are used to apply known pressures to the fluid and the flow rate is measured. Dies can be changed to allow some variation of shear rate. The simplest of this type of rheometer is the flow cup<sup>(1,15)</sup> where flow pressure is supplied by the head of liquid (therefore decreases during the test) and the volume of liquid flowing out is measured. The melt flow index (MFI) test for polymer melts is an example of a single rate test. These systems, although cheap to purchase and simple to operate, do not have the capability to fully characterise viscous or rate dependent adhesives.

Factors influencing the accuracy of capillary flow measurements are discussed in Appendix I.

### 3.2. ROTATIONAL VISCOMETERS

These instruments shear the test fluid between rotating cylinders, cones or plates<sup>(1-3, 10, 16)</sup>. The method of testing has two basic advantages over tube viscometers in that i) a sample can be sheared for as long as required, thus allowing the time dependent behaviour of the fluid to be determined and ii) by use of suitable test geometries, a uniform shear rate can exist through the sample.

However there are some disadvantages. Rotational viscometers are considerably more expensive than 'U' tube systems. High shear rates cannot be achieved without an increase in the sample temperature due to shear heating effects. However, the flow curve can be derived more precisely than by tube viscometry. The measured angular velocity is proportional to the shear rate. Whereas for tube viscometers, the shear rate will vary across the radius of the tube. Rotational rheometers operate by constant stress or constant strain rate control. These control systems are described further in section 4.

The majority of rotational viscometers are based on the rotation of combinations of cylinders (Figure 4a), cones (Figure 4b, 4c, and 4d) or plates (Figure 4e and 4f) about a common axis.

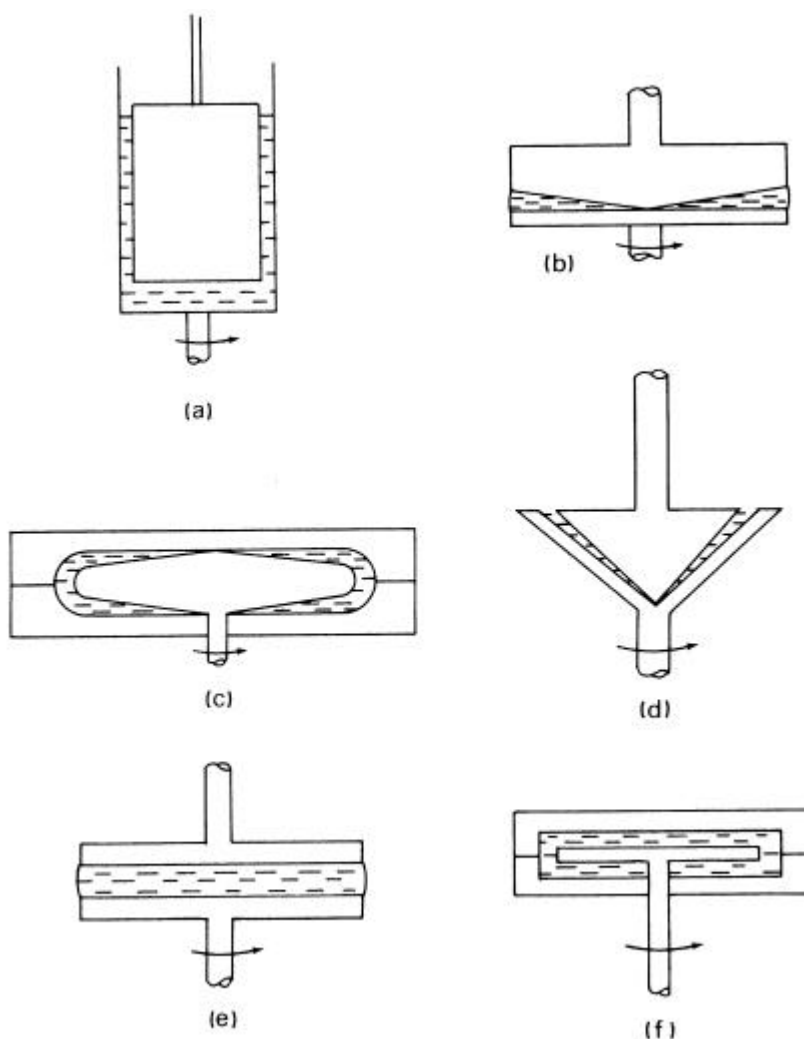


Figure 4: Geometries used for rotational rheometry.

Some of the analysis factors for the most common measurement system geometries are outlined in Appendix II. Additional mathematical solutions for the measurement geometries are given in the TA Instruments rheometer manual<sup>(16)</sup> and by Walters<sup>(1)</sup>. In general, the rheometer's operating manual or analysis software will contain the appropriate correction factors for the instrument's measurement geometries. Inaccuracies in the manufacture or set-up of the measurement geometries can lead to significant errors in the measurements. The measurement geometries should be symmetrical, of precise dimensions and accurately aligned in order to make accurate measurements. Rotational rheometers are generally calibrated using standard reference fluids (although these are of comparatively low viscosity) but it is possible in many instruments to directly calibrate the torque and position sensors.

Early designs of rotational rheometers had several user-set motor speeds and gave an output as a voltage proportional to torque. The operator then used conversion factors pertaining to the measurement geometry and motor speed setting to calculate shear rate and viscosity. With the development of cheap accessible computing, a number of instruments have been developed with computerised control, data acquisition and analysis functions. These provide solutions for qualitative, quality control functions in many industries and quantitative laboratory investigations of fluid properties. There are a large number of manufacturers and suppliers of rotational rheometers. For example Rheometrics, TA Instruments, Bohlin Instruments and Haake all supply this type of rheometer.

For the determination of the shear flow properties of adhesives, pastes and other 'stiff' materials using rotational rheometers, cone and plate geometries are recommended. The measurement gap should be set to allow the free movement of any filler materials in the test material. 'Clogging' problems may occur when solid particles are present and the gap is too small. If the material has a very high viscosity (e.g. bitumens, rubbers or highly filled adhesive pastes) then a small diameter geometry, large measurement gap system is required. This is so that torque limits for the instrument are not exceeded. Specialist testing instruments have been developed for 'stiff' materials (e.g. the Monsanto 2000 range).

A variation of the parallel plate rheometer is a compression instrument. The Wallace Rapid Plastimeter measures the 'viscosity' of unvulcanised rubbers. This instrument uses a modified parallel plate compression technique with automatically timed "conditioning" (pre-loading at 100°C) and loading periods. The test piece, cut from a 3 mm thick sheet, is compressed to a thickness of 1 mm over a period of 15 seconds at 100°C. A compressive force of 100N is then applied for 15 seconds and the final thickness of the sample is a measure of "plasticity" (viscosity).

### 3.3 FALLING BALL VISCOMETRY

The falling ball viscometry method<sup>(8)</sup> is the oldest and simplest viscometry method<sup>(1)</sup>. In this method, the time for the ball to fall a known distance in the fluid is measured and the terminal velocity,  $u$ , is determined. The relationship between viscosity and terminal velocity depends on the constitutive relationship of the liquid. However, shear rates in this test are low and in this region a Newtonian approximation can be used to determine an apparent viscosity ( $\eta$ ) which depends on the difference in density ( $\rho$ ) between the ball and fluid and the radius,  $R$ , of the ball and gravitational constant ( $g$ ):

$$\mathbf{h} = \frac{2(\mathbf{r}_b - \mathbf{r}_f)gR^2}{9u}$$

(Equation 6)

The falling ball technique can be sealed to prevent evaporation or even to permit measurements at high pressure. However, to avoid complex flow patterns there must be a significant gap between the falling ball and the wall which limits the method to materials that have a reasonable degree of transparency. The range of strain rates that can be covered is low. This method is not particularly suitable for rate-dependent, visco-elastic materials such as adhesives. A variation on the falling ball method is the rolling ball method<sup>(9)</sup> where the tube is inclined at known angles and the velocity of the rolling ball measured. As the ball is in contact with the wall even opaque liquids can be measured. Varying the angle of incline allows variation in the shear stress and shear rate. However, analysis of the flow is much more complex.

#### 4. OSCILLATORY RHEOMETERS

Oscillatory measurements on visco-elastic fluids are usually carried out using rotational rheometers<sup>(12)</sup>, for example TA Instruments, Bohlin Instruments or the Rheometrics range of rheometers. Oscillatory instruments fall into two classes; i) constant stress, in which an oscillatory stress of constant amplitude is applied and the resultant displacement amplitude in the material under test is measured and ii) constant strain, in which an oscillatory strain is applied and the torque is constantly monitored.

The two types of instrument are fundamentally different in their approach to the measurement of the rheological properties of materials and both offer specific advantages for different analytical studies.

##### 4.1. CONSTANT STRESS RHEOMETERS

The principal components of a constant stress rheometer are shown in Figure 5a. The angular deformation imparted to the test material in the rheometer is derived from a constant torque direct drive motor attached to the drive shaft with an air bearing. An angular position sensor detects the movement of the measuring system attached to the shaft. This mode of construction allows constant stress rheometers to measure the creep properties of visco-elastic materials.

Manufacturers' software converts the applied value of torque to a shear stress by using the form factor information derived from the physical dimensions of the selected measuring geometry. The reading from the position sensor is converted to strain and strain rate by again using the dimensions of the measurement geometry.

The only data being produced by the rheometer is a deflection reading from the angular position sensor. Hence, it follows that the lowest shear rate achievable is determined only by how long the operator is prepared to wait and the minimum control torque of the drive system. The sensor must turn a measurable amount for the software to calculate a speed and hence a shear rate.

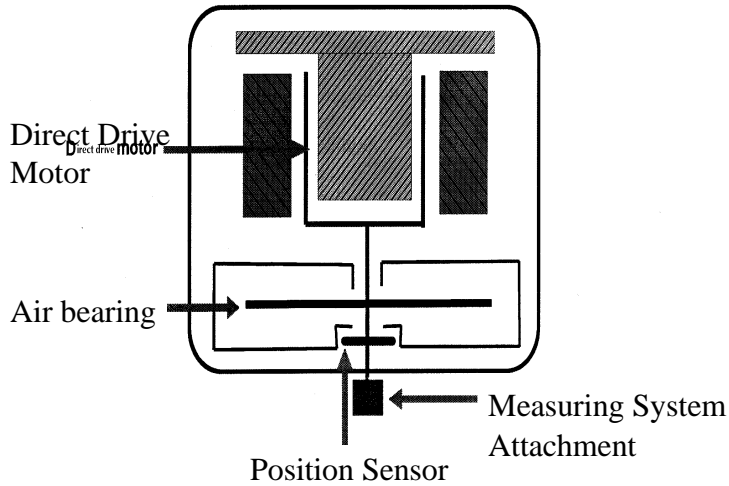


Figure 5a: Components of a controlled stress Rheometer

#### 4.2. CONSTANT STRAIN RHEOMETERS

The basic components that make up a controlled rate rheometer are shown in Figure 5b. The instrument is based around a constant speed motor with a torque detection system.

As the drive system rotates at a controlled angular velocity, the sample resistance (viscosity/elasticity) twists the torsion bar. By measuring the resultant rotation and knowing the stiffness of the bar, the torque is measured. Software supplied with the instrument automatically converts the measured torque to a shear stress when displaying data.

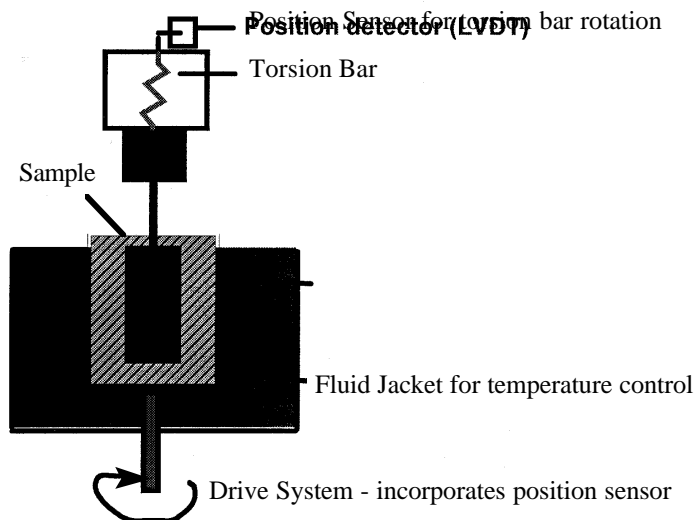


Figure 5b: Basic components of a constant strain rheometer

This system allows a feedback loop from the position detector to the motor constantly updating the applied oscillatory displacement to maintain a constant strain. Elasticity effects, so-called normal

forces which act in the direction perpendicular to the rotational axis, are also monitored. A further development of both constant stress and constant strain rheometers is their ability to input a complex oscillatory waveform composed of a number of selected test frequencies. This allows a frequency sweep of the visco-elastic behaviour of a test material to be performed in a single experimental run.

With increasing processor speed of the controlling computer, the basic distinctions between these instruments are becoming increasingly blurred. Most instruments will now work in pseudo constant strain or pseudo constant stress modes under computer control. Only for the very complex analysis of materials is there a specific need for a specific type of instrument.

#### 4.3 THEORY OF OSCILLATORY RHEOMETRY.

The basic principles of operation of the oscillation technique for measuring the mechanical or rheological properties of visco-elastic materials whether it be for constant strain or constant stress instruments are quite simple. The description of an ideal viscous fluid behaviour is Newton's Law:

$$\text{Stress} = \text{viscosity} \times \text{shear strain rate} \quad \tau = \eta \dot{\gamma} \quad (\text{Equation 7})$$

The description of a perfect elastic solid behaviour is described by Hooke's Law:

$$\text{Stress} = \text{elasticity} \times \text{strain} \quad t = Gg \quad (\text{Equation 8})$$

If a sinusoidal stress is applied then, from Hooke's Law, stress is proportional to strain. A sinusoidal stress wave applied to an ideal elastic will produce a sinusoidal strain wave completely in phase, Figure 6.

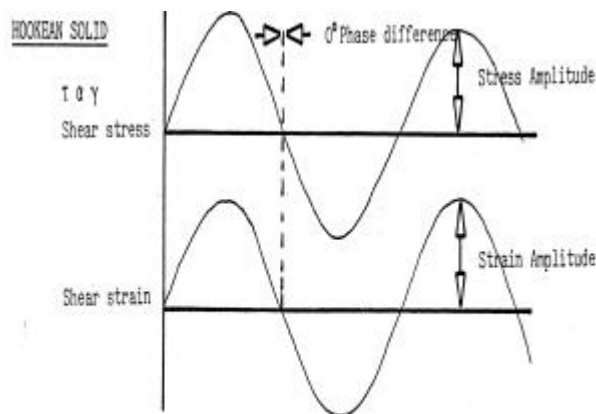


Figure 6: Strain response of a solid

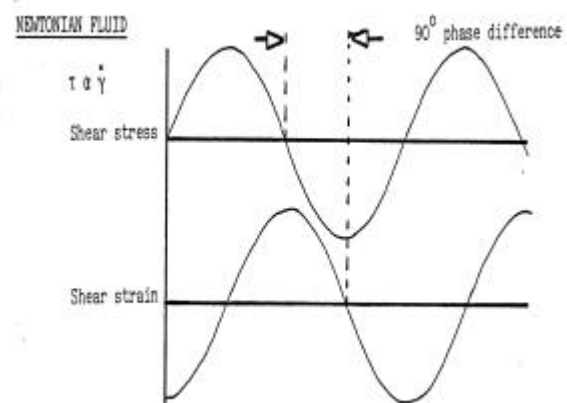
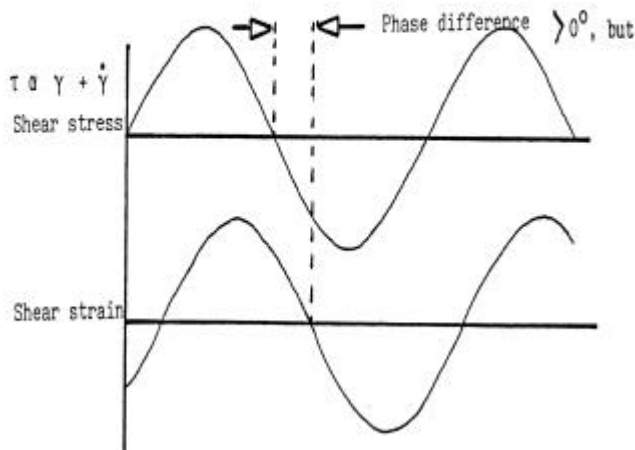


Figure 7: Strain response of a Newtonian liquid

For a Newtonian fluid, if a sinusoidal stress wave is applied then the resultant strain wave will be out of phase by 90°, as the stress is proportional to the strain rate (the differential of the strain). Therefore, when the stress is at a maximum, the shear rate (or strain rate) is also at a maximum. Therefore the stress maximum will coincide with the zero crossing point of the strain wave. Thus the stress and strain maxima are 90° apart, Figure 7.

The elastic solid and a Newtonian liquid represent limiting cases. For a visco-elastic material, the phase difference is greater than zero but less than  $90^\circ$ . Figure 8.

VISCO-ELASTIC MATERIAL



$$\mathbf{t}^* = \mathbf{t}_0 \exp(i\omega t)$$

(Equation 9)

$$\mathbf{g}^* = \mathbf{g}_0 \exp(i\omega t - \mathbf{d})$$

(Equation 10)

Figure 2: Strain response of a visco-elastic material

The complex modulus,  $G^* = \frac{\mathbf{t}^*}{\mathbf{g}^*}$  can be expressed as  $G^* = G' + G''$  (Equation 11)

where the elastic (storage) modulus,  $G' = \frac{\mathbf{t}_0}{\mathbf{g}_0} \cos(\mathbf{d})$  (Equation 12)

and

the viscous (loss) modulus,  $G'' = \frac{\mathbf{t}_0}{\mathbf{g}_0} \sin(\mathbf{d})$ . (Equation 13)

From these definitions, the phase difference,  $\delta$ , can be expressed,  $\tan(\mathbf{d}) = \frac{G''}{G'}$ .

Oscillatory tests, whether using a controlled strain or a controlled stress machine, measure or control the stress amplitude,  $\tau_0$ , strain amplitude,  $\gamma_0$ , and phase difference,  $\delta$ . From these the storage and loss moduli can be determined.

Oscillatory tests can be performed at different frequencies and amplitudes. The oscillation frequency ( $\omega$ ) can be related to shear strain rate ( $\dot{\mathbf{g}}$ ) and these tests can be used to explore the rate dependence of the visco-elastic properties<sup>(13)</sup>. The amplitude of the oscillation will also influence the moduli measured as stress-strain curves of visco-elastic materials are non-linear. However, in the low strain amplitude region the behaviour can be assumed to be linear visco-elastic and independent of amplitude.

Oscillatory tests separate the elastic and viscous responses of the material. This separation of these components allows for the determination of properties for applications such as hydraulic damping.

Oscillatory rheometry is analogous to dynamic mechanical testing for solids. Since strain amplitudes are small, the internal structure of the material will be little disturbed during testing. This fact makes oscillatory testing useful for studying the development of properties over significant periods of time (e.g. when curing an adhesive<sup>(17)</sup>).

One potential source of error in this type of test arises from the compliance of the measurement instrument. When testing ‘stiff’ materials where large torques are needed, a significant proportion of the deformation measured may occur in the shaft of the rheometer rather than in the specimen. The measurements will underestimate the stiffness properties  $G'$  and  $G''$ . Methods for determining instrument compliance and applying corrections have been developed to improve the accuracy of oscillatory tests<sup>(17)</sup>.

## 5. TRANSIENT TESTING

Testing of this nature is usually carried out on ‘stiffer’ materials, materials with a storage modulus of approximately 1 GPa. Several types of rheometer have the capability of performing transient tests. As mentioned in Section 4, constant stress rheometers are capable of creep testing and constant strain rheometers can be used for stress relaxation tests. Creep testing involves measuring the time-dependent strain response of a specimen subjected to a constant static load. Stress relaxation testing involves measuring the load response of a specimen subjected to a constant strain<sup>(14)</sup>. In using rotational rheometers for transient testing, the same types of measurement geometry as outlined in section 3.2 can be used. However, as transient tests are normally concerned with higher stiffness materials the parallel plate geometry is normally preferred.

In creep tests, the creep compliance,  $J(t) = \frac{\mathbf{g}(t)}{\mathbf{t}}$ , (Equation 14) is measured. In stress relaxation tests, the relaxation modulus,  $G(t) = \frac{\mathbf{t}(t)}{\mathbf{g}}$ , (equation 15) is determined. The creep compliance and relaxation moduli are related through a convolution integral:

$$\int_0^t G(t-u)J(u)du = t$$

(Equation 16)

In the limits  $t \rightarrow 0$  and  $t \rightarrow \infty$ ,  $G(t) \rightarrow \frac{1}{J(t)}$  but in general  $G(t) \neq \frac{1}{J(t)}$  (Equation 17).

Transient tests allow data on the time-dependence of shear properties to be obtained over many orders of magnitude of time.

## 6. ROUND ROBIN INTERCOMPARISONS OF RHEOMETRY METHODS

Two intercomparison exercises have been recently completed:

1. Round robin for parallel plate oscillatory rheometry<sup>(18)</sup>
  2. Capillary extrusion rheometry intercomparison<sup>(19)</sup>
- 1) The round robin for parallel plate oscillatory rheometry<sup>(18)</sup> was based on the standard ISO 6721-10:1997 - Plastics, Determination of dynamic mechanical properties, Part 10:Complex shear viscosity using a parallel plate rheometer<sup>(12)</sup>. Time sweep and strain sweep measurements were carried out to determine the duration of thermal stability of the sample and the limiting strain for linear visco-elasticity. Measurements to determine the frequency response of the materials were also performed. Repeatability and reproducibility at selected frequencies were determined for the storage modulus  $G'$  and loss modulus  $G''$ . The repeatability of measurements for the HDPE and PP materials was in the range 4 - 8%, and the reproducibility was in the range 21 - 32%, at the 95% confidence level.
  - 2) The round robin for capillary extrusion<sup>(19)</sup> was based on the use of the standard ISO 11443:1995 - Plastics, Determination of the fluidity of plastics using capillary and slit-die rheometers<sup>(7)</sup>. The repeatability of measurements of shear viscosity of high density polyethylene, HDPE and glass fibre filled polypropylene, GFPP, was in the range 20 - 24%, and the reproducibility 27 - 35%, 95% confidence level. The repeatability of measurements of extrusion pressure was in the range 20 - 38%. The reproducibility of measurements of entrance pressure drop was 42 - 56%. In all cases the GFPP had values that were at the upper end of these ranges whereas HDPE had values at the lower end. Analysis of the uncertainties in the measurement method, using the specification of the standard, indicated that the uncertainties were in the range 2.5 - 19% depending on the test conditions used. The analysis indicated that a potentially large contribution to the uncertainty level was due to the use of the pressure transducer. If used in the lower part of its range, it could potentially contribute significantly to the overall level of uncertainty.

## 7. CONCLUSIONS

The large range of equipment available means that it is possible to select a measurement system that is suited to determine the 'apparent' viscosity of almost any material. However, adhesives do not generally have simple Newtonian behaviour. Many of the less expensive viscometry methods (such as U-tube viscometers, flow cups or falling ball) do not have sufficient ranges of flow stress or shear rate to perform adequate characterisation. Capillary or rotational rheometers<sup>(20)</sup> have the capability to characterise the viscosity of the adhesive over wide ranges of shear rate and, therefore, will generate much more useable data.

Oscillatory methods enable measurements of both elastic and viscous properties of the fluid and therefore give a much more complete characterisation of material properties. They are more suitable for 'stiff' materials such as adhesive pastes. Oscillatory measurements have the capability of measuring changes occurring in the properties of the adhesive (e.g. during cure). However, instruments with oscillatory capabilities tend to be more expensive than simple rotational

viscometers. Transient measurements, such as creep or stress relaxation, are only really applicable for the study of extremely slow rate behaviour.

As the round robin exercises have shown, great care is required in interpreting rheological data obtained from capillary and rotational instruments. Factors such as the parallelism of the plate geometries in rotational rheometers can introduce an error of up to 50% depending upon the selected measurement gap. In capillary rheometry, difficulties in accurate pressure measurement coupled with poor selection of the range of the pressure transducer can lead to significant errors in measurements.

As a general conclusion, it is best to use a measurement method which most closely approximates the processes that the adhesive will experience. Where this is not possible, the measurement method employed should use comparable strain rates and temperatures. The main features of each measurement technique are summarised in Appendix III.

## **8. ACKNOWLEDGEMENTS**

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## APPENDIX 1: CORRECTIONS FOR CAPILLARY RHEOMETRY

The basic quantities measured in capillary flow rheometers are volumetric flow rate and pressure drop. However, there are a number of differences between practical instruments and the idealised flow situations described by the various capillary flow equations. To address these differences, a number of correction methods have been devised. These are outlined in this Appendix.

### I.1 ENTRY FLOW CORRECTION

It is common to use the Bagley correction<sup>(7)</sup> to remove the effect of the pressure drop at the entry point of the capillary. This requires measuring the pressure drop,  $\Delta P$ , for a number of capillary lengths,  $L$ , and radii,  $r_o$ , at selected values of the shear rate (determined at the capillary wall). Plots of the form shown in Figure I.1 ( $\Delta P$  against  $L/r_o$ ) are derived and the entry pressure drop,  $\Delta P_{ent}$ , is simply the intercept on the y axis.

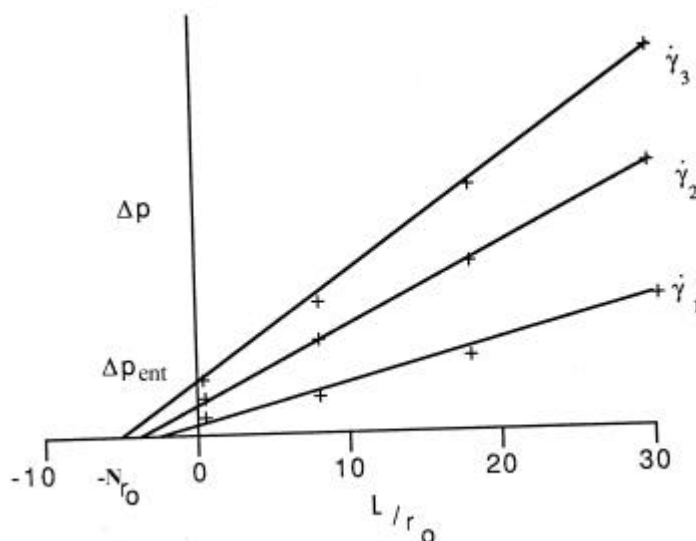


Figure I.1: Entry pressure drop as a function of capillary length for a number of shear rates.

It can also be assumed that the entry pressure drop is equivalent to an additional section of capillary, of length,  $N$  and radius,  $r_o$ . The intercept ( $\Delta P = 0$ ) on the x axis from Figure I.1 yields the value of  $N$  for the given shear rate curve. However, the simple correction to obtain the true pressure drop along the length of the die,  $\Delta P_{true}$ , is to subtract  $\Delta P_{ent}$  from the measured pressure drop  $\Delta P$ .

$N$  and  $\Delta P_{ent}$  are functions of flow rate, temperature and geometry. The use of twin barrel rheometers, such as the range manufactured by Rosand, in which one barrel is set for the zero  $L/r_o$  condition permits the immediate correction for the entry pressure drop term and thus allows the 'true' capillary pressure drop to be determined.

In the special case of Newtonian fluids, the Couette correction can be applied. It is assumed that the effective length of a tube of radius  $a$ , is approximately  $0.6a$  greater than its physical length. Thus

by selecting a suitable tube length to radius ratio, this correction can be set below 1%. However it must be mentioned that for non-Newtonian fluids this error can be much larger.

## I.2 KINETIC ENERGY CORRECTION

The kinetic energy correction is normally only of any significance for low viscosity liquids. It allows correction for the part of the work imparted by the applied pressure that is converted to kinetic energy of the fluid emerging from the tube.

For the special case of 'U' tube viscometers, widely used for testing "Newtonian" fluids at high precision, the correction term can be applied:

$$Q = \frac{\rho r^4}{8\eta L} (\Delta P - \alpha \rho u^2)$$

Equation I.1

where	$v$ = mean velocity of the fluid	$Q$ = volume flow rate
	$\alpha$ = is a correction factor	$\Delta P$ = pressure drop
	$\rho$ = fluid density	$\eta$ = viscosity
	$L$ = length of capillary	$r$ = capillary radius

Standards specify that flow times through the viscometer should be extended to make the correction term negligible.

## I.3 PISTON FRICTION AND BARREL CORRECTION

In measuring 'stiff' fluids some instruments hold the fluid in a barrel and use a piston to force the material through the capillary. If the measured force on the piston is used to calculate the extrusion pressure, then the friction between the piston and the barrel wall is not accounted for leading to errors in the pressure drop determined for the capillary. If a pressure transducer is mounted close to the capillary entrance then the piston friction effect is avoided.

A barrel correction is required if the capillary length is short with respect to the barrel or the radii of the barrel and die are similar. This correction is for the pressure drop in the barrel between the die and the pressure transducer. For example, for a Newtonian fluid, the pressure drop per unit length is proportional to  $1/r^4$ , if the barrel radius is an order of magnitude greater than that of the capillary, (10:1), then the pressure drop per unit length in the capillary is 10,000 times greater than that in the barrel and the correction is negligible. However for power law fluids and more complex materials this pressure difference may be reduced significantly. For example, Equation I.2 describes the situation for a power law fluid;

$$\Delta P = 2LK \left( \frac{(3n+1)}{pnr_b^{(3n+1)/n}} \right)^n Q^n$$

Equation I.2

where  $K$  = viscosity constant (=  $\eta$  when  $n = 1$ )  
 $r_b$  = radius of barrel between the die and the pressure transducer  
 $n$  = power index ( $n = 1$  implies Newtonian fluid)

Thus  $\Delta P \propto r_o^{-(3n+1)}$ . If  $n = 1/3$ , then  $\Delta P$  is proportional to  $\frac{1}{r_o^2}$ . Therefore the corresponding pressure gradient ratio is much smaller, and the error due to the pressure drop in the barrel is significant.

If the form of the flow law governing the fluid under test is known, then it is possible to estimate the barrel correction by treating the barrel as another viscometer capillary.

#### I.4 WORK INDUCED TEMPERATURE INCREASES IN CAPILLARY VISCOMETERS

Work applied to a viscous fluid will be dissipated as heat, leading to a rise in temperature of the material being tested. Since the visco-elastic properties of polymeric materials are temperature sensitive, any flow induced heating will lead to errors in the determination of the rheological properties. To estimate the temperature increase, the following approach can be followed. The work done per second, for a pressure drop,  $\Delta P$ , producing a volume flow of  $Q$  is  $\Delta PQ$ . Therefore it follows that the temperature increase  $\Delta T$  is given by:

$$\Delta T = \frac{\Delta PQ}{rQC_v} = \frac{\Delta P}{rC_v}$$

Equation I.3

where  $\rho$  = density  
and  $C_v$  = specific heat capacity.

Typical values for a polymer are  $r \approx 1000 \text{ kg m}^{-3}$  and  $C_v \approx 2000 \text{ J kg}^{-1} \text{ K}^{-1}$

For a change in temperature ( $\Delta T$ ) around  $1^\circ\text{C}$ , the pressure drop ( $\Delta P$ ) would be  $\approx 2 \text{ MPa}$  which is approximately 20 times atmospheric pressure. Thus for pressures below 20 atmospheres, temperature changes will be small and may be neglected.

#### I.5 PRESSURE EFFECTS

Increasing the pressure of a fluid will lead to increased viscosities. Where adhesives are dispensed at low pressures, the increase in adhesive viscosity may be negligible. However, where pressures are high, there may be significant effects. Denn<sup>(1b)</sup> considered a Newtonian fluid with a pressure dependence of viscosity given by an Arrhenius type equation

$$\eta = \eta_0 e^{\beta P}$$

Equation I.4

where  $\eta$  = viscosity at pressure P  
 $\eta_0$  = viscosity at atmospheric pressure  
P = pressure  
 $\beta$  = pressure coefficient of viscosity.

Approximate solutions for the dependence of the viscosity on pressure have been derived<sup>(1b)</sup> for Newtonian and non-Newtonian fluids. Adiabatic flow with temperature and pressure dependent viscosity can be represented by Equation I.5:

$$\eta = \eta_0 e^{\beta P} e^{-\alpha(T - T_1)}$$

Equation I.5

where  $T_1$  = reference temperature  
T = temperature  
 $\alpha$  = temperature viscosity coefficient

Viscosity increases with pressure and this should be considered when determining the rheology of the adhesive using capillary techniques where there may be large pressure drops, or for adhesive applications where high pressures will be experienced. Most other measurement techniques, for example rotational rheometry, do not operate at elevated pressures.

In most likely adhesive applications, such as dispensing or extruding, the applied pressures will be relatively low. Pressure dependence of viscosity tends to have more significant influence during high pressure processes such as injection moulding. In a study of the pressure dependence of polymer melt viscosities, Chakravorty et al<sup>(1c)</sup> showed that viscosities of polystyrene melts increased by 200-300 % between atmospheric pressure and 70 MPa. This was in agreement with published results showing increases of 400-500 % for pressures up to 125 MPa.

## I.6 ADDITIONAL REFERENCES

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## APPENDIX II: GEOMETRICAL FACTORS IN ROTATIONAL RHEOMETRY

The rheological properties of the test material are calculated from the shear rate and stress factors which can be calculated for the various test geometries<sup>(1-3, 16)</sup>. This Appendix outlines how the stress and shear rate factors are calculated for the most popular geometries used in rheological measurements.

The following notation is used

Shear Strain =  $\gamma$

Shear rate =  $\dot{\gamma}$

Shear stress factor =  $F_\tau$

Shear rate or shear strain factor =  $F_{\dot{\gamma}}$

Torque =  $T$  (N.m)

Angular Displacement =  $\omega$  (rad)

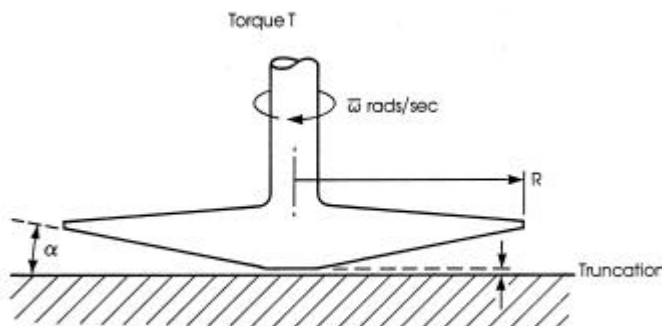
Angular velocity =  $\bar{\omega}$  (rad/sec)

Cone angle (radians) =  $\alpha$

Component radius =  $R_1... R_2... (m)$

Immersed (shear effective) height of component =  $H$  (m)

### II.1 CONE AND PLATE GEOMETRY



$$\text{Shear rate (s}^{-1}\text{)} = F_{\dot{\gamma}} \times \bar{\omega}$$

$$\text{where } F_{\dot{\gamma}} = \frac{1}{\tan \alpha}$$

Equation II.1

$$\text{Shear Stress (Nm}^{-2}\text{)} = F_\tau T$$

$$\text{where } F_\tau = \frac{3}{3} p R^3$$

Equation II.2

Figure II.1: Cone and plate geometry

## II.2 PARALLEL PLATE GEOMETRY

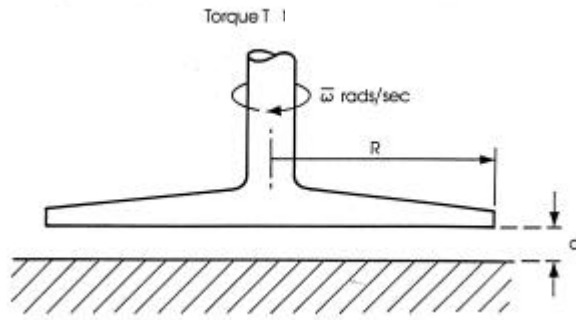


Figure II.2: Parallel plate geometry

Stress can be calculated explicitly as a function of the radius:

$$\mathbf{t}_r = \frac{2T}{pR^3} \left[ \frac{3}{4} + \frac{1}{4} \frac{d \ln \left( \frac{2T}{pR^3} \right)}{d \ln (\mathbf{g} \times r)} \right]$$

Equation II.6

The parallel plate system provides a convenient solution to problems involving stiff materials for which neither a cone and plate nor a concentric cylinder system may be quite suitable. Adjustment of the shear gap,  $d$ , overcomes 'clogging' problems where solid particles may be present, and has the added advantage of increasing the strain range of the instrument, when used in the creep or oscillation modes.

$$\text{Strain } \gamma = F_\gamma \mathbf{w}$$

$$\text{where } F_\gamma = \frac{R}{d} = F_{\dot{\mathbf{g}}}$$

and  $\mathbf{w}$  = angular displacement

Equation II.3

$$\text{Shear rate, } (\dot{\mathbf{g}})_{S^{-1}} = F_{\dot{\mathbf{g}}} \times \bar{\mathbf{w}}$$

Equation II.4

Shear stress ( $\tau$ ) in  $\text{Nm}^2 = F_\tau T$  where

$$F_\tau = \frac{2}{\pi R^3}$$

Equation II.5

The above formulae apply to conditions at the rim.

### II.3 RECESSED CONCENTRIC CYLINDER

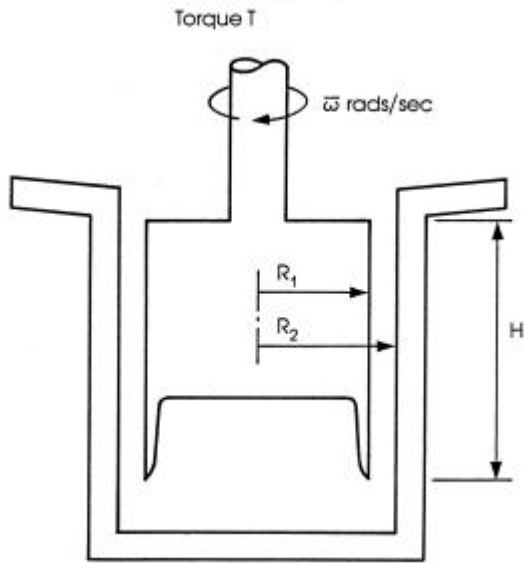


Figure II.3: Recessed concentric cylinder

Assuming no end effects

$$\text{Shear rate (s}^{-1}\text{)} = F_{\dot{\gamma}} \times \bar{\omega}$$

$$\text{where } F_{\dot{\gamma}} = \frac{R_2^2 + R_1^2}{R_2^2 - R_1^2}$$

Equation II.7

$$\text{Shear Stress (N m}^{-2}\text{)} = F_t \times T$$

$$\text{where } F_t = \frac{R_2^2 - R_1^2}{4\pi \times H \times R_2^2 \times R_1^2}$$

Equation II.8

### II.4 CONCENTRIC CYLINDER WITH CONE AND PLATE END

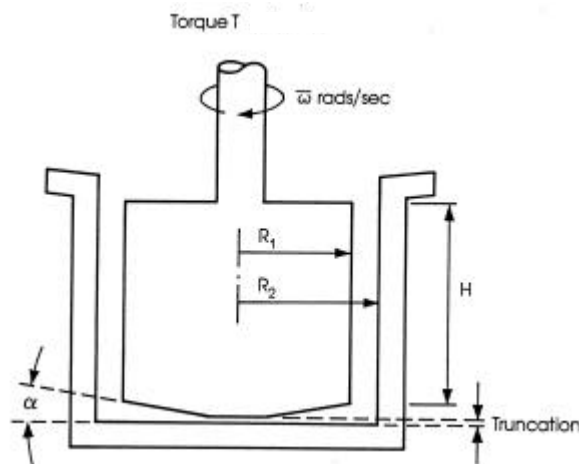


Figure II.4: Recessed concentric cylinder with cone and plate end - Mooney-Ewart geometry

In order to achieve corresponding shear rate conditions the angle of the conical section must so adjusted that:

$$\frac{1}{\tan \alpha} = \frac{R_2^2 + R_1^2}{R_2^2 - R_1^2} = F_{\dot{\gamma}}$$

and

$$\text{Shear rate (s}^{-1}\text{)} = F_{\dot{\gamma}} \times \bar{\omega}$$

Equation II.9

Shear stress calculations combine  $F_t$  for the cone and for the cylindrical sections in the formula

$$F_t \text{ (Mooney)} = \frac{F_t \text{ (cone)}}{F_t \text{ (cone)} + F_t \text{ (cylinder)}} \times F_t \text{ (cylinder)}$$

Equation II.10

From which: resultant shear stress (Nm<sup>2</sup>) =  $F_t$  (Mooney) x T

$F_t$  (cone) is calculated from Equation II.2,  $F_t$  (cylinder) is calculated from Equation II.8.

### APPENDIX III SUMMARY OF MEASUREMENT TECHNIQUES

Technique	Advantages	Disadvantages	Typical Measurement Ranges	Cost
Hydrostatic Head Viscometers (including flow cups and MFI)	<ul style="list-style-type: none"> <li>• Accurate;</li> <li>• Simple to perform;</li> <li>• Small, portable equipment;</li> <li>• Used for quality control;</li> <li>• Standardised</li> </ul>	<ul style="list-style-type: none"> <li>• Limited range of strain rates;</li> <li>• Simple tube viscometers limited to low viscosity liquids;</li> <li>• Flow corrections required;</li> <li>• Large samples sizes;</li> </ul>	<ul style="list-style-type: none"> <li>• low flow rates &amp; strain rates;</li> <li>• low viscosities (simple tube viscometers &lt; 0.1 PaS);</li> </ul>	Low to Medium
Capillary Viscometers (mechanically driven, incorporating differential pressure measurements)	<ul style="list-style-type: none"> <li>• Accurate;</li> <li>• Strain rates can be controlled;</li> <li>• High strain rates;</li> <li>• Flow similar to extrusion;</li> <li>• Quality control and research;</li> </ul>	<ul style="list-style-type: none"> <li>• Flow corrections required;</li> <li>• Entrance/exit effects;</li> <li>• Trained operators needed;</li> <li>• Large sample sizes;</li> <li>• Equipment tends to be large;</li> <li>• Shear heating at high rates;</li> </ul>	<ul style="list-style-type: none"> <li>• low - high strain rates (0.1 to <math>10^6 \text{ s}^{-1}</math>);</li> <li>• medium - high viscosity (1 to <math>10^8 \text{ PaS}</math>)</li> </ul>	High
Falling Ball Viscometry	<ul style="list-style-type: none"> <li>• Cheap;</li> <li>• Simple to Perform;</li> <li>• Used for quality control;</li> <li>• Standardised</li> </ul>	<ul style="list-style-type: none"> <li>• Low accuracy;</li> <li>• Limited range of strain rates;</li> <li>• Flow difficult to analyse;</li> <li>• Not suitable for opaque materials;</li> </ul>	<ul style="list-style-type: none"> <li>• low speeds (&lt; 5 <math>\text{mms}^{-1}</math>);</li> <li>• low - medium viscosities (&lt; 100 PaS);</li> </ul>	Low
Rotational Viscometry	<ul style="list-style-type: none"> <li>• Accurate;</li> <li>• Small sample size;</li> <li>• Strain rates can be controlled;</li> <li>• Measurement geometries can be selected to suit material;</li> <li>• Quality control and research;</li> <li>• Time dependence of properties can be measured;</li> <li>• Standardised;</li> </ul>	<ul style="list-style-type: none"> <li>• Strain rates may not be constant across geometry;</li> <li>• Edge effects;</li> <li>• Test may alter sample properties;</li> <li>• Low instrument compliance may be a problem with high viscosity materials;</li> <li>• Shear heating at high rates;</li> </ul>	<ul style="list-style-type: none"> <li>• strain rates 0.001 to <math>10^4 \text{ s}^{-1}</math>;</li> <li>• low - high viscosities (<math>10^{-4}</math> to <math>10^9 \text{ PaS}</math>);</li> </ul>	Medium to High

Technique	Advantages	Disadvantages	Typical Measurement Ranges	Cost
Oscillatory Viscometry	<ul style="list-style-type: none"> <li>• Accurate;</li> <li>• Small sample size;</li> <li>• Frequencies can be controlled;</li> <li>• Viscous and Elastic properties;</li> <li>• Quality control and research;</li> <li>• Measure changes in properties (eg cure);</li> <li>• Standardised;</li> <li>• Instruments normally versatile (eg. based on rotational rheometers)</li> </ul>	<ul style="list-style-type: none"> <li>• Usually limited to low strains;</li> <li>• More complex measurement;</li> <li>• Interpretation of data required;</li> <li>• Low instrument compliance may be a problem with high viscosity materials;</li> <li>• Edge effects</li> </ul>	<ul style="list-style-type: none"> <li>• frequency range typically 0.01 - 100 Hz;</li> <li>• medium - high viscosities/modulus (0.1 to 10<sup>9</sup> PaS);</li> </ul>	High
Transient Techniques	<ul style="list-style-type: none"> <li>• Long time/low rate measurements;</li> <li>• Spreading phenomena;</li> <li>• Research measurements;</li> </ul>	<ul style="list-style-type: none"> <li>• Applicable only to long time properties;</li> <li>• Long test times required;</li> <li>• Data interpretation can be complex;</li> <li>• Lack of standards;</li> </ul>	<ul style="list-style-type: none"> <li>• times from 1s, strain rates &lt; 0.01 s<sup>-1</sup></li> <li>• normally medium - high viscosities</li> </ul>	Low to High

Cost: Low = < £1,000; Medium = £1,000 to £10,000; High = > £10,000