BOHLIN INSTRUMENTS

A BASIC INTRODUCTION TO RHEOLOGY

Part No MAN0334 Issue 2

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Section 1 - Introduction to rheology

This gives a brief introduction to the basic terms and definitions encountered in rheology.

Section 2 - Selecting measuring geometries

This covers the selection of measuring geometries.

Section 3 - Flow characterisation

Covers viscometry tests, flow curves and rheological models. Time and temperature dependence are looked at as sources of rheological error.

Section 4 - Creep analysis

Looks at the creep test.

Section 5 - Viscoelastic characterisation

Covers oscillatory, relaxation and stress growth tests.

Appendix-A - Some practical applications of rheology

Contains various practical applications / equations.

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References & Bibliography- A list further reading material.

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Shear rate and shear stress form factors.

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SECTION 1 - INTRODUCTION TO RHEOLOGY

(A) Simple deformation under an applied constant force (Hookean response)

To define the term STRAIN we will consider a cube of material with its base fixed to a surface (See Figure-1).

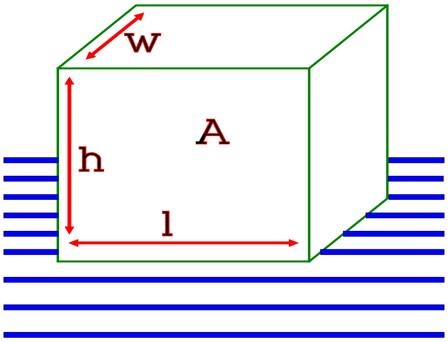


Figure-1

If we now apply a constant 'pushing' force, F, to the upper part of the cube, assuming the material behaves as an ideal solid, it will obey Hooke's law of elastic deformation and will deform to a new position (Figure-2)

This type of deformation (lower fixed, upper moving) is defined as a SHEAR DEFORMATION.

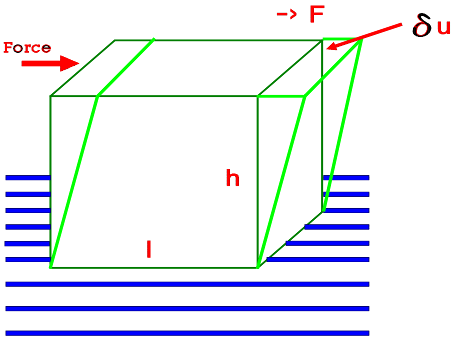


Figure-2

The deformation δu and h are used to define the SHEAR STRAIN as :

Shear Strain = δu/h

The shear strain is simply a ratio of two lengths and so has no units. It is important since it enables us to quote pre-defined deformations without having to specify sizes of sample, etc.

The SHEAR STRESS is defined as F/A (A is the area of the upper surface of the cube l x w) Since the units of force are Newtons and the units of area are m^2 it follows that the units of Shear Stress are N/m^2 This is referred to as the PASCAL (i.e. 1 N/m^2 = 1 Pascal) and is denoted by the symbol σ (in older textbooks you may see it denoted as τ).

For a purely elastic material Hooke's law states that the stress is proportional to the strain i.e.

Stress = G x Strain where G is defined as the SHEAR MODULUS (a constant)

Thus doubling the stress would double the strain i.e. the material is behaving with a LINEAR RESPONSE. If the stress is removed, the strain returns instantaneously (assuming no inertia) to zero i.e. the material has undergone a fully recoverable deformation and so NO FLOW HAS OCCURRED.

This Hookean behaviour is analogous to a mechanical spring which stretches when a weight is suspended from it (see Figure-3).

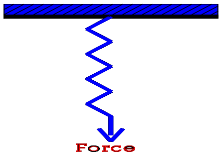


Figure-3

(B) Simple flow under an applied constant shear stress (Newtonian response)

Let us again consider the case of the cube of material as described above but in this case assume that the material behaves as an ideal fluid. When we apply the shear stress (force) the material will deform as before but in this case the deformation will continually increase at a constant rate (Figure-4).

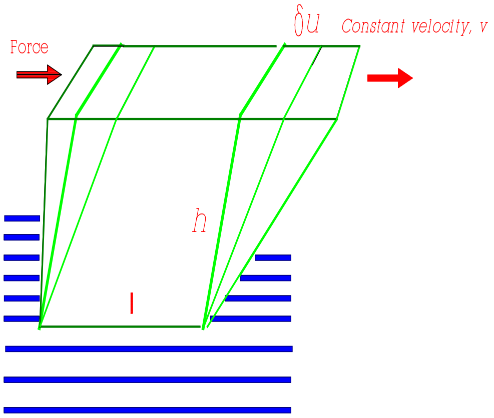


Figure-4

$$\gamma = \frac{\delta u \times 1}{h \times S}$$

The rate of change of strain is referred to as the SHEAR STRAIN RATE often abbreviated to SHEAR RATE and is found by the rate of change of strain as a function of time i.e. the differential δ.SHEAR STRAIN / δ .TIME.

The Shear Rate obtained from an applied Shear Stress will be dependant upon the material's resistance to flow i.e. its VISCOSITY.

Since the flow resistance ≡ force / displacement it follows that ;

VISCOSITY = SHEAR STRESS / SHEAR RATE $\eta = \frac{\sigma}{\gamma}$

The units of viscosity are $Nm^{-2}S$ and are known as Pascal Seconds (Pas).

If a material has a viscosity which is independent of shear stress, then it is referred to as an ideal or NEWTONIAN fluid. The mechanical analogue of a Newtonian fluid is a viscous dashpot which moves at a constant rate when a load is applied (see Figure-5).

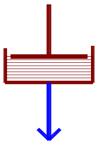


Figure-5

Although the definitions covered so far are based on applying a shear stress and measuring the resultant shear rate, the viscosity is simply the ratio of the one to the other, thus it follows that we will obtain the same answer for viscosity no matter which we apply and which we measure.

In theory therefore it does not matter if the instrument you are using (rheometer or viscometer) is controlled shear rate or controlled shear stress, you will still be able to measure the same flow characteristics. In practice however there are sometimes good reasons for using one type in preference to the other and a well equipped rheological laboratory should have access to both types of instrument.

Throughout this guide, I will try out show the good and bad points to both measurement techniques.

SUMMARY OF TERMS

Shear stress	= Force / Area (NM^{-2} or Pascal, Pa)	σ
Shear strain	= δu / h (Simple ratio and so No units)	
Shear rate	= d.Shear strain / d.Time	γ
Viscosity	= Shear stress / Shear rate ($NM^{-2}S$ or Pascal Second, Pas)	η

TYPICAL SHEAR RATE'S FOR SOME STANDARD PROCESSES

Process	Typical range (S^{-1})
Spraying	10^4 - 10^5
Rubbing	10^4 - 10^5
Curtain coating	10^2 - 10^3
Mixing	10^1 - 10^3
Stirring	10^1 - 10^3
Brushing	10^1 - 10^2
Chewing	10^1 - 10^2
Pumping	10^0 - 10^3
Extruding	10^0 - 10^2
Levelling	10^{-1} - 10^{-2}
Sagging	10^{-1} - 10^{-2}
Sedimentation	10^{-1} - 10^{-3}

TYPICAL VISCOSITIES OF SOME COMMON MATERIALS [1]

Material	Approximate Viscosity (Pas)
Air	10^{-5}
Acetone (C_3H_6O)	10^{-4}
Water (H_2O)	10^{-3}
Olive Oil	10^{-1}
Glycerol ($C_3H_8O_3$)	10^{+0}
Molten Polymers	10^{+3}
Bitumen	10^{+8}

SECTION 2 - SELECTING MEASURING GEOMETRIES

Measuring geometries fall into three basic categories. These are:

(1) Cone and Plate
(2) Parallel Plates
(3) Cup and bob

Each type has its associated advantages and disadvantages which will be described in the following sections.

(A) Cone and plate

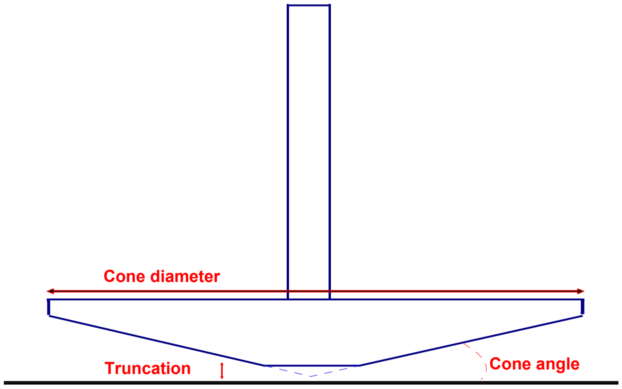


Figure-6

This is in many instances the ideal measuring system. It is very easy to clean, requires relatively small sample volumes and with a little care can be used on materials having a viscosity down to about ten times that of water (10 mPas) or even lower.

Cone and plate measuring geometries are referred to by the diameter and the cone angle. For instance a CP4/40 is a 40mm diameter cone having an angle of 4°.

Often cones are truncated. These types of cone are positioned such that the theoretical (missing) tip would touch the lower plate. By removing the tip of the cone, a more robust measuring geometry is produced.

Since strain and shear rate are calculated using the angular displacement and the gap it follows that the smaller the cone angle, the greater the error is likely to be in gap setting and hence your results. By using a relatively large angle (4°) it becomes easier to get reproducibility of gap setting. Unfortunately, the larger the cone angle the more the shear rate across the gap starts to vary!

In considering what cone angle to use it is worth looking at variations of shear against the gap compared to reproducibility of gap setting. The following table of expected errors comes from work by Adams and Lodge [2].

CONE ANGLE (^{O})	VARIATION OF SHEAR RATE ACROSS GAP %	TYPICAL ERROR IN CALCULATIONS %
1	0.03	0.02
2	0.21	0.08
3	0.28	0.18
4	0.49	0.32
5	0.77	0.50
7	1.5	0.98
10	3.1	2.0

This shows that for a 4° cone the shear rate will vary by less than 0.5% across the gap giving data with around 0.3% error. If a smaller cone angle is used, although the shear distribution error is small, the operator to operator gap settings could easily introduce errors of over 5% even by experienced operators and so the larger angle gives a more acceptable error since it is a reproducible error.

When NOT to use a cone and plate.

Because of the importance of correct positioning (often referred to as 'gap setting') a cone and plate is not recommended when performing temperature sweeps unless your rheometer is fitted with an automatic system for thermal expansion compensation.

If you must use a cone, use the largest cone angle and diameter available to you to minimise the errors and try to set the gap at approximately the mid-range temperature of your sweep.

You should also avoid using a cone if the sample you are testing contains particulate material. If the mean particle diameter is not some five to ten times smaller than the gap, the particles can 'jam' at the cone apex resulting in noisy data.

Materials with a high concentration of solids are also prone to being expelled from the gap under high shear rates, another reason to avoid the use of the cone.

(B) Parallel plate

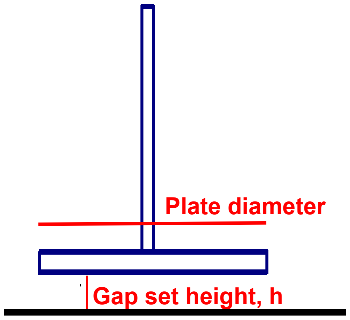


Figure-7

The parallel plate (or plate-plate) system, like the cone and plate, is easy to clean and requires a small sample volume. It also has the advantage of being able to take preformed sample discs which can be especially useful when working with polymers. It is not as sensitive to gap setting, since it is used with a separation between the plates measured in mm. (See Figure-7) Because of this it is ideally suited for testing samples through temperature gradients.

The main disadvantage of parallel plates comes from the fact that the shear rate produced varies across the sample. In most cases you will find that your software actually takes an average value for the shear rate.

Note also that the wider the gap, the more chance there is of forming a temperature gradient across the sample and so it is important to surround the measuring system and sample with some form of thermal cover or oven.

Parallel plate geometries are referred to by the diameter of the upper plate. For instance, a PP40 is a 40mm diameter plate. The lower plate is either larger than or the same size as the upper plate.

When NOT to use parallel plates.

When it is important to test samples at a known shear rate for critical comparisons the use of Parallel plates is not recommended.

(C) Sample loading for cone and plate and parallel plate measuring geometries.

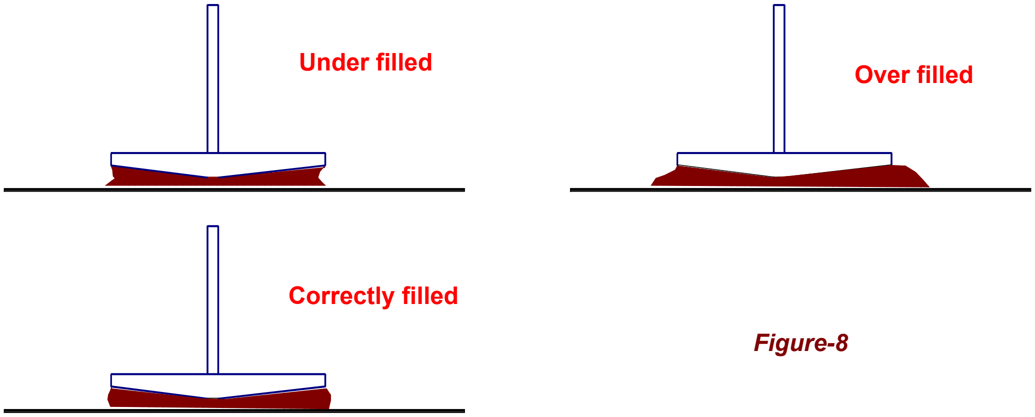


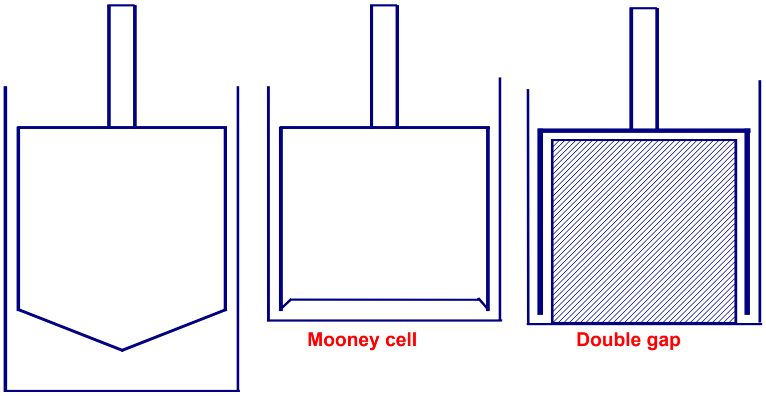
Figure-8

The sample should just fill the gap between the upper and lower elements. If the sample is likely to shrink during the test (due to solvent loss etc.) it is advisable to aim for a slight bulge as shown in Figure-8. If too much or too little sample is used, the torque produced will be incorrect leading to the data being higher or lower respectively.

When using stiff materials with parallel plates, the best results can often be obtained by pre-forming the sample into a disc of the same diameter of the upper plate. The thickness should be very slightly thicker than the required value so that the plates may be brought down such that they slightly compress the material, thus ensuring a good contact.

Some samples may be prone to skinning or drying. This will happen at the edge of the sample to its exposure to atmosphere. To overcome this fit a solvent trap to the measuring system. Another technique is to apply a fine layer of low viscosity (approximately 10 times thinner than the sample) silicon oil around the measuring systems. This works well provided that the oil and sample are not miscible and also that relatively small rotational speeds are being used so as not to mix the oil into the sample.

(D) Cup and bob



Mooney cell

Double gap

DIN Coaxial cylinder

Figure-9

Cup an bob type measuring systems come in various forms such as coaxial cylinder, double gap, Mooney cell etc (see Figure-9).

For DIN standard coaxial cylinders they are referred to by the diameter of the inner bob. i.e. a C25 is a coaxial cup and bob having a 25mm diameter bob. The diameter of the cup is in proportion to the bob size as defined by the DIN Standard.

For double gap measuring systems they are usually referred to by the inner and outer diameters i.e. DG 40/50.

Cup and bob measuring geometries require relatively large sample volumes and are more difficult to clean. They usually have a large mass and large inertia's and so can produce problems when performing high frequency measurements (see 'Viscoelastic Measurement' section for more information).

Their advantage comes from being able to work with low viscosity materials and mobile suspensions. Their large surface area gives them a greater sensitivity and so they will produce good data at low shear rates and viscosities.

The double gap measuring system has the largest surface area and is therefore ideal for low viscosity / low shear rate tests. It should be noted that the inertia of some double gap systems may severely limit the top working frequency in oscillatory testing (See later).

Some test materials may be prone to 'skinning' with time due to sample evaporation etc. To overcome this fit a solvent trap onto the measuring system. Another technique is to float a very low viscosity (10 to 100 times thinner viscosity) silicon oil on the top of the sample in the cup. This works well provided that the oil and sample are not miscible and also that relatively small rotational speeds are being used so as not to mix the oil into the sample.

RULES OF THUMB FOR SHEAR RATE/ SHEAR STRESS; SELECTION.

Decrease cone/plate diameter to increase available shear stress.

Decrease bob surface area to increase shear stress

Decrease cone angle (or gap in a parallel plate) to increase available shear rate
Remember: smaller the angle the more difficult to set gap correctly)

Use large surface areas for low viscosity and small surface areas for high viscosities.

(E) Measurement of large shear rates on CS rheometers

To achieve very high shear rates on controlled stress rheometers can pose a few problems as described below.

High shear rates on low viscosity materials using CS rheometers.

The angular position / speed sensing system in controlled stress rheometers will have a maximum 'tracking' rate before it is no longer able to measure the angular velocity correctly. If this velocity is exceeded the instrument will normally indicate some sort of over speed error.

If this happens at shear rates lower than you would like to obtain, change the measuring geometry to one with a smaller gap (a decrease in gap will increase the shear rate for the same angular velocity.) The highest shear rates can be obtained with a parallel plate with a very small gap or a tapered plug system.

High shear rates on high viscosity materials using CS rheometers.

Since the shear rate = shear stress / viscosity it follows that to obtain a high shear rate with a high viscosity material you will need a high shear stress and so you may find that full stress will not produce the shear rate you require. Remember that small changes in the dimensions of the measuring systems will make large changes to the available shear stress since the equations contain squared (coaxial cylinder) and cubed terms (cones and plates).

Example :

Maximum shear stress with a 1° 40mm cone = 596.8 Pa

Maximum shear stress with a 1° 20mm cone = 4775 Pa

i.e. halving the diameter increase the shear stress by a factor of eight.

(F) Summary of measuring geometry selection

Thick materials can be tested with a cone and plate unless they contain particulate matter, in which case use a parallel plate. (remember that the shear rate will then only be an averaged value).

If you are performing a temperature sweep, use a parallel plate in preference to a cone and plate due to variations in the gap with thermal expansion of the measuring system.

For low viscosity materials and mobile suspensions use a cup and bob type system. Maximum sensitivity is obtained with a double concentric cylinder (double gap).

For oscillatory measurements at high frequencies on low viscosity materials, the C25 cup and bob or a parallel plate with a small gap will produce the optimum test conditions.

For testing low viscosity materials when only small sample volumes are available, use a Mooney Cell (such as a 'small sample cell').

For all samples, if drying or skinning of the sample is likely to be a problem, use a solvent trap with the measuring system or alternatively use a low viscosity silicon oil as a barrier if it is not likely to alter the samples properties.

SECTION 3 - FLOW CHARACTERISATION

(A) The viscometry test

There are generally two types of simple flow characterisation tests for viscometry . These are Stepped shear stress / shear rate or Ramped shear stress / shear rate.

The types available on your particular instrument will depend upon the configuration of your rheometer software.

Stepped shear.

Individual shear values are selected. Each shear is applied for a user set time and the shear rate, shear stress and viscosity are recorded for each value.

The individual points are then either joined up 'dot to dot' fashion or using a rheological model to produce the flow curve and the viscosity curve.

This test method is the generally the preferred way of generating flow and viscosity curves.

Ramped shear

This test applies a continuously increasing or decreasing shear (in a ramp) throughout the complete test. Measurements are taken at user defined intervals along this shear gradient.

The three main uses of this technique are:

1. To perform rapid 'loop' tests of viscosity for use in QC type environments.
2. To simulate processes where the shear changes in a ramped fashion (e.g. start up of a roller, chewing etc..)
3. To determine some point where the material starts to flow (the yield point) although this is normally only done on controlled stress rheometers.

(B) Flow curves

The measured viscosity of a fluid can be seen to behave in one of four ways when sheared, namely :

1. Viscosity remains constant no matter what the shear rate (Newtonian behaviour)
2. Viscosity decreases as shear rate is increased (Shear thinning behaviour)
3. Viscosity increases as shear rate is increased (Shear thickening behaviour)
4. Viscosity appears to be infinite until a certain shear stress is achieved (Bingham plastic)

Over a sufficiently wide range of shears it is often found that the material has a more complex characteristic made up of several of the above flow patterns.

Since it is the relationship of shear stress to shear rate that are strictly related to flow we can directly show the flow characteristics of a material by plotting shear stress v shear rate. A graph of this type is called a Flow Curve.

The graphs in Figure-10 show the flow curves and viscosity curves of the four basic flow patterns.

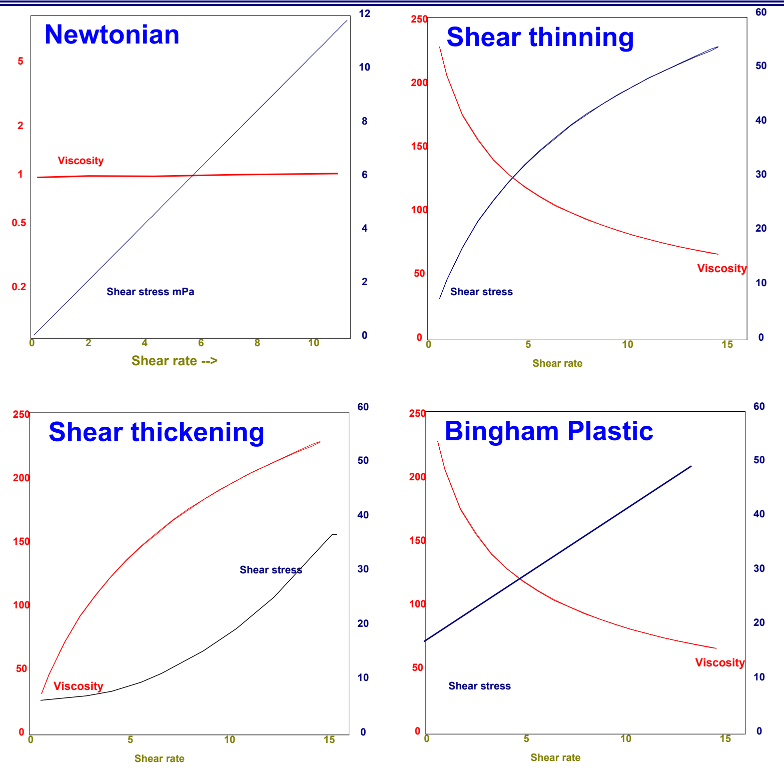


Figure-10

The exact behaviour of materials can often be described by some form of rheological model. Some of the more commonly used models are described in the following section.

Models for fundamental flow behaviour

These models describe the simple flow behaviour as shown in the previous graphs. Most materials will start to deviate from these relationships over a sufficiently large shear range. They are well suited to studying materials over a small shear range or where only a simple relationship is required.

Newtonian

This is the simplest type of flow where the materials viscosity is constant and independent of the shear rate. Newtonian liquids are so called because they follow the law of viscosity as defined by Sir Isaac Newton:

$$\sigma = \gamma * \eta$$

Shear Stress = Shear rate * viscosity

Water, Oils and dilute polymer solutions are some examples of Newtonian materials.

Power law - (or Ostwald model)

Many non-Newtonian materials undergo a simple increase or decrease in viscosity as the shear rate is increased. If the viscosity decreases as the shear rate is increased the material is said to be Shear Thinning or Pseudo plastic. The opposite effect is known as shear thickening. Often this thickening is associated with an increase in sample volume; this is called ‘dilatency’.

The power law is good for describing a materials flow under a small range of shear rates. Most materials will deviate from this simple relationship over a sufficiently wide shear rate range.

$$\sigma = \eta * \gamma^n$$

Shear stress = viscosity * Shear rate ^{n}

Where 'n' is often referred to the power law index of the material.

If n is less than one, the material is shear thinning, if n is more than one then material is shear thickening. Polymer solutions, melts and some solvent based coatings show Power law behaviour over limited shear rates.

Bingham

Some materials exhibit an 'infinite' viscosity until a sufficiently high stress is applied to initiate flow. Above this stress the material then shows simple Newtonian flow. The Bingham model covers these materials:

Shear Stress = Limiting shear Stress + viscosity*shear rate

The limiting stress value is often referred to as the Bingham Yield Stress or simply the Yield Stress of the material. It should be noted that there are many definitions of Yield stress. For further information on this topic see the section on Yield values later.

Many concentrated suspensions and colloidal systems show Bingham behaviour.

Herschel Bulkley

This model incorporates the elements of the three previous models

Shear stress = limiting stress + viscosity * shear rate^n

Special Cases of the model:

A pure Newtonian material has limiting stress=0 and n=1
A power law fluid has limiting stress=0 and n=power law index
A Bingham fluid has limiting stress= 'Yield value' and n=1

This model many 'industrial' fluids and so is often used in specifying conditions in the design of process plants.

Vocadlo

This is similar to Herschel Bulkley although it will some times prove a better representation of the fluid.

Models for more complex flow behaviour

These relationships have been developed as 'enhancements' to the fundamental models. They tend to give a more realistic prediction of flow over a wider range of conditions.

Ellis

This describes materials with power law behaviour at high shear rates but Newtonian behaviour at low shear rates.

Shear rate = K1* shear stress + K2*shear stress^^{n}

Where K1 and K2 are simple constants and n is material index.

This model is often used to describe polymeric systems as it generally gives a better representation than the power law model.

Casson

This model is used for materials that tend to Newtonian flow only at stresses much higher than the materials Yield stress.

shear stress^$^{0.5}$ = Yield stress^$^{0.5}$ + K*shear rate^$^{0.5}$

This model is often used for suspensions. It is also used by some confectionery manufactures to describe the properties of molten chocolate.

Moore

This model is capable of predicting flow properties over a wide range of shear rates since it incorporates terms for both limiting low shear rate and high shear rate viscosities.

Cross

This is an extension of the Moore model but with containing four independent parameters (Moore has three) It is often able to accurately describe the shear thinning behaviour of disperse systems.

Sisko

This describes a material with a limiting high shear rate viscosity. Although the limiting low shear rate viscosity is infinite, the model does not in general describe a material with Yield.

Viscosity = high shear viscosity + k*(1/shear rate)^^{m}

Note : if m=1 then this equation is the same as the Bingham.

(C) Yield values

If we think back to our basic definitions (section 1) we recall that when the applied shear stress is removed after a deformation has occurred, the strain should return to zero. If it does not eventually return to zero, we say that flow has occurred.

The yield stress of a material is usually defined as the maximum stress below which no flow will occur. However the accurate measurement of this point requires the determination of whether the strain has reached a value of zero. It is generally believed that if you wait long enough and can measure sufficiently small strains, you will find that no materials have a true yield stress.

In practical terms however the yield stress (or yield point) is defined in terms of whether the material has undergone a degree of deformation that is significant to the size and time scales of a particular process. Thus yield becomes dependant upon not only the stress but also the measured strain and the elapsed time.

There are three commonly used methods for determining yield, each of which has its own advantages and disadvantages. These are as follows:

Flow curve method

Use the Flow Curve for the material and extrapolate back to where the shear rate = zero to find the shear stress value. The disadvantage of this method is that you are not measuring the value but calculating it by assuming the material follows simple Newtonian behaviour immediately after it yields i.e. Bingham flow. For controlled shear rate instruments this is the only method that can be used.

Step stress test

This consists of applying a small stress, holding for a pre-defined time and measuring the strain response. The stress is gradually stepped up until a measurable 'flow' is obtained. This method is probably the most accurate way of characterising the yield point of a material but it can be a very time consuming process. As this test is essentially a multiple creep test, it will be covered more fully in section-4.

Ramp stress test

This involves applying a gradually increasing stress and monitoring the instantaneous viscosity for an inflexion of the curve i.e. the onset of flow. By altering the ramp rate, time effects can be taken into consideration. This method is used by the Bohlin Yield Stress test and will be explained in greater detail later.

(D) Time and temperature dependence

As well as looking at the rheological characteristics of a material as a function of shear, two other factors, namely time and temperature dependence must be looked at as well.

Temperature dependence

The viscosity of a material is usually found to decrease with an increase in temperature, assuming no physical/chemical changes are being induced by the applied heat energy. The temperature dependence can be determined by running a temperature gradient programme. Samples usually have some degree of heat capacity, known informally as 'thermal inertia' i.e. if the surrounding temperature is altered then they will take time to change their overall temperature. This is an important point to consider when selecting the rheometer's temperature ramp rate. To find a measure of this lag, manually increase or decrease the temperature and monitor the time it takes for the sample viscosity to change.

Note that you will also need to be certain that the sample does not exhibit any significant time dependant properties throughout the time scale of the test.

It is important to establish the temperature dependence of your sample if you wish to state degrees of accuracy for your measurements. As an example consider the viscosity of water which alters by some 3% per °C. To maintain a ± 1% accuracy in the measurements you must hold the temperature to ± 0.3°C.

Arrhenius model

The viscosity of Newtonian liquids decreases with an increase in temperature approximately in line with the Arrhenius relationship.

This model describes a materials variation in viscosity with ABSOLUTE temperature.

$$\text{Viscosity} = c * e^{(k/\text{temperature in Kelvin})}$$

(k is related to the flow activation energy E and Boltzmann's constant R by k=E/R).

Time dependence

Some materials have flow characteristics that are dependant on the 'shear history' of a material. A well known example of this is tomato ketchup. When left long enough, the inter-particle interaction causes the ketchup to 'stiffen' up, seen as an increase in viscosity. To get the sauce to flow out you have to shake the bottle (i.e. shear it) This destroys the samples structure and the viscosity decreases.

A reversible decrease of viscosity with time under steady shear is referred to as thixotropy (if the shear gives a temporary increase in viscosity, it is termed negative thixotropy, sometimes referred to as rheopexy although this is not the preferred term).

If the act of shearing a material produces a non-recoverable change in the viscosity it is referred to as rheodestruction (or rheomalaxis). Again, theoreticians argue that there is no such thing as rheodestruction but that the time required for complete rebuild is just very long and so does not appear to happen.

It should be noted that these changes are purely time related and the materials flow characteristic need to be studied as well. It is possible that a material could be, say, both thixotropic and shear thickening.

When materials have time dependence it is important to take steps to pre-condition them such that flow curves can be compared with a common shear history. The best method to do this is to put the sample into the rheometer and subject it to a high shear rate for a time sufficient to destroy any structure, (this is why it is not a good idea to use a syringe to apply the sample if you wish to measure the structure of the material since you will produce very high shear rates and could destroy the samples structure) then allow it to rest for a fixed time to recover again before taking any measurements.

You will need to study the time dependence of the material in order to design a conditioning regime since the changes can happen over time scales of a few seconds to many hours or even days. In addition, the rate of change of viscosity may also be affected by the sample temperature!

Figure-11 shows the rebuild in viscosity of a material after pre-shear. After approximately 100 seconds most of the recovery has occurred. Thus you could design a test that pre-sheared the sample, waited for two minutes and then performed the rest of the test. This way all materials should be starting from the same reference point.

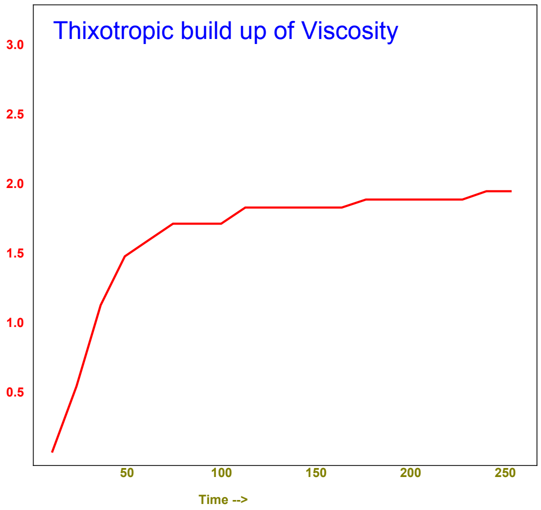


Figure-11

(E) Other factors

You should be aware that the rheology of your material can also be influenced by factors such as pressure, pH and electric fields and so these should be maintained at constant values throughout the test.

(F) Equilibrium flow curves

We stated earlier in this chapter that the viscometry test could produce either a ramp or a stepped flow curve . It is important to be aware of the differences between these two.

If we look at the case of a controlled stress rheometer, we see that we impose a constant force i.e. stress and measure the resultant deformation as a function of time. If the material is a pure Newtonian liquid we will obtain a linearly changing deformation i.e. simple Newtonian flow. For all other materials the effect will not be as simple. If the applied stress is relatively small, it may be fighting against the materials 'structural' properties i.e. elastic elements, time dependant changes etc.

The response of the material will follow something along the following lines ;

ELASTIC DEFORMATION
VISCOUS FLOW ON TOP OF ELASTIC DEFORMATION
PURE VISCOUS FLOW

If the material is a pure solid, we will either obtain a fixed but fully recoverable deformation (i.e. below the materials yield point) or a rapid fracture if we are above it. Since in rheology we are only interested in looking at fluids it follows that there will also be some viscous elements in the material and these will work to resist the applied stress and hence the 'fracture' of the elastic component will be delayed a small instant.

Depending on the strength of the viscous and elastic elements and the value of the applied stress, it is possible that we may need to wait a considerable length of time until we have deformed the material sufficiently to remove all elastic deformation and are just measuring the pure viscous flow. Even in controlled shear rate instrumentation the delay may be of a noticeable interval.

In stress viscometry tests the software monitors how 'compliant' the material is as a function of time. The compliance of a material is simply defined as the STRESS APPLIED / STRAIN PRODUCED and as we have seen should be a linear function as a function of time for pure viscous flow (Figure-12).

When this state is achieved it will be found that the measured shear rate is constant and the slope of the compliance curve as a function of time is constant ie. the differential gives a value of 1.00. This is the number shown by the Bohlin software.

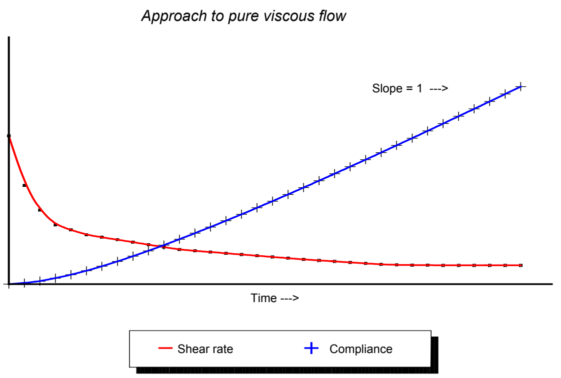


Figure-12

Under these conditions we know that we can measure the viscosity of the material without it containing any effects due to elasticity. This is very important since many processes are shear rate controlled and can be thought of as being able to apply up to an infinite torque if required to obtain the specified shear rate. In controlled shear rate rheometers the time to reach equilibrium is generally small and so the normal delay interval is sufficient.

Thus, the stepped shear test allows us to wait for this equilibrium condition at each applied value whereas the ramped test does not. There are occasions however where the use of a ramp is preferred to the use of step. This is covered in the next section.

(G) Ramp viscometry tests

In ramp testing, if the shear range is sufficiently large and the ramp rate fast enough, the materials non-flow structure will be largely destroyed before any measurements are taken and so a simple flow curve can be produced. This method is fine for quick QC type applications although you should be aware that it may not give absolute readings of viscosity since no check is made that you are only recording steady flow conditions. If you change the test conditions (e.g. the ramp rate of the shear range) the data produced can not be directly compared to results generated by the previous test conditions.

Many people use this test to measure a materials time dependant properties (i.e. thixotropy) by sweeping up and then down in shear and measuring the area of the looped flow curve (known as the hysteresis loop). Again, although this is fine for a simple QC test, you should be aware that changing any of the test parameters will invalidate comparisons with previously generated data. For measurement of thixotropy / structure rebuild you are best to perform a pre-shear followed by a single frequency or multiwave oscillation test (please refer to the section on oscillatory testing for more information).

Yield stress measurements on a controlled stress rheometer

Suppose we limit the ramp to small stresses and put a longer sweep time (say the minimum stress available, up to 1 Pa over 120 seconds) then we will be able to see the effect of the elastic elements as an increase in the 'instantaneous' viscosity since this value is calculated assuming that the relationship Viscosity = Stress / Shear rate holds, which it will not do until we break into pure viscous flow. As the material starts to flow, the instantaneous viscosity will be seen to change rapidly from an increasing value to a decreasing value and the stress being applied at this instant is recorded as the Yield Stress (see Figure-13).

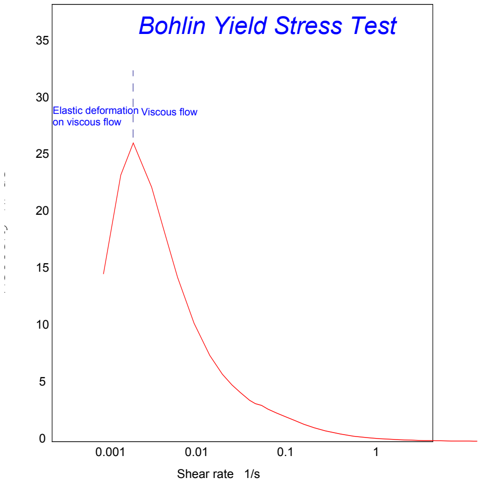


Figure-13

DESIGNING YOUR OWN FLOW CHARACTERISATION TESTS

The above section has now hopefully given an insight into the many type of flow characteristic that can be expected from a material. All of these points must be borne in mind if you are to design tests that produce valid and useful data.

Questions to ask when designing a test protocol.

The following 4 points should always be considered when designing your tests :

(1) WHY !

Perhaps the most important question to be asked is why do you want to characterise the material. For example, is it for use on the factory floor for QC or is it to enable the design of a new formulation?

Once this is established the range of variables and conditions can often be radically reduced. Also the protocol can be designed to give the required balance between precision, speed and reproducibility.

For instance, if you know what shear rates or shear stresses you require, pick a measuring system and measurement head capable of generating and recording the data.

(2) WHAT ARE YOU TRYING TO DETERMINE ?

Do you wish to simply measure a viscosity value at a certain shear rate ? Do you wish to study ageing characteristics or dependence upon temperature ? Are you trying to obtain as full a characterisation of the material as possible for use on comparative purposes either for QC or in developing new formulations / better products?

(3) DOES MATERIAL HAVE TIME / TEMPERATURE DEPENDENCY?

If this is suspected or not known it should be determined first. There is no point trying to measure a material if the time taken for the test allows a significant change in the material to take place. Some form of preconditioning will be required if you are trying to obtain comparative data. This could consist of changing the samples temperature for a fixed time or pre-shearing the material.

An important consideration is the temperature of a material **before** it is placed into the rheometer. If it is likely to vary widely use a long equilibrium time to ensure that the material has sufficient time to reach test temperature.

(4) WHAT TYPE OF MEASUREMENT SYSTEM IS BEST ?

The selection of measuring geometry is relatively straightforward if you consider the following points:

What shear rates / stresses / viscosities are you working with ? Use the data sheets and the information contained previously in the course to obtain the required combination.

What is the material like ? Is it 'pourable' or highly viscous ? Is it a gel or a suspension ? Does it contain particulate material ? Does it have a solvent base ?

The previous section on measuring system selection covers the selection on the above points.

PITFALLS

When you produce data on any computer controlled instrument, you should be aware that sometimes there are errors arising from the conditions you have selected. The software can not always point these out to you. The following section lists some of the more common rheological problems that may occur.

Turbulent or secondary flow

For rotational rheometers and viscometers it is assumed that at all times the flow of the fluid in the measuring systems is steady, or laminar and one dimensional. That is, no variation with time exists and the fluid moves only in the direction of rotation (see Figure-14).

Laminar Flow

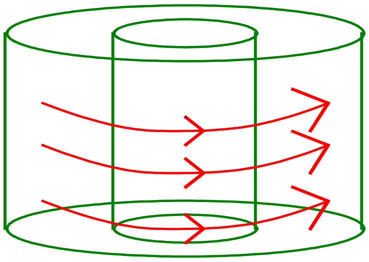


Figure-14

In general, for narrow gaps and modest rotational speeds, this type of flow is attained and satisfactory viscosity data may be recorded. However, as the rotational speed is increased, a transition from a steady one dimensional flow pattern to a more complex but steady three dimensional flow takes place. This flow pattern takes the form of vortices whose axes lie in the circumferential direction (see Figure-15).

This type of flow was first described by Taylor (1936) and is termed TAYLOR VORTEX FLOW.

Taylor Vortex Flow

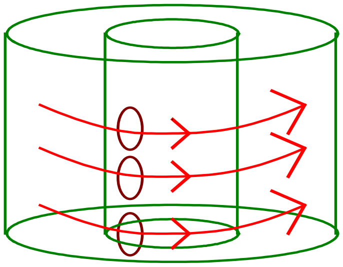


Figure-15

In most cases the onset of this SECONDARY flow will be seen as a sharp and distinct increase in the torque required to obtain a given shear rate. The consequence of this is an apparently rapid increase in the recorded viscosity.

At even higher speeds the flow becomes turbulent but in viscometry we are primarily interested in ensuring we remain below the threshold at which the development of Taylor vortex flow takes place.

When the inner cylinder rotates, the fluid at the inside of the measuring system is moving rapidly and tends to move outwards under centrifugal action. This must be replaced by fluid from elsewhere and so a recirculating vortex flow structure develops. Simplistically, this is the mechanism responsible for the onset of secondary or ‘Taylor Vortex’ flow.

Secondary flow problems are largely restricted to tests using coaxial cylinders since cone and plates are generally used with more viscous samples.

As an example we will consider the flow curve for water measured on a controlled stress rheometer using a large double gap concentric cylinder.

Example - Water on a double concentric cylinder

According to Taylor's theory [3] , the onset of secondary flow should occur at the critical stress of 27 mPa or a shear rate of 27 S^{-1}. This can be seen on the graph as a marked increase in viscosity, Figure-16.

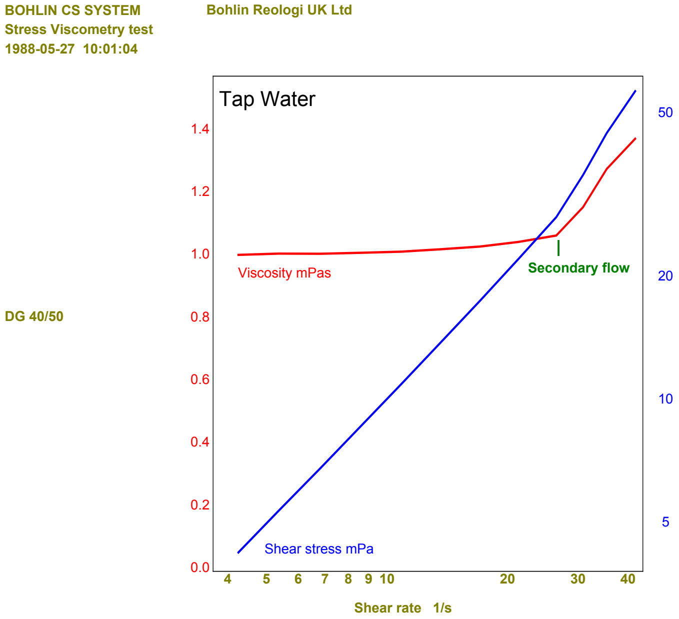


Figure-16

REMEMBER
Results above the critical stress are not valid Refer to your User manual for information on limiting viscosity values.

Wall slip

If you recall back to the original definitions of shear stress and shear rate you will recall that we imagined a cube of material with one surface fixed and one moving.

Since we do not physically 'glue' the material onto the measuring systems used in the rheometer it is possible that there may be some movement on the surface that is supposed to be fixed. This will result in the rheometer measuring a greater strain than should be correct and so the measured value of viscosity will appear lower than it should be. The lower the expected strain the larger the effects will appear.

If the flow curve of a material at low stresses seems to deviate away from the expected try using a roughened measuring system and see if that alleviates the problem. As a quick check, use a piece of fine gauze wrapped around the bob as a roughening agent.

Ageing effects

It is important to design your test procedures such that no significant change in the material occurs during the time of the test. If you plan to do experiments over long periods it is advisable to first of all monitor the samples viscosity as a function of time at one or more shear rates. If the material changes, first find if it is something that can be overcome i.e. if the material forms a skin, use a solvent trap. You may find that the only solution is to split the test into two or more parts, using fresh sample for each. If you do this you must be aware of the reproducibility you can expect.

Centrifugal effects

Certain materials will start to be thrown out of measuring systems if the rotational rate becomes too large. This is most noticeable for large angle cone and plates. If the sample is thrown out of the measuring system, the measured viscosity will be seen to drop. To overcome the problem you could use a cup and bob although you will not be able to achieve such high shear rates. To obtain high shear rates with least risk of sample expulsion use a small angle cone or a parallel plate with a small gap or a tapered plug measuring system.

Remember that you may start to generate noisy data when running particulates with small gaps since the particles may jam into each other (a rough rule of thumb often used to ensure good data is to use a gap at least 10 times larger than the mean particle size).

Measurement of small shear rates on controlled stress rheometers

The angular position sensor on the Bohlin CS is a digital based system, that is it produces discreet steps for angular movement and is thus limited to the smallest angular position it can measure. If you wish to measure very small shear rates you must therefore be prepared to wait such that a large enough angular deflection is obtained to give you good data. Make sure also that you have optimised on the measuring system best suited to give you low shear rates.

SECTION 4 CREEP ANALYSIS

Most materials are formed by a combination of viscous and elastic components. If a sufficiently large strain is applied it is possible to break the 'structure' of the material i.e. the elastic part, resulting in purely viscous flow. This is the principle of the viscometry tests that we have looked at so far.

At low strains however, the elastic component will play a major part in contributing to the materials behaviour and so it is important to be able to measure and characterise it.

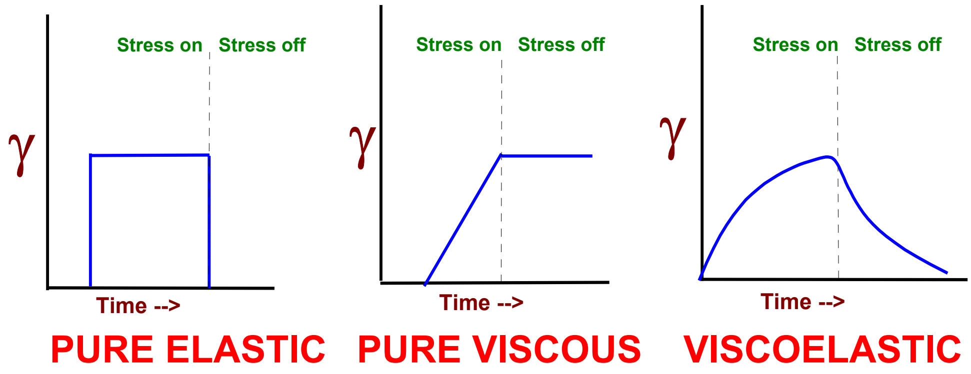
One method available to us on controlled stress rheometers is the creep test. (a similar test, stress growth, is available on controlled shear rate instruments. See later for more information on this test.)

Creep is defined as 'the slow deformation of a material, usually measured under a constant stress'. If we apply a small stress to a viscoelastic material and hold it constant for a long period of time whilst measuring the resultant strain we will see behaviour initially from elastic components followed shortly by viscoelastic effects. At sufficiently long time scales we will obtain effects only from the viscous components since the resultant strain is large enough to have 'used up' the elastic component (see Figure-17). If we refer back to the section on equilibrium flow curves you will remember that we only recorded data in this later stage when we knew that what we were measuring was pure viscous flow. The creep test records the information from the moment we apply the stress and hence gives a measure of elastic, viscoelastic and viscous components.

By applying small stresses it is also possible to mimic gravitational effects on a sample to assist in predicting effects such as sedimentation, sagging and levelling. The shear rates produced under these conditions will typically be of the order 10^{-5} - 10^{-6} S^{-1}.

(A) Principle of operation

In a creep test a user selected shear stress is 'instantaneously' applied to a sample and the resultant strain monitored as a function of time. After some predetermined time the stress is removed and the strain is again monitored. The three typical response curves are shown in figure-17



PURE ELASTIC PURE VISCOUS VISCOELASTIC

Figure-17

The third case shows a typical curve produced by a viscoelastic material. The actual shape will be determined by the interaction of the viscous and elastic components.

Since the actual change of strain will be dependant upon the applied stress, it is usual to talk about the **compliance** rather than the strain. The compliance is defined simply as the ratio of the strain to the applied stress and is denoted by the letter J (J=strain/stress). By using this notation, creep curves may be directly compared even if they were not measured under the same applied stress.

(B) Time scales and the Deborah Number

To fully recognise the concept of creep, time factors must be understood with respect to mechanical behaviour of the samples. Rapid response times (often fractions of a second) are mainly indicative of elastic phenomenon whereas viscous phenomenon usually take seconds or even minutes to occur. The correct experiment time is important to enable fast and slow phenomenon to be accurately resolved. To enable us to put numbers to a materials response characteristics we use a function called the **Deborah number.**

The Deborah Number

To understand whether a material will tend to behave more as a fluid or more as a liquid two factors must be looked at. These are the time scale of the process/experiment, T and the characteristic relaxation time of the system, τ.

The Deborah number is defined as $D_e = \tau / T$

$D_e < 1$ liquid like behaviour $D_e = 1$ viscoelastic behaviour $D_e > 1$ solid like behaviour

The time τ is infinite for a Hookean elastic solid and zero for a Newtonian viscous liquid and is actually the time taken for an applied stress (or strain) to decay to 2/3 its initial value. (The decay is exponential.) The relaxation time can be found by performing a frequency sweep on the sample and taking $\tau = 1/\omega_x$ where ω_x is the angular velocity ($2 * \pi$ * frequency) within the linear region at the point where G'=G" or by use of the relaxation test. (see later)

The above can be summarised simplisticaly by saying 'everything flows if you wait long enough' (the name Deborah comes from an Old Testament prophetess who told of "mountains flowing before the Lord" !)

It can be seen therefore that a sample may show solid-like behaviour either because it has a relatively long characteristic relaxation time or it is being subjected to a process of time scales considerably shorter than the materials characteristic relaxation time. The creep test takes the sample through short time scale response to long time scale response. This can be seen in the example creep curve in Figure-18.

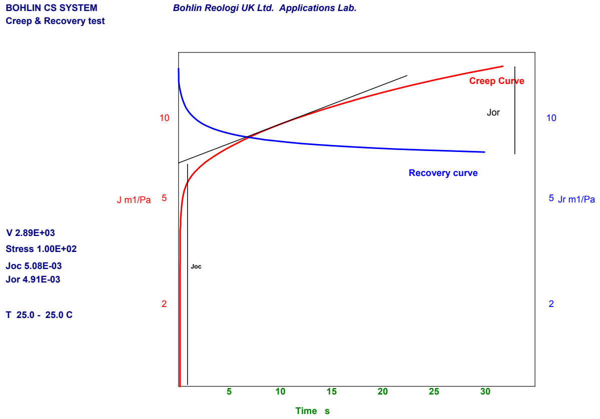


Figure-18

Data at the very start of the test relates primarily to a pure elastic deformation and is referred to as the 'instantaneous' or 'glassy' compliance. At longer time scales the deformation will be due to both viscous and elastic elements and is referred to as damped or delayed elastic compliance. At sufficiently large enough time scales the resultant deformation will be purely due to viscous flow. When the material is in pure viscous flow the differential of the slope of the curve will be 1.00. The Bohlin software gives a readout of the slope as the test progresses and can be made to automatically accept the data when this 'steady state' is attained. This is presented as dLn.j/dLn.t (i.e. the change in compliance as a function of time) in the software.

Zero shear viscosity

After sufficiently long time scales where the steady viscous flow is achieved, the samples viscosity can be estimated from the slope of the compliance curve.

At sufficiently low shear rates it is found that most materials either have a viscosity that tends to infinity (yield stress) or have a viscosity that becomes independent of shear rate (the low shear Newtonian plateau). To verify the materials behaviour you would run a creep test to obtain the low shear viscosity, then repeat the creep test but with a lower shear stress (hence producing a lower shear rate) If the two tests produce the same reading of viscosity then you have found the materials zero shear viscosity. If you keep decreasing the stress and the viscosity keeps increasing, it is possible that the material has a measurable yield stress (see next section).

A materials zero shear viscosity is useful in predicting such factors as storage stability, levelling etc. Equations for these are given in Appendix-B.

Measurement of yield stress by 'stepped creep' tests

By repeating creep tests at lower and lower shear stress values you can determine the yield stress of a material quite accurately.

In the ramped stress viscometry test mentioned previously, we gradually ramp up the stress and determine the point that the structure breaks down or 'ruptures' Since the yield point of a material is dependent not only upon the applied stress but also the time the stress is applied for, a much more accurate way of determining yield would be to hold a stress for a pre-set period of time, then step up to a slightly higher stress and hold, continuing this process until the material started flowing. In a creep test, if we apply a stress below the materials yield value, we find that the sample will deform due to viscoelastic properties, but will not start to flow. This will be seen as the compliance curve tending to level off to a horizontal curve (slope -> 0) Therefore we can determine if the material is likely to flow by seeing if the slope of the curve (dLn.J/dLn.t) is increasing towards unity (tending to flow) or decreasing towards zero (no flow).

NOTE: Since this technique can be lengthy you will need to determine that the material does not have significant time dependant properties over the observation time of this test.

It is important that we let the sample recover after applying each stress i.e apply stress for 30 seconds, remove stress and rest for 30 seconds, then repeat at a higher stress and so on.

The ramped viscometry test is a good method of determining the yield stress and of course is very rapid. The method of stepped stresses is more accurate and therefore may produce significantly different answers from the other test. It is a good idea to try both techniques and see which best suits your materials and requirements.

Measurement of elasticity

The creep test provides a method of determining the amount of elasticity in a sample. This value is denoted as J_o and is calculated by extrapolating back along the creep curve when in steady viscous flow. The intercept is then a measure of J_o and since it is obtained from the creep test it is recorded as J_{oc}. This method is fine for estimating J_o but it is prone to error since it generally involves extrapolating back from a large number to obtain a small number. A far better method of obtaining J_o would be to measure it directly and this is done by the Creep Recovery test.

When we have obtained a state of steady viscous flow, if we remove the stress and wait for at least as long as it took us to obtain viscous flow, the material will recoil due only to the elasticity. By measuring this recoil, or recoverable compliance, we obtain a value for J_o denoted in the software as J_{or}. Generally you will find that J_{oc} and J_{or} have the same order of magnitude but that J_{or} is more accurate.

When to do creep recovery tests.

If the value of J becomes quite large during the creep test, it is more likely that J_{oc} will not be as accurate as could be obtained by performing a creep recovery test. The disadvantage of doing the full creep followed by creep recovery is that you must run the recovery part for at least as long as the creep part to guarantee that all of the elasticity has been recovered (since the viscous part produces viscous damping). This effectively doubles the time required and could cause problems if the material is likely to change due to drying, skin formation etc. The accuracy of J_{oc} should thus be looked at in relationship to the reliability of obtaining good J_{or} data.

SECTION 5 - VISCOELASTIC CHARACTERISATION

Flow characterisation tests do just that, i.e. tell you how a material is likely to flow under an imposed constant shear rate or shear stress. They tell only about the materials VISCOUS properties (resistance to flow).

To measure a materials viscoelastic properties we can use creep testing (as described in the previous section) or alternatively we can use oscillatory techniques. The technique used is to apply a stress or strain whose value is changing continuously according to a sine wave equation. Thus the induced response (strain or stress) will also follow a sine wave.

Thus it can be seen that we can continuously excite the sample but never exceed a certain strain and hence we do not destroy the sample structure. (providing steps are taken to keep the strain small enough).

If we 'over strain' the sample, we will start to destroy the elastic structure of the material and so it is important to keep the strain low. The technique used by the software in controlled stress instruments is to continuously adjust the applied stress so that the resultant strain is held at a specified value.

If you remember back to section 1 we talked about Hookean deformation (analogous to a spring being extended) and Newtonian flow (analogous to a viscous dashpot) most materials are made up of a combination of these two properties. Hooke's law is a simple linear relationship, that is if you double the applied stress you double the measured strain. Provided the strain produced is small enough it is said that you are working in the materials REGION OF LINEAR STRAIN RESPONSE or more simply LINEAR REGION.

The calculations used in the software are only valid in this linear response region.

Thus, before performing oscillation tests on a material you must verify that the test conditions fall into this regime. This is easily tested by oscillating at a fixed frequency and slowly increasing the applied amplitude (strain or stress). The measured values for the viscoelasticity will remain constant. When the applied stress becomes too great, the induced strain will start to cause the material to 'rupture' i.e. you will obtain some flow on top of the deformation. This will be seen as the measured value of elasticity falling whilst the measured viscous component will start to increase. Provided you work at strains below this point you will be working in the materials linear region. If it is difficult to find the linear region, increase the cone angle or the parallel plate gap to produce lower strains in oscillation.

(A) Definition of elastic and viscous components

As stated earlier, if we apply a sinusoidally varying stress to a sample, we will induce a sinusoidally varying strain (and vice versa for applied strain) response. If we think back to how the stress effects the sample for a pure solid and a pure liquid you will remember the following :

For a Hookean Solid :

Shear Stress = Shear Strain x G (a constant)

For a Newtonian liquid :

Shear Stress = Shear Strain rate x Viscosity (a constant)

So for a pure solid the strain is controlled by the absolute value of shear stress, whereas for a liquid it is the rate of change of strain that is controlled by the stress

If we consider one complete cycle of the sine wave as 360° then we can talk about differences of phase between the two waves as PHASE ANGLES.

In the case of a pure solid, since the strain is directly related to the stress, it will be at a maximum when the stress is a maximum and zero when the stress is zero. The strain response is said to be totally IN PHASE with the applied stress i.e. the PHASE ANGLE = 0° (see Figure-19).

If the material is a pure viscous liquid we find that it will be the **strain rate** that is exactly following the stress. If you look at the graph of strain rate as a function of time you can see that the strain alternates between a positive and negative extreme accelerating and decelerating between these two values.

Therefore, when the strain rate is at a maximum the rate of change of strain will be zero, likewise when the strain is zero, the rate of change will be a maximum. The resultant strain will therefore be totally (90°) out of phase to the applied stress (see Figure-20).

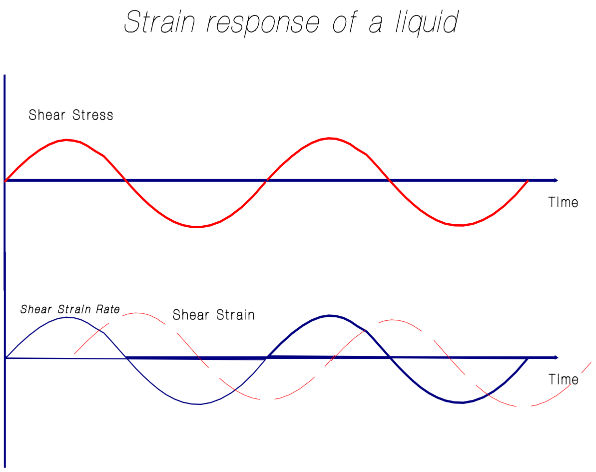


Figure-19

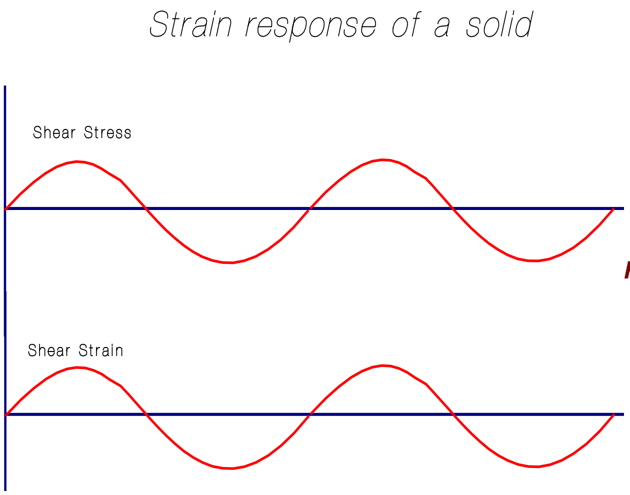


Figure-20

In practice, most materials are a combination of viscous and elastic components and so the measured phase angle will be somewhere between 0° and 90°. The closer to 90° the more fluid like the behaviour of the material under test.

Modulus Values

We stated earlier that Hooke's law relates the strain to the stress via a material constant known as the MODULUS, G. (G = stress / strain)

In the oscillation test the stress and strain are constantly changing but we can consider any number of 'instantaneous' values to obtain a value of 'viscoelastic G'. This is referred to as the materials COMPLEX MODULUS, G^* and is obtained from the ratio of the stress amplitude to the strain amplitude. This modulus is the 'sum' of the elastic component (referred to as G' often called the STORAGE MODULUS to signify elastic storage of energy since the strain is recoverable in an elastic solid), and the viscous component (referred to as G'' often called the LOSS MODULUS to describe viscous dissipation [loss] of energy through permanent deformation in flow).

We define the complex modulus as:

$$G^* = G' + i \times G''$$

By measuring the ratio of the stress to the strain (G^*) as well as the phase difference between the two (delta, δ) we can define G' and G'' in terms of sine and cosine functions as follows:

$$G' = G^* \cos \delta$$
$$G'' = G^* \sin \delta$$

Since G* is essentially Stress/strain, G' and G'' have units of Pascal (N/m^2).

(B) Frequency

The combination of viscous and elastic components in a material will respond in different ways depending on the 'speed' at which you try to move it.

By oscillating over a wide range of frequencies you will obtain the characteristics over a range of time scales as high frequencies relate to short times whereas low frequencies relate to long time scales. (remember back to the Deborah number as discussed in the section on creep).

Inertia effects

Controlled stress rheometers use a drag cup motor. This literally operates by 'dragging' the spindle by use of a rotating electromagnetic field. The transient movement of the spindle will contain a delay introduced from the inertia of the drag cup motor and measuring geometry. In viscometry testing this is not a problem since you are taking long time / equilibrium data (although you should be aware of it if you use the Yield Stress test as a 'loop' test and set a very rapid ramp rate) In oscillation however inertia becomes relevant since it will introduce a phase difference between the sine wave you apply in torque and the actual sine wave that the sample sees. Obviously it is important to know the value of this phase lag so that you can remove it from the phase angle produced by the sample. The software automatically calculates this value using the built in inertia constant for the drag cup motor and the C4 inertia constant for the measuring geometry in use. It should be noted that the inertia term is proportional to the frequency squared and hence grows rapidly as the frequency increases. Under certain combinations of measuring systems and materials the inertia term may become large which will make the raw data difficult to analyse.

Controlled strain oscillation is not so prone to inertia effects but can suffer from other problems such as resonant frequency error.

Resonant frequency of torsion bars

The measuring head on a controlled shear rate (strain) rheometer consists of a torsion bar suspended via a virtually frictionless bearing. This is mechanically equivalent to a freely suspended spring. The measuring system attached to the air bearing acts as a damping weight and therefore each combination of torsion bar and measuring system will have some natural resonant frequency. When making oscillatory measurements it is therefore important to work at frequencies away from this natural resonance.

Gap Loading

Many rheometers work on the principle of shearing a fluid between two surfaces separated by a narrow gap. The reason for this narrow gap is to obtain a shear rate distribution across the gap which is effectively constant. The ‘gap loading limit’ is the maximum gap that a sample can fill whilst still giving a uniform velocity distribution across the gap.

In oscillatory tests, inside this limit, sample inertia effects are negligible and the shear wave propagation properties of the sample give a shear rate distribution which is uniform and in phase with the driving surface. The velocity distribution throughout the gap is thus independent of material properties and depends only upon the motion of the driving surface.

However, even for small gaps, at a sufficiently high frequency the gap loading condition is not satisfied and a complex standing shear wave results within the gap. This effect is accentuated for high density and low viscosity fluids and gives meaningless experimental results. It is therefore important to appreciate the upper limit of the practical operating frequency appropriate to a particular set of test conditions.

This limit has been determined by Schrag[4] (1977) and an outline is given in the Bohlin CS Reference guide. A nomograph is included in the Bohlin CS User manual to show the practical limits of the various measuring systems. The VOR is not so prone to gap loading since the strain is applied on one surface and measured on the other.

Gap loading effects manifest themselves as elastic response being seen where viscous should be and vice-versa.

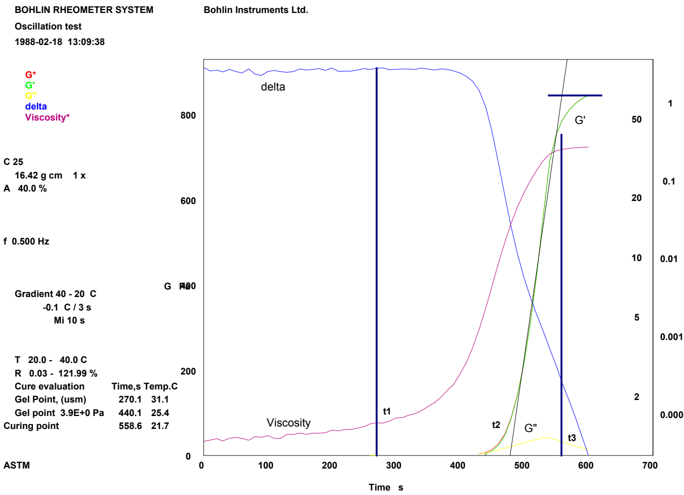
Controlling the strain on controlled stress rheometers

Consider the fact that a controlled stress rheometer controls the stress and measures the strain. If we hold one stress and step down in frequency we will find that the measured strain will increase since we are holding the stress for longer and longer time scales and hence the displacement increases. As the linear response region is strain dependent and not stress dependant it becomes apparent that we require a method of adjusting the stress at each frequency to produce a strain in the linear region. The Auto Stress function in the Bohlin software does this job. If we were to start at a low frequency and step up the first stress that is used by the programme may produce a very large strain and so it is usual to sweep down in frequency (highest first, lowest last) so that the software can adjust the stress and maintain a fixed strain without deviating too far.

It should be noted that occasionally a material will be tested where the value of modulus (G*) increases for a decrease in frequency (eg. thixotropic materials). In this case the frequency sweep should go from low to high.

Cure Analysis

The Oscillation software is capable of performing a cure test and analysis to ASTM D 4473 standard. This is done by using one frequency (1 Hz) to monitor the materials viscoelastic properties as a function of time or temperature.



Cure evaluation	Time,s	Temp.C
Gel Point, (usm)	270.1	31.1
Gel point 3.9E+0 Pa	440.1	25.4
Curing point	558.6	21.7

Figure-21

At the end of the test, pressing the C key will invoke the cure analysis.

Maximum in the phase angle, δ, is called the gel point of the unsupported material (USM) E1. Cross over point between G' and G'' (i.e. δ=45° or Tan δ=1) is called the gel point, E2. A tangent is constructed on the G' curve on the region of steepest ascent. The intersection of the tangent with the asymptotic G' value is termed the cure point, E3. The software will also show the maximum fluidity (minimum viscosity) This is not part of the ASTM spec. but is useful in predicting process problems if the value of viscosity is too low.

Multiwave oscillation

The ASTM cure analysis looks for the cross over of G' and G" as a means of determining the gel point. It is stipulated in the specification that the frequency used is 1 Hz. If a different frequency was used it is quite possible that you will obtain different results since, as we have already seen, a material shows different viscoelastic properties for different frequencies.

If we wish to study the viscoelastic properties as a function of frequency on a material that is changing with time (or temperature) we must use some technique other than the discrete frequency methods we have looked at so far. In a multiwave test, we generate a compound wave consisting of several frequencies summed together. This signal can then be used for discrete point measurements with the data being displayed as frequency dependence as a function of time or temperature.

Rapid Frequency sweeps

Using multiwave, a frequency sweep only takes as long as the time to take a measurement at the lowest frequency. Thus you can perform a 'frequency sweep' with many points at the low frequency end in a fraction of the time it would take with a conventional frequency sweep.

The relative amplitude of each discrete frequency can be set, enabling you to ensure that the signal measured is within an acceptable range at each individual frequency. To assist in setting the relative amplitudes, three functions are available which are used as follows:

Amplitude	*Use*
Constant	***Solids***
1/f	***Viscoelastic materials***
1/SQRT(f)	***Liquids***

The overall amplitude can either be set or the AutoStrain function used. Set this amplitude as you would a normal single frequency (i.e. to be in linear region).

(C) Relaxation

Stress relaxation is a rather neglected technique that can give very useful information about viscoelastic materials. The test sample is subjected to a rapidly applied strain which is then held for the remainder of the test. The relaxation behaviour is then studied by monitoring the steadily decreasing value of shear stress. For a pure Newtonian material, the stress will decay instantaneously whereas for a pure Hookean material there will be no decay. The simplest type of viscoelastic response is an exponential decay.

For long time scale tests the stress relaxation method is substantially faster than standard oscillation testing to obtain the viscoelastic response as a function of time.

The stress relaxation test is also useful in quality control to obtain a ‘finger print’ which may indicate several rheological properties - viscosity, initial modulus and decay time.

(D) Stress Growth

The stress growth test is the controlled shear rate rheometer’s counterpart to the creep test. The sample is subjected to a linearly increasing strain normally over a long period of time. When the shear stress becomes constant as a function of time, the material is in steady state flow and the zero shear viscosity can be obtained. (Remember, in a creep test we have a fixed value of shear stress and wait for the shear rate to become constant. The stress growth test applies a constant shear rate and waits for the shear stress to become steady - thus the two tests are mathematically interchangeable)

The limitation of the stress growth test comes from the fact that the rheometer may not be able to apply a sufficiently large enough strain to overcome the elastic component in the sample. Controlled stress rheometers can apply an infinite strain and so do not suffer from this problem.

APPENDIX-A

SOME PRACTICAL APPLICATIONS OF RHEOLOGY

(A) Coatings

Sagging

Sagging is usually due to the action of gravitational forces on a coating applied to an inclined surface as show in Figure-22

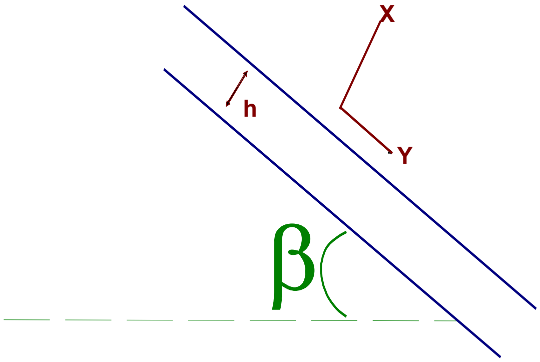


Figure-22

Since the flow does not involve acceleration, a balance exists between the gravitational forces and the stresses in the fluid:

$$\frac{\delta\sigma}{\delta y} + \rho g.\mathrm{Sin}\,\beta = 0$$

This gives the maximum shear stress σ_{max} as ρgh Sin ß i.e. sagging will not occur for coatings with yield stresses greater than σ_{max}

For viscous materials the maximum shear rate will be : ρgh Sin ß / η

The distribution of velocity across the film is given by (h-½y) yρg Sin ß / η with the maximum velocity occurring at the surface. A consequence of this is that thicker areas of coating will sag with a higher speed thus promoting runs.

If the drying time of the film is T_d, then sagging will not occur if ρgh Sin ß T_d / 2 η << 1

Notation key

ρ = density (kg m^{-1})
g = acceleration due to gravity
h = film thickness
ß = tilt angle (degrees)
η = film viscosity (Pas)
T_d = drying time of the film

Levelling

Under certain conditions levelling depends upon the balance between the surface tension and viscous forces which oppose levelling. A sinusoidal film is produced as shown in figure-23

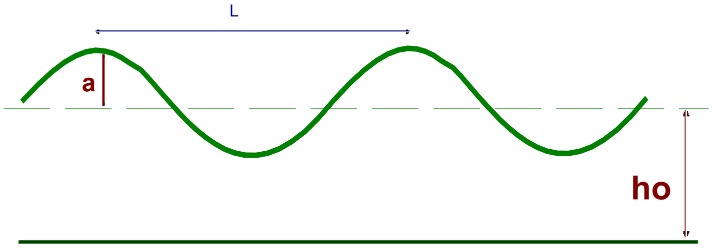


Figure-23

Analysing the equations of motion it can be shown that the film levelling occurs exponentially with time according to :

$$h(t) = h_o + a\, e^{-t/\tau} \text{Sin } (2\pi\, x / L)$$

The time constant τ is given by :

$$\tau = 3\, \eta\, L^4 / ((2\, \pi)^4\, \sigma\, h_o^3)$$

An approximate shear rate is :

$$\text{Shear rate}_{\text{approx.}} = 2a / \text{Ln } 2\, \tau\, L$$

This gives :

$$\tau_{max} = 8\, \pi^3\, \sigma\, a\, h / L^3$$

Notation key

$h = h_o + a \text{ Sin } (2\, \pi\, x / L)$
σ = surface tension
L = wave length
τ = time constant

Sedimentation

The sedimentation velocity in a suspension is given by Stokes Law:

$$V_s = \frac{2\, r^2\, g\, (d-p)}{9\, \eta_0}$$

From this we find that the maximum shear rate obtained by the particles in the suspension is :

$$\text{Shear rate}_{max} = \frac{3\, V_s\, \eta_0}{2r}$$

The limiting stress is thus given by :

$$\sigma_{limit} = \frac{rg\, (d-p)}{3}$$

Thus, if the material has a yield stress greater than σ_{limit} you will not have a problem with sedimentation otherwise the sedimentation rate can be determined from the maximum shear rate.

Notation key

r = particle radius
g = acceleration due to gravity
p = density of suspending fluid
d = particle density
η_0 = Zero shear viscosity

Flow rates to shear rate conversion

When pumping a material it is often useful to be able to predict the rate at which it will flow from an orifice. For a power law fluid (determine this by the Power law model in Data Processing) we can obtain values for the material constants k and n and use them as follows.

The shear rate will vary across the output nozzle and is zero at the centre of the jet. At the edge of the jet it is given by :

$$\text{shear rate}_{edge} = \frac{4Q}{(\pi r^3)\,(3/4 + 1/4n)}$$

This equation can be used to check that k and n are being determined in the right range of shear rates. (As a first approximation you could set n=1 i.e. assume Newtonian behaviour, to get a rough idea of shear rate range involved).

The flow rate from the tube orifice is determined by the pressure drop and the rheological properties k and n by means of the following equation :

$$Q = \pi r^3 / (1/n + 3) \times (Pr / 2k)^{1/n}$$

Notation key

Q = flow rate ($M^3\ S^{-1}$)
r = radius of the tube
P = pressure gradient along nozzle
k = from power law fit
n = power law index (from power law fit)

(B) Polymers

Generation of heat in rapid oscillating deformation [5]

Materials undergoing rapid oscillating deformations will generate heat energy. An example of this is a vehicle tyre travelling along an uneven surface. The following is an equation to predict the energy dissipated per second from the material :

$$\Sigma^{\circ} = w\, G''\, y_o^2 / 2 = w j'' \sigma_o^2 / 2$$

Further information can be found in Ferry's book **[5]**

Notation key

y_o = peak shear strain
σ_o = peak shear stress
w = angular velocity ($2\pi f$)

MWD and MW determination

For many commercial polymer melts, it is generally accepted that the elasticity measured from a creep test, J_o, is related to molecular weight distribution, independent of molecular weight. In contrast, it is also generally accepted that the zero shear viscosity, η_o, is only a function of weight-average molecular weight (the higher the MW, the higher η_o)

It has been found that η_o is proportional to $M^{3.4}$ over a considerable range of molecular weights for many polymers**[6]**

Consequently, creep (and creep recovery to give a more accurate J_o, see section 4) provide a convenient way to separate the effects of molecular weight and distribution.

(C) Typical linear regions for materials

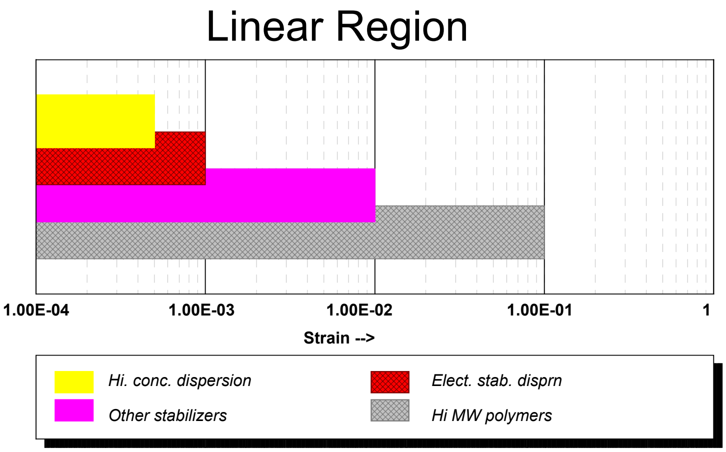


Figure-24

APPENDIX-B

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APPENDIX-C

CALCULATION OF SHEAR RATE AND SHEAR STRESS FORM FACTORS.

Rheometers and viscometers work with torque and angular velocity. Since we normally work with shear stress and shear rates a method is needed to convert from 'instrument numbers' to 'rheology numbers'.

Each measuring system used in an instrument will have its associated 'form factors' to convert torque to shear stress and to convert angular velocity to shear rate.

We will call the shear stress form factor C1 and the shear rate factor C2

Shear Stress = C1 x Torque
Shear Rate = C2 x angular velocity *
Viscosity = Shear Stress / Shear Rate

- For some measuring systems such as parallel plates, the gap between the measuring systems can be set by the user. In this case the equation used is :

Shear Rate = C2 x angular velocity / gap.

The following section shows how the form factors are calculated for each measuring system.

(A) Cone and plate

$$C1 = \frac{3}{2 \pi r^3} \qquad C2 = 1 / \theta$$

Where r = radius of cone θ = cone angle in radians

(B) Parallel plates

$$C1 = \frac{3}{2 \pi r^3} \qquad C2 = 3r / 4$$

Where r = radius of cone

NOTE: The shear stress varies across the radius for a parallel plate. The above formula refers to the 3/4 radius position if the test sample is Newtonian.

(C) Coaxial cylinders

$$C1 = \frac{1}{2 \pi r_a^2 H} \qquad C2 = \frac{2\ r_i^2\ r_o^2}{r_a^2 (r_o^2 - r_i^2)}$$

Where $r_a = (r_i + r_o) / 2$
r_i = inner radius
r_o = outer radius
H = height of cylinder

NOTE: C1 takes the shear stress as that occurring at an average radius position r_a

APPENDIX-D

PRINCIPLE OF OPERATION OF RHEOMETERS AND VISCOMETERS.

The following information is based around the Bohlin range of rheometers and viscometers but should be equally applicable to other instruments of similar types.

(A) Principle of operation of controlled stress (CS) rheometers

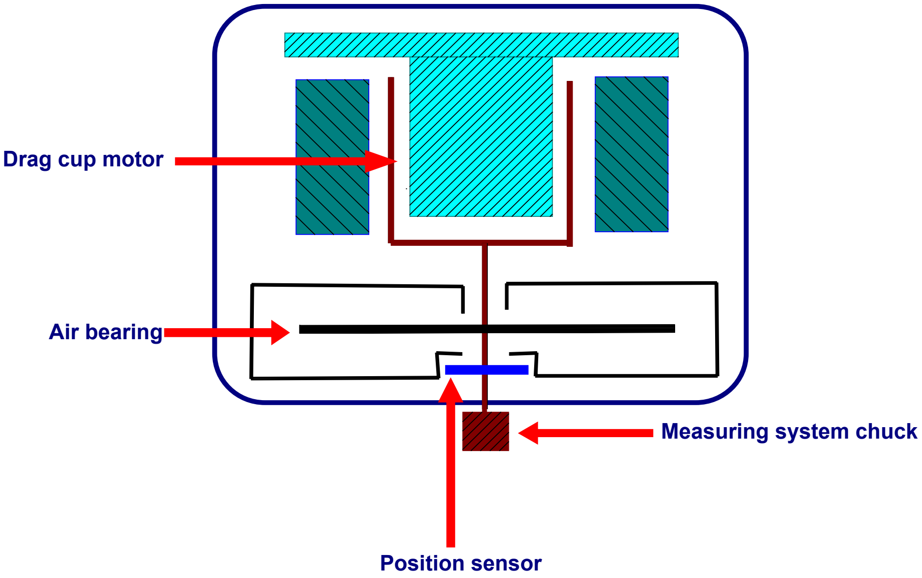

Figure-25

The principal components of a CS Rheometer are shown in figure-25. The rheometer is a constant torque motor which works by a drag cup system. An angular position sensor detects the movement of the measuring system attached to the shaft.

The software automatically converts the applied value of torque to a shear stress when displaying data. The reading from the position sensor is converted to a strain, again by using the information about the current measuring system. By monitoring the change of strain as a function of time we can obtain the shear rate.

Since the only data being produced by the rheometer is a deflection reading (from the angular position sensor) it follows that the lowest shear rate you can achieve is determined only by how long you are prepared to wait, since the sensor must turn a measurable amount for the software to calculate a speed and hence a shear rate.

(B) Principle of operation of controlled shear rate rheometers

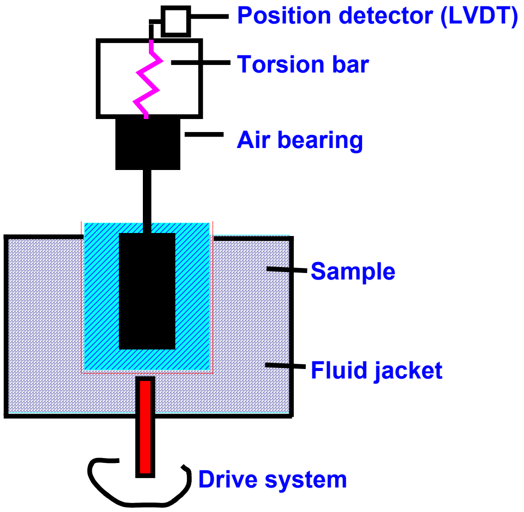

Figure-26

The principal components of a controlled rate rheometer are shown in figure-26. The rheometer is a constant speed motor with a torque detection system.

The torsion bar is suspended on an air bearing to give a virtually friction less bearing. When the drive system turns, the sample resistance (viscosity) tries to twist the torsion bar. By measuring the resultant twist and knowing the stiffness of the bar, the torque is measured.

The software automatically converts the measured torque to a shear stress when displaying data.