POLYMER PROCESSING

MODULE - I

Module 1:

Rheology of Polymer melts, Viscosity models,

Dependence of viscosity on Temperature, Pressure, molecular weight.

Viscoelastic models. Extensional viscosity,

Rheometers: Capillary, Rotational, cone & plate.

Die swell.

[8]

FLOW OF FLUIDS

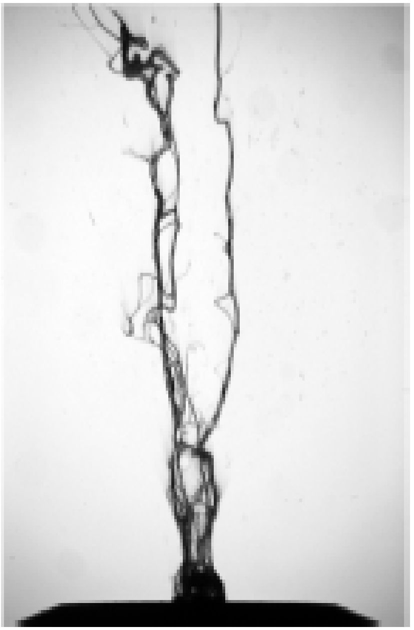
- ✓ Different fluids flow differently

Flow of Water	Flow of Honey	Flow of Toothpaste
		

- ✓ Type of flow depends on the nature of the materials, how the molecules are interacted, the processing conditions etc.

What is “Rheology”…

- Rheology; from the Greek word *rheos* & *logos*
  - **Rheos - stream current (i.e. flowing)**
  - **Logos – the study of…**
- The technical definition is:
  - **“The science of *deformation* and *flow*”**
- In practice it is used as a problem solving tool…
  - **My material….**
    - will not pour
    - is not stable
    - will not spray
    - is settling
    - leaves trail marks
- Can be used to measure internal structure and properties under processing conditions



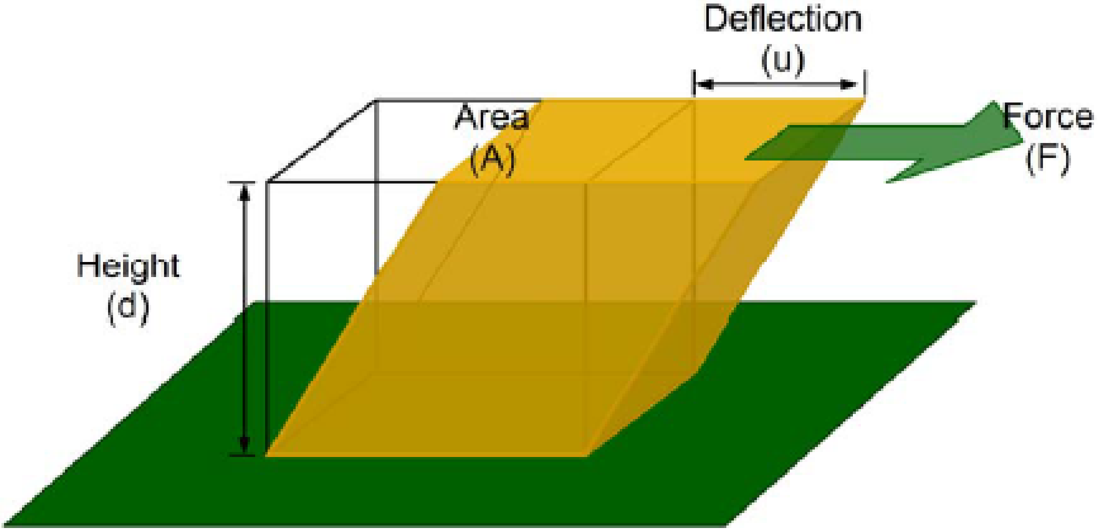
Using a simple illustrative picture:

„The Rheology Road“

viscous ← ***viscoelastic*** → ***elastic***

ideally viscous liquids **like water, oils** **Law of Newton**	***viscoelastic liquids*** **like glues, shampoos**	***viscoelastic solids*** **like pastes, gels, rubbers**	***ideally elastic*** (rigid) ***solids*** **like stone, steel** **Law of Hooke**

Rheology Definitions



			Units
Shear stress	$= \dfrac{\text{force (N)}}{\text{surface area (m}^2\text{)}}$	$\sigma = \dfrac{F}{A}$	Pa
Shear strain	$= \dfrac{\text{deformation}}{\text{height}}$	$\gamma = \dfrac{u}{d}$	None (or strain units)
Shear rate	$= \dfrac{\text{change in strain}}{\text{change in time (s)}}$	$\dot{\gamma} = \dfrac{d\gamma}{dt}$	1/s or s^{-1}

Absolute (dynamic) viscosity:

$$\text{Viscosity} = \eta = \frac{F'}{S} = \frac{\text{shear stress}}{\text{shear rate}} = \frac{\text{dyn m}^{-2}}{\text{sec}^{-1}} = \text{dyn m}^{-2}\text{ s}$$

The fundamental unit of viscosity measurement is the *poise.* A material requiring a shear stress of one dyne per square meter to produce a shear rate of one reciprocal second has a viscosity of one poise, or 100 centipoise.

Fluidity:

It is the reciprocal of viscosity ($\varnothing = 1/\eta$)

Kinematic Viscosity:

It is the absolute viscosity divided by the density of liquid at a specified temperature.

Kinematic viscosity **=** η **/** ρ; where ρ is the density of the liquid.

The unite is Stock (S) or centi-Stock (cS)

Relative viscosity:

is the relation of the solution viscosity η with respect to the viscosity of the solvent “standard” η_o

$$\eta_{rel} = \eta / \eta_0$$

- **Viscosity:**
- Thus, the fluid element, when subjected to shear stress, ζ_{yx}, experiences a rate of deformation {shear rate) given by du/dy.
- The rate of shearing strain is increased in direct proportion—that is,

$$\tau \propto \frac{du}{dy}$$

- This result indicates that for common fluids, such as water, oil, gasoline, and air, the shearing stress and rate of shearing strain (velocity gradient) can be related with a relationship of the form:

$$\tau = \mu \frac{du}{dy}$$

- where the constant of proportionality is designated by the Greek symbol μ (mu) and is called the absolute viscosity, dynamic viscosity, or simply the viscosity of the fluid.

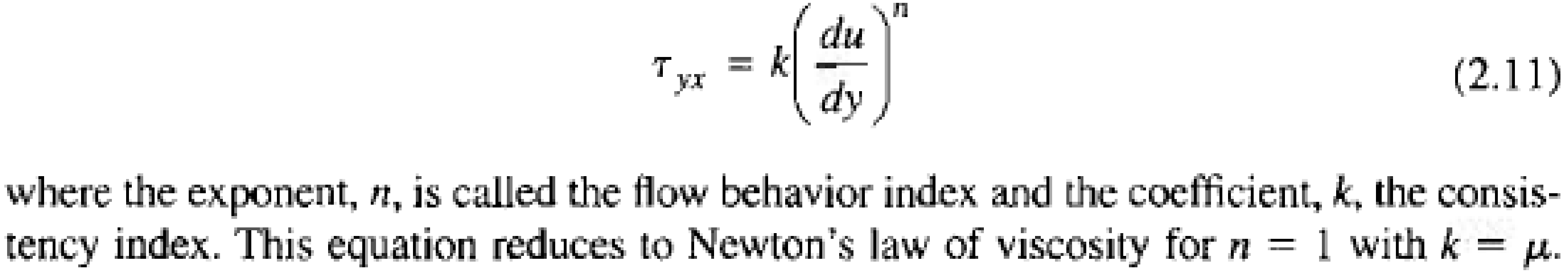
- **Newtonian Fluid:**
- Most common fluids such as water, air, and gasoline are Newtonian under normal conditions.
- If the fluid is Newtonian, then

$$\tau_{yx} \propto \frac{du}{dy}$$

- It states that the shear stress on a fluid element layer is directly proportional to the rate of shear strain or velocity gradient.
- The constant of proportionality is called the co-efficient of viscosity.

$$\tau = \mu \frac{du}{dy}.$$

- **Non-Newtonian Fluid:**
- Fluids in which shear stress is not directly proportional to deformation rate are non-Newtonian.
- Non-Newtonian fluids commonly are classified as having time-independent or time-dependent behavior.
- Familiar example is toothpaste.
- Toothpaste behaves as a "fluid" when squeezed from the tube. However, it does not run out by itself when the cap is removed.
- There is a threshold or yield stress below which toothpaste behaves as a solid.
- This may be adequately represented for many engineering applications by the **power law model**, which for one-dimensional flow becomes



$$\tau_{yx} = k\left(\frac{du}{dy}\right)^n \tag{2.11}$$

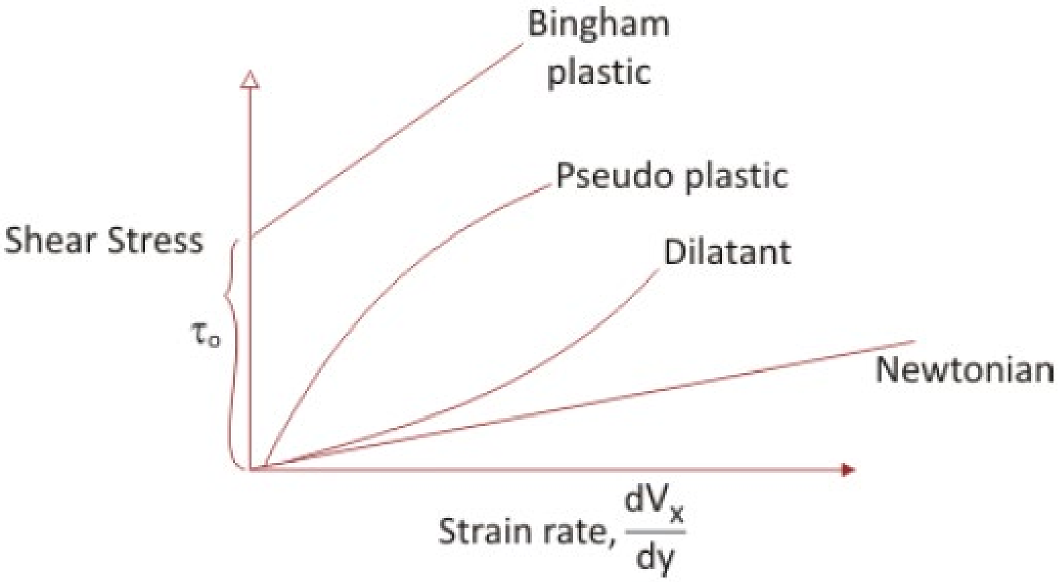
where the exponent, n, is called the flow behavior index and the coefficient, k, the consistency index. This equation reduces to Newton's law of viscosity for $n = 1$ with $k = \mu$.

VISCOSITY MODELS

Time Independent Fluid Flow

(Generalized Newtonian Fluids)

- **Newtonian Fluid:**



- **Newtonian:** $\tau = \mu \frac{dv_x}{dy}$: air, water, glycerin
- **Bingham Plastic:** $\tau = \underset{\text{yield stress}}{\tau_o} + \mu \frac{dV_x}{dy}$: toothpaste

  (Fluid does not move or deform till there is a critical stress)
- **Dilatant:** $\tau = K \left(\frac{dv_x}{dy}\right)^n, n > 1$: starch or sand suspension

  or shear thickening fluid

  (Fluid starts 'thickening' with increase in its apparent viscosity)
- **Pseudo plastic:** $\tau = K \left(\frac{dv_x}{dy}\right)^n, n < 1$: paint or shear thinning fluid

  (Fluid starts 'thinning' with decrease in its apparent viscosity)

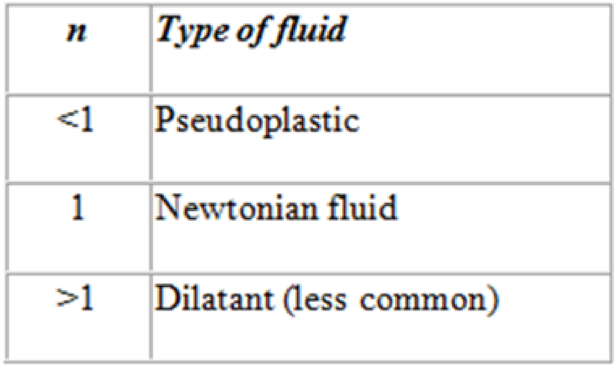
Power-law fluid/ Ostwald–de Waele power law (2 Parameters Model)

A Power-law fluid is a type of generalized Newtonian fluid for which the shear stress, σ , is given by

$$\sigma = m(\dot{\gamma})^n$$

Where ***n*** is the flow behavior index or power law index (dimensionless) and ***m*** is the flow consistency index (SI units Pa.s^n),
In terms of the apparent viscosity,

$$\eta = m(\dot{\gamma})^{n-1}$$



n	*Type of fluid*
<1	Pseudoplastic
1	Newtonian fluid
>1	Dilatant (less common)

The value of n in the range 0.3-0.7 depending upon the concentration and molecular weight of the polymer, etc. Smaller is the value of n, more shear-thinning is the material.

Drawback

It predicts neither the upper nor the lower Newtonian plateaus in the limits of $\dot{\gamma} \rightarrow 0$ or $\dot{\gamma} \rightarrow \infty$

Cross Law (3 Parameters Model)

- New parameter incorporated here is zero shear viscosity
- Another difference is Cross law index (m) is introduced in place of power law index

$$\eta = \frac{\eta_0}{1 + (\lambda\dot{\gamma})^m}$$

where η_0 = zero-shear-rate viscosity

λ = natural time (i.e., inverse of the shear rate at which the fluid changes from Newtonian to power-law behavior)

m = Cross-law index ($= 1 - n$ for large shear rates)

- Applicable at the low-shear-rate behavior of the viscosity.
- Differs from the Bird-Carreau law primarily in the curvature of the viscosity curve in the vicinity of the transition between the plateau zone and the power law behavior

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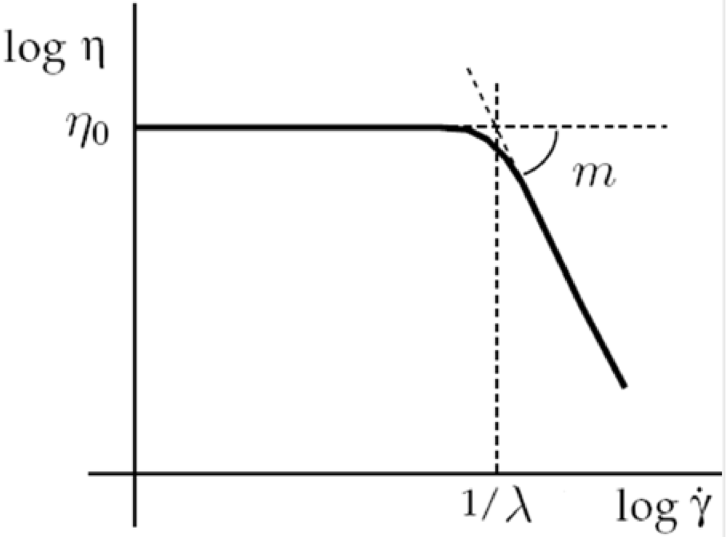


✓At low shear rate ($\dot{\gamma} \ll 1/\lambda$) cross fluids behave as Newtonian fluids

✓At high shear rate ($\dot{\gamma} \gg 1/\lambda$) as power-law fluids.

Bird-Carreau Law (4 Parameters Model)

- New parameter incorporated here is infinite shear viscosity

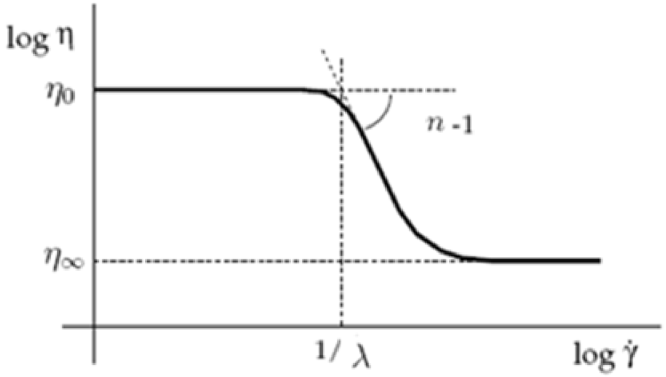
$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)\left(1 + \lambda^2 \dot{\gamma}^2\right)^{\frac{n-1}{2}}$$

where η_∞ = infinite-shear-rate viscosity

η_0 = zero-shear-rate viscosity

λ = natural time (i.e., inverse of the shear rate at which the fluid changes from Newtonian to power-law behavior)

n = power-law index



✓At low shear rate ($\dot{\gamma} \ll 1/\lambda$) Carreau fluid behaves as a Newtonian fluid

✓At high shear rate ($\dot{\gamma} \gg 1/\lambda$) Carreau fluid behaves as a power-law fluid.

It differs from the Cross law primarily in the curvature of the viscosity curve in the vicinity of the transition between the plateau zone and the power law behavior.

Carreau-Yasuda Law (5 Parameters Model)

New parameter incorporated here is an index **a** that controls the nature of transition

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)\left[1 + (\lambda\dot{\gamma})^a\right]^{\frac{n-1}{a}}$$

where η_0 = zero-shear-rate viscosity

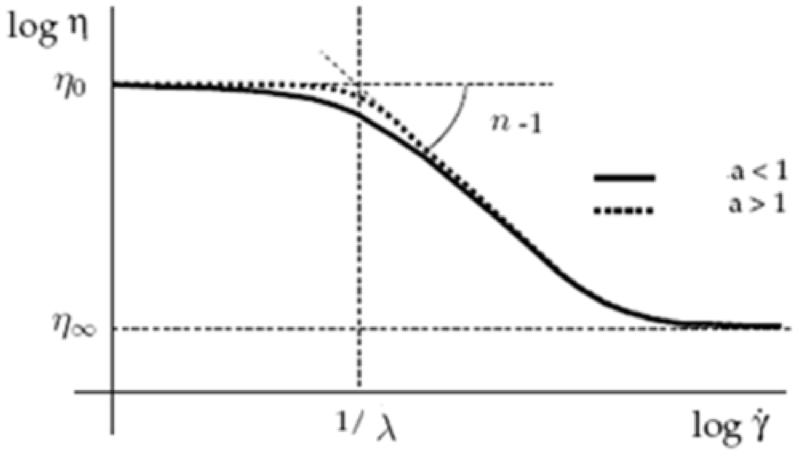
η_∞ = infinite-shear-rate viscosity

λ = natural time (i.e., inverse of the shear rate at which the fluid changes from Newtonian to power-law behavior)

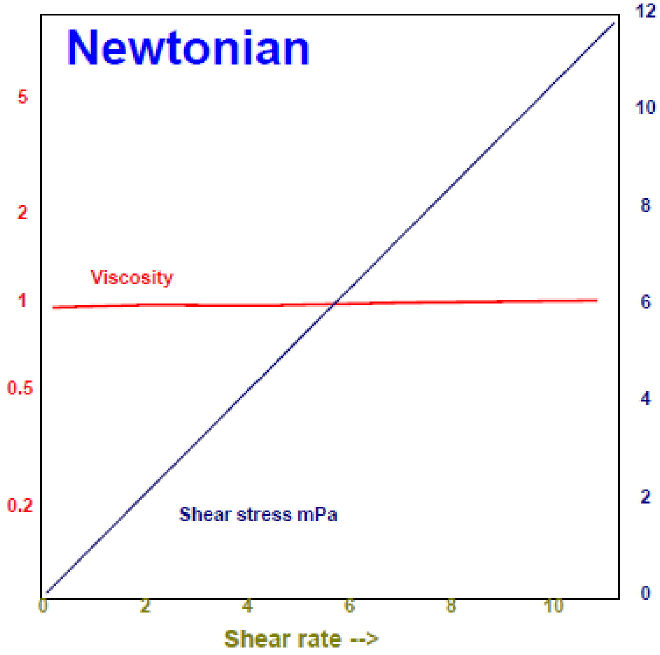
a = index that controls the transition from the Newtonian plateau to the power-law region

n = power-law index

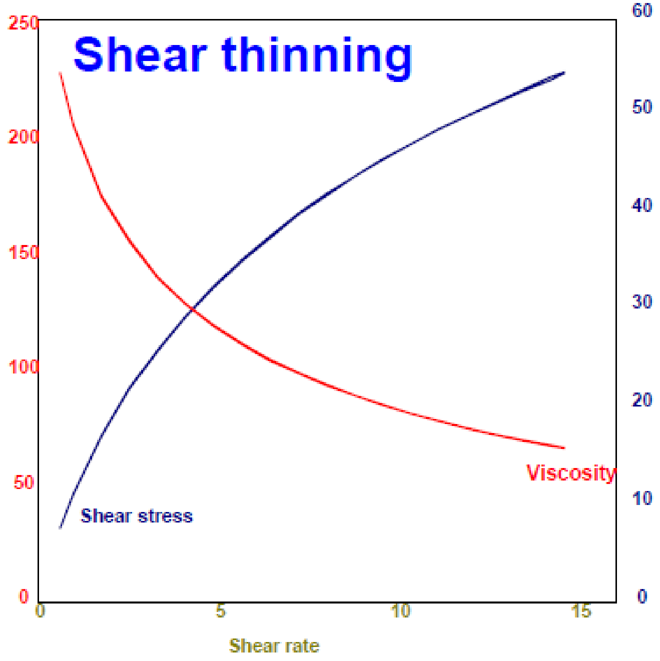
The Carreau-Yasuda law is a slight variation on the Bird-Carreau law. The addition of the exponent '*a*' allows for control of the transition from the Newtonian plateau to the power-law region.



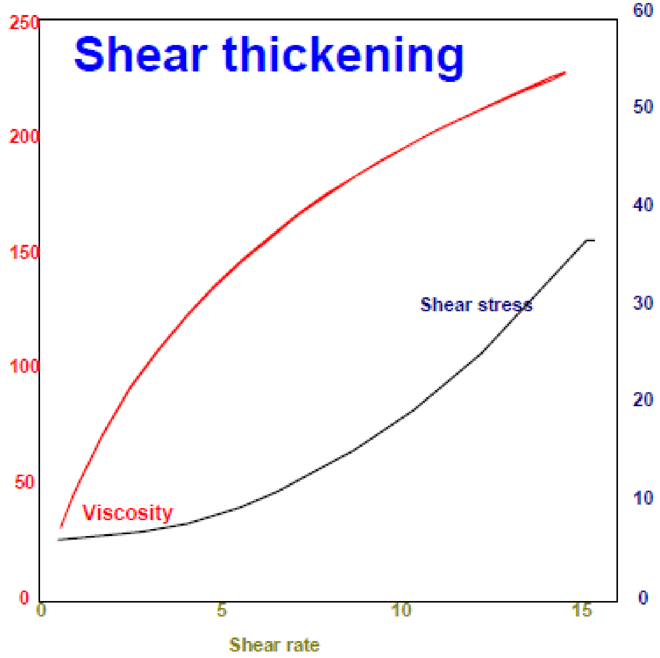
- ✓ low value of parameter *a* (*a* < 1) lengthens the transition.
- ✓ high value of parameter *a* (*a* > 1) results in an abrupt transition.



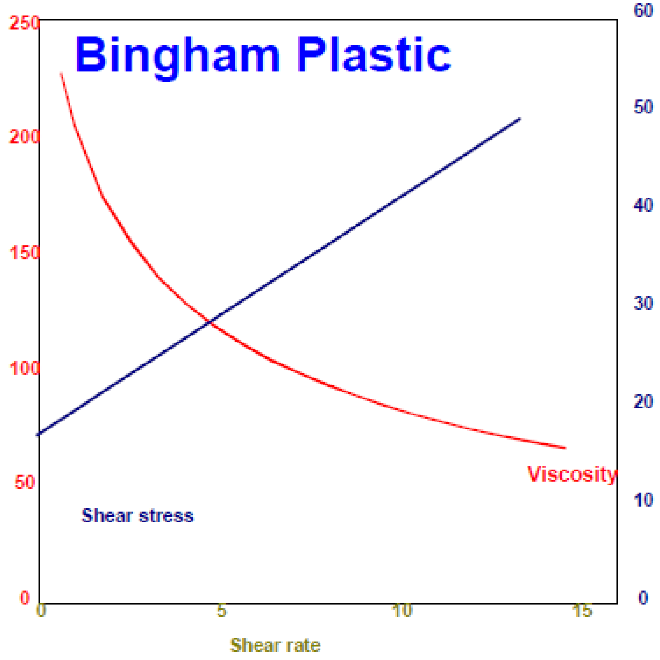
Newtonian



Shear thinning



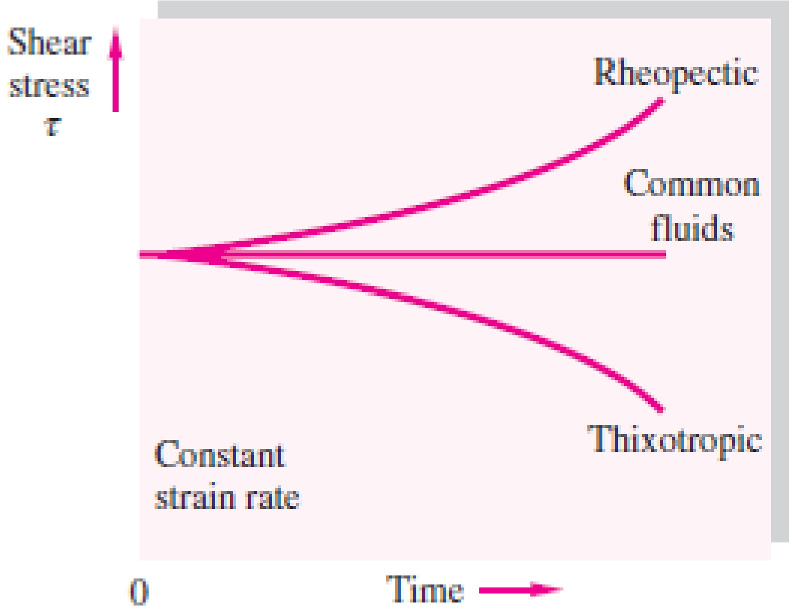
Shear thickening

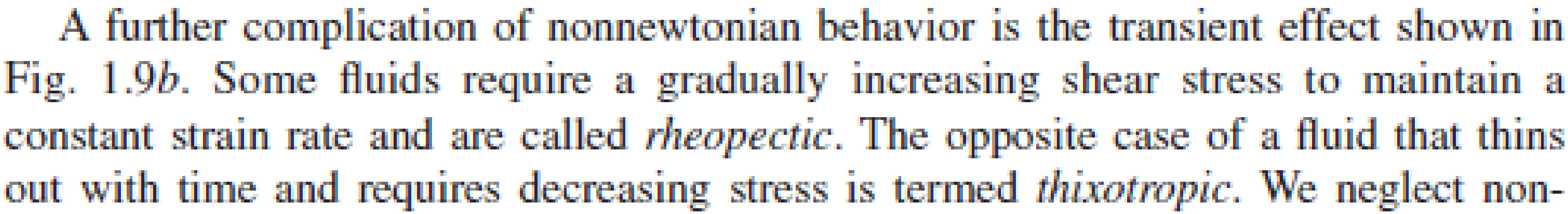


Bingham Plastic

Time Dependent Fluid Flow

- **Newtonian Fluid:**

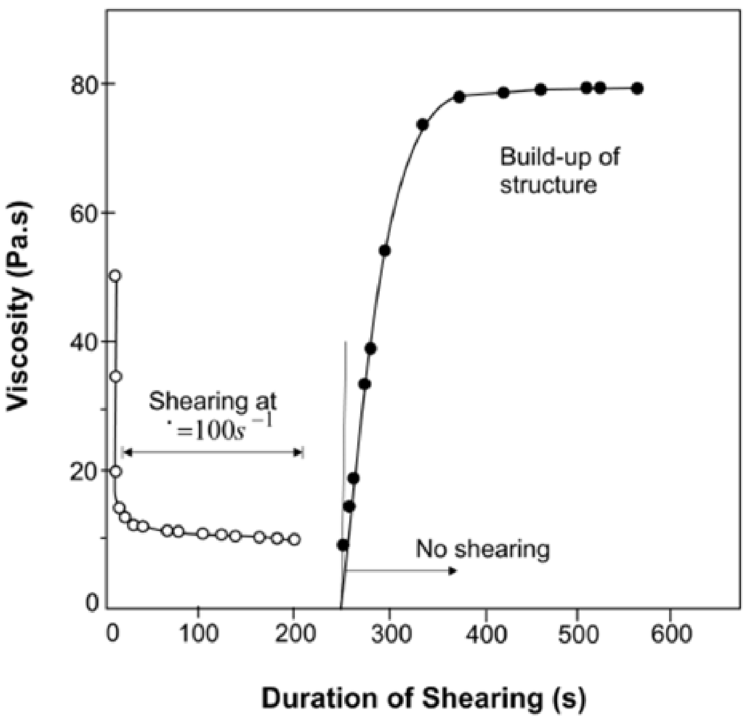




A further complication of nonnewtonian behavior is the transient effect shown in Fig. 1.9*b*. Some fluids require a gradually increasing shear stress to maintain a constant strain rate and are called *rheopectic*. The opposite case of a fluid that thins out with time and requires decreasing stress is termed *thixotropic*. We neglect non-

THIXOTROPY

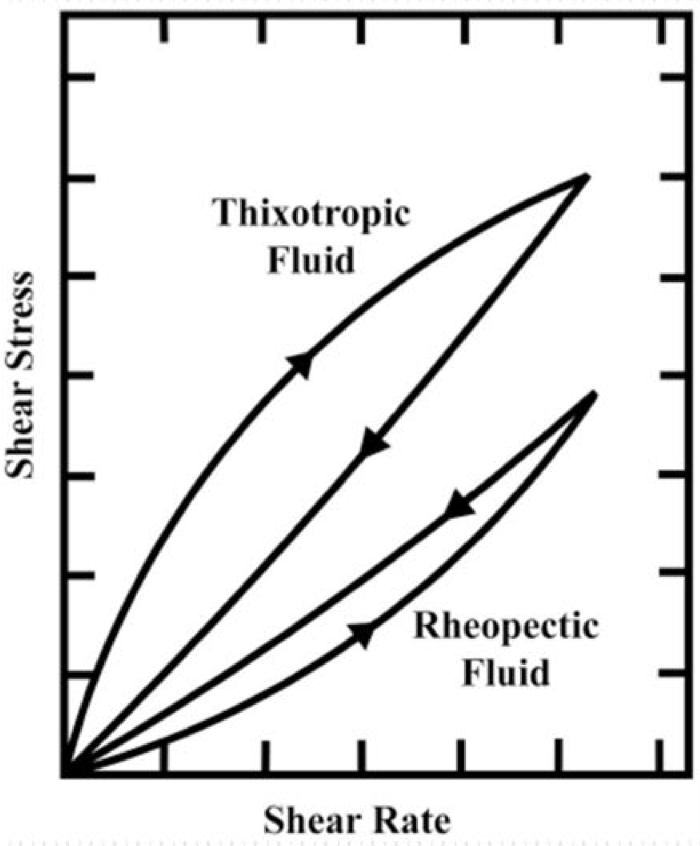
- When material is sheared at a constant rate, its apparent viscosity decreases with the duration of shearing.
- As the value of $\dot{\gamma}$ is gradually increased, the time needed to reach the equilibrium value is seen to drop dramatically.
- The breakdown of structure may be reversible, i.e., upon removal of the external shear and following a long period of rest, the fluid may regain (rebuilding of structure) the initial value of viscosity.



Rheopexy

- Fluids which show the negative thixotropy, i.e., their apparent viscosity (or the corresponding shear stress) increases with time of shearing
- The hysteresis loop is obviously inverted
- As opposed to thixotropic fluids, external shear raises the build up of structure

Example : gypsum pastes, printer inks, coal-water slurries and protein solutions



INTRODUCTION

Effect of Temperature on viscosity

- The procedure is based on the idea that increasing temperature has an equivalent effect on viscosity as decreasing shear rate.
- This trend can be seen by inspection of Fig., noting that increasing the temperature moves data to lower curves.

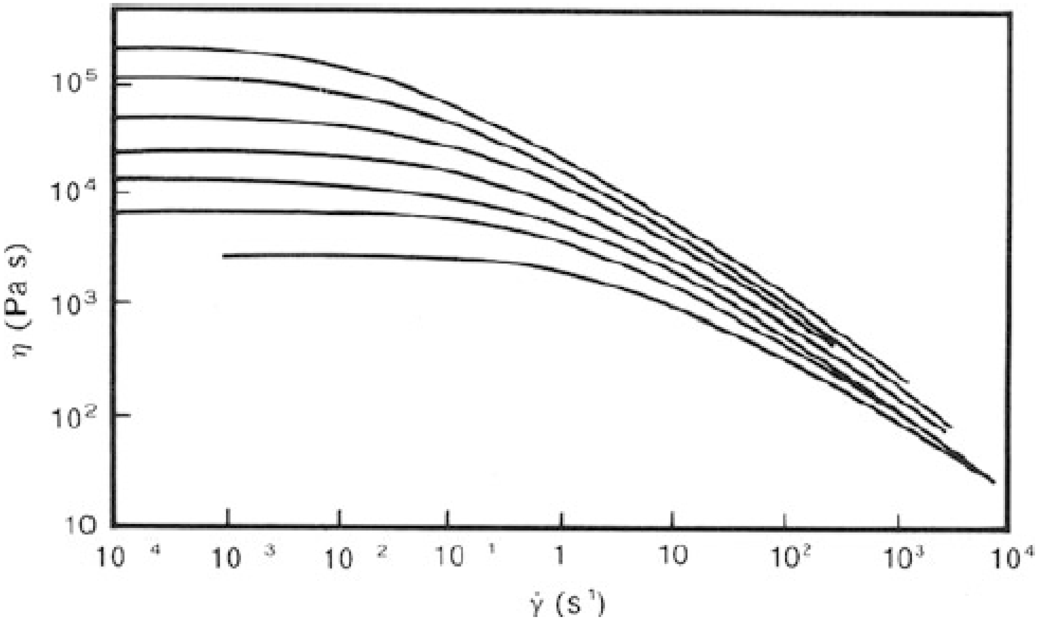


Fig. 2.4 Viscosity versus shear rate of a LDPE at several temperatures; from *top* to *bottom*: T(°C) = 115, 130, 150, 170, 190, 210, and 240. Data of Meissner [2]

INTRODUCTION

Effect of Temperature on viscosity

- If this effect is quantitatively the same at all shear rates, this implies that a single horizontal shift factor can be used to shift data on a log–log plot taken at several temperatures along the shear rate axis to coincide with those measured at a reference temperature T0.
- This idea is expressed by Eq (1).

$$\eta(\dot{\gamma}, T_0) = [1/\alpha_T(T)]\eta(\dot{\gamma} a_{\mathrm{T}}, T)$$

- For greater precision, a second shift factor, bT(T), normally equal to (T0ρ0/Tq), should also be applied to the viscosity, but it is usually close to unity and is often neglected.
- Such a representation is called a master curve and is a plot of reduced viscosity versus reduced shear rate.

INTRODUCTION

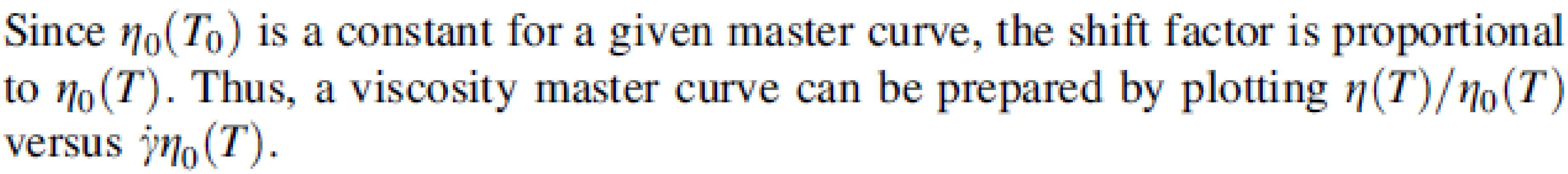
Effect of Temperature on viscosity

- For a polymer well above its glass transition temperature, it is often found that the zero-shear viscosity obeys the well-known Arrhenius relationship shown by Eq (2).

$$\eta_0(T) = \eta_0(T_0)\exp\left[\frac{E_\mathrm{a}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]$$

- The constant Ea is called the activation energy for flow.
- But this is the special case of Eq. (1) for shear rates where the viscosity equals ɳ0, which implies that the shift factor is give by Eq. (3).

$$a_T(T) = \frac{\eta_0(T)}{\eta_0(T_0)} = \exp\left[\frac{E_\mathrm{a}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]$$



Since $\eta_0(T_0)$ is a constant for a given master curve, the shift factor is proportional to $\eta_0(T)$. Thus, a viscosity master curve can be prepared by plotting $\eta(T)/\eta_0(T)$ versus $\dot{\gamma}\eta_0(T)$.

- It should be mentioned that time–temperature superposition is of limited utility with crystallizable polymers, because the range of temperatures over which measurements can be made is limited to that between the melting point and the temperature at which the polymer star
- Time–temperature superposition is not useful for long-chain branched systems although such materials are sometimes characterized in terms of specially-defined activation energies.ts to decompose.

INTRODUCTION

Effect of Pressure on Viscosity

- Whereas increasing temperature decreases the viscosity of melts, increasing pressure increases it, because compression of the melt decreases free volume.
- Pressure shift factors can be used to generate master curves just as temperature shift factors are used in time–temperature superposition.
- The Barus equation is often found to describe the pressure dependence of viscosity.

$$\ln\left[\frac{\eta_0(P)}{\eta_0(P_0)}\right] = \beta(P - P_0)$$

- This implies that the pressure shift factor aP is given by:

$$\ln[a_P(P)] = \beta(P - P_0)$$

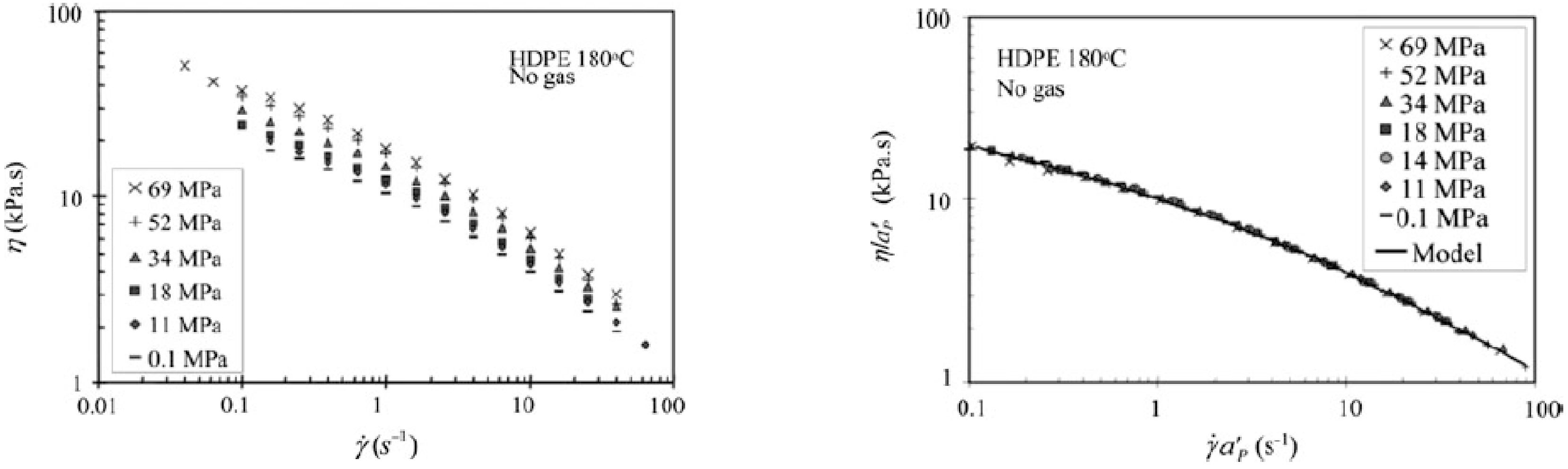
INTRODUCTION

Effect of Pressure on Viscosity

- Figure (a) shows the effect of pressure on the viscosity of a high-density polyethylene at 180 C and Fig. (b) is a maser curve based on the same data.
- The horizontal shift factor is a0 PðPÞ; the prime indicating that the vertical shift factor was neglected, i.e., set equal to unity.

(a) Effect of pressure on the viscosity versus shear rate curve of HDPE. From Park and Dealy.

(b) Shifted viscosity curve taking bP to be unity; reference pressure is 0.1 MPa. From Park and Dealy



INTRODUCTION

Effect of Pressure on Viscosity

- The Barus Eq. was found to fit the entire viscosity curve very well with bP set at unity.
- Increasing the pressure from atmospheric 0.1 to 69 MPa (&10,000 psi) increases the viscosity by a factor of about two.

INTRODUCTION

Effect of Molecular Weight on Viscosity

- Small molecules in the liquid state interact primarily through intermolecular forces that give rise at the microscopic level to friction and at the macroscopic level to viscosity.
- The viscosity of such a liquid is independent of shear rate.
- A polymeric liquid with a low molecular weight behaves in this way, and its viscosity increases linearly with molecular weight.
- For example, for linear polyethylene this behavior obtains up to a molecular weight around 3,500.
- But over a fairly narrow range of molecular weights the viscosity starts to decrease with shear rate and the increase of $\eta0$ with molecular weight becomes much stronger than linear.
- In the same range of rates, the viscosity depends increasingly on shear rate.

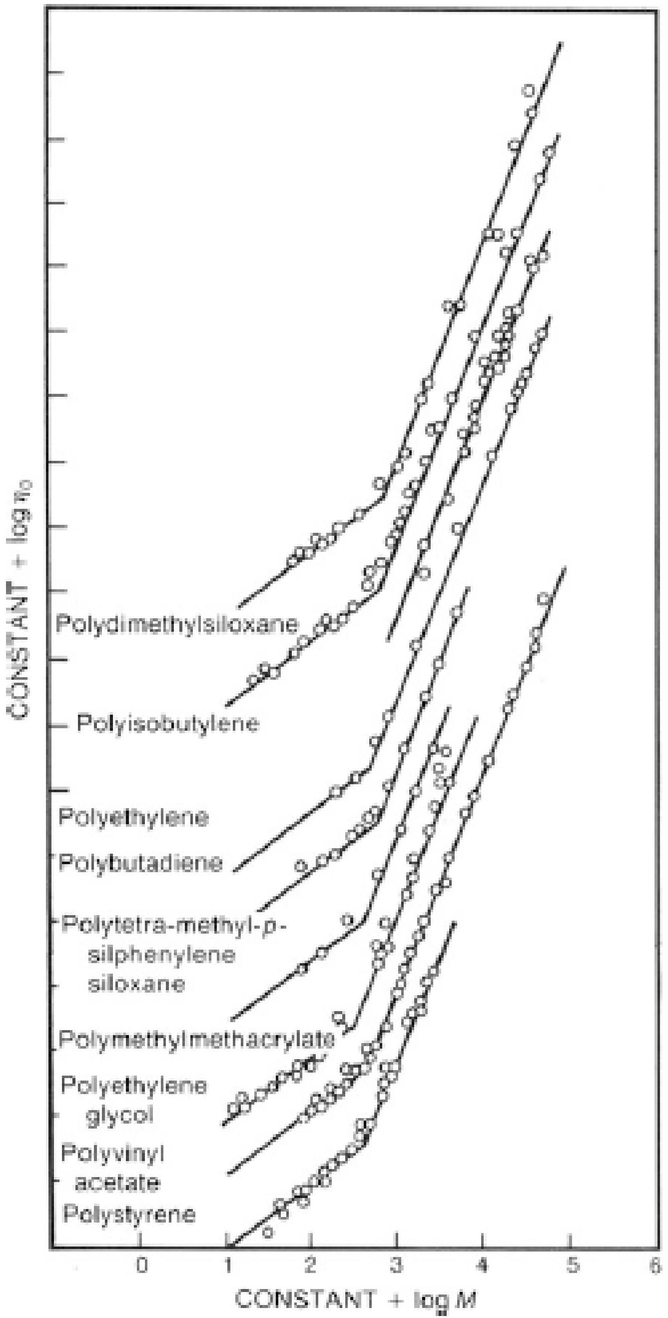
INTRODUCTION

Effect of Molecular Weight on Viscosity

- At low molecular weights the viscosity is proportional to molecular weight and varies little with shear rate over a wide range of shear rates.
- As the molecular weight increase, ɳ0 starts to increase much more rapidly with M, and the viscosity starts to depend strongly on shear rate.

Effect of Molecular Weight on Viscosity

Fig. 2.10 Zero-shear viscosity versus molecular weight (logarithmic scales) for several polymers. The axes have been shifted to avoid crowding. The *low-MW lines* correspond to unentangled samples and have slopes of unity, while the *high-MW lines* correspond to entangled polymers and are fitted to lines having slopes of 3.4. From Berry and Fox [16]



INTRODUCTION

Effect of Molecular Weight Distribution on Viscosity

- The effect of molecular weight distribution, MWD, is somewhat more subtle but still very important. In general, commercial polymers have a rather broad molecular weight distribution.
- Figure is a sketch of viscosity curves for two polymers having the same weight average molecular weight but different molecular weight distributions.
- The upper curve is for a nearly monodisperse sample, while the lower one is for a sample with a moderately broad MWD.
- The broadening of the distribution stretches out the range of shear rates over which the transition from the zero-shear viscosity to the power law region occurs.

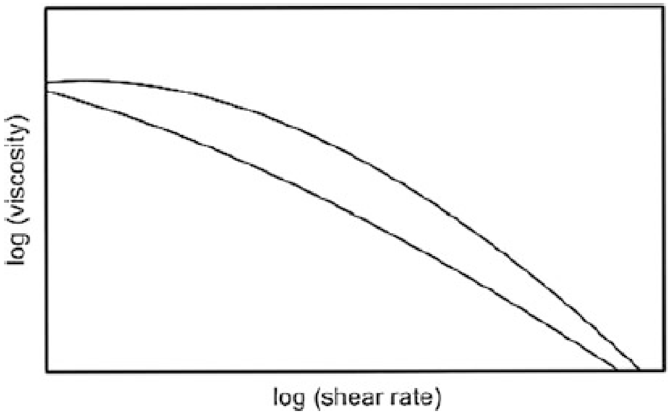


Fig. 2.11 Shapes of viscosity curves for two samples having the same M_w but with narrow (*upper curve*) and broad (*lower*) molecular weight distributions. The narrow MWD sample moves

LONG TERM MECHANICAL PROPERTIES

- **VISCOELASTIC MODELS:**
- Over the years there have been many attempts to simulate the behaviour of viscoelastic materials.
- This has been aimed at (i) facilitating analysis of the behaviour of plastic products, (ii) assisting with extrapolation and interpolation of experimental data and (iii) reducing the need for extensive, time-consuming creep tests.
- The most successful of the mathematical models have been based on spring and dashpot elements to represent, respectively, the elastic and viscous responses of plastic materials.
- In a perfectly elastic (Hookean) material the stress, a, is directly proportional to be strain, E, and the relationship may be written, for uniaxial stress and strain, as

$$\sigma = \text{constant} \times \varepsilon$$

where the constant is referred to as the modulus of the material.

- In a perfectly viscous (Newtonian) fluid the shear stress, ***t is directly proportional*** to the rate of strain

$$\tau = \text{constant} \times \dot{\gamma}$$

LONG TERM MECHANICAL PROPERTIES

- **VISCOELASTIC MODELS:**
- MAXWELL MODEL:
- The Maxwell Model consists of a spring and dashpot in series.
- The spring is the elastic component of the response and obeys the relation.

$$\sigma_1 = \xi \cdot \varepsilon_1 \tag{2.27}$$

where σ_1 and ε_1 are the stress and strain respectively and ξ is a constant.

- The dashpot is the viscous component of the response

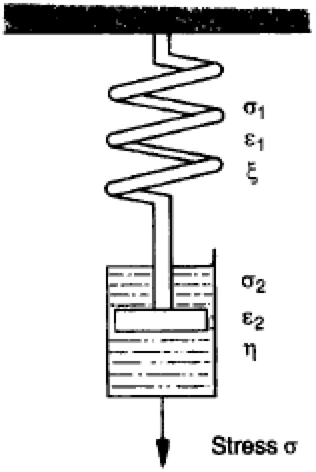
$$\sigma_2 = \eta \cdot \dot{\varepsilon}_2 \tag{2.28}$$

where η is a material constant.

Equilibrium Equation

For equilibrium of forces, assuming constant area

$$\text{Applied Stress, } \sigma = \sigma_1 = \sigma_2 \tag{2.29}$$



LONG TERM MECHANICAL PROPERTIES

- **VISCOELASTIC MODELS:**
- MAXWELL MODEL:

Geometry of Deformation Equation

The total strain, ε is equal to the sum of the strains in the two elements. So

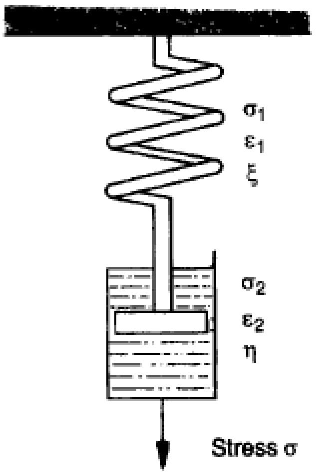
$$\varepsilon = \varepsilon_1 + \varepsilon_2 \tag{2.30}$$

From equations (2.27), (2.28) and (2.30)

$$\dot{\varepsilon} = \frac{1}{\xi}\dot{\sigma}_1 + \frac{1}{\eta}\sigma_2$$

$$\dot{\varepsilon} = \frac{1}{\xi}\cdot\dot{\sigma} + \frac{1}{\eta}\cdot\sigma \tag{2.31}$$

- This is the governing equation of the Maxwell Model.



LONG TERM MECHANICAL PROPERTIES

- **VISCOELASTIC MODELS:**
- KELVIN-VOIGHT MODEL:
- In this model the spring and dashpot elements are connected in parallel.

Stress–Strain Relations

These are the same as the Maxwell Model and are given by equations (2.27) and (2.28).

Equilibrium Equation

For equilibrium of forces it can be seen that the applied load is supported jointly by the spring and the dashpot, so

$$\sigma = \sigma_1 + \sigma_2 \tag{2.36}$$

Geometry of Deformation Equation

In this case the total strain is equal to the strain in each of the elements, i.e.

$$\varepsilon = \varepsilon_1 = \varepsilon_2 \tag{2.37}$$

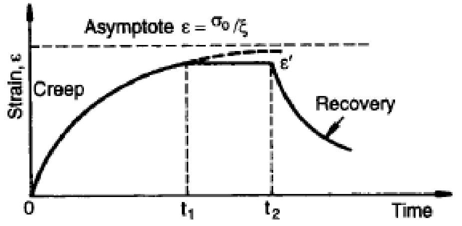
From equations (2.27), (2.28) and (2.36)

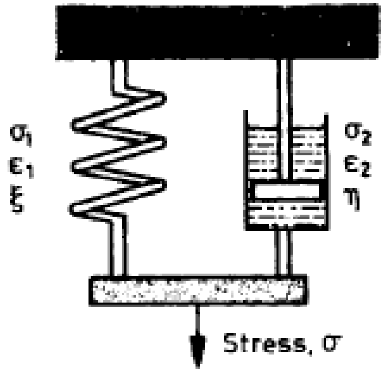
$$\sigma = \xi \cdot \varepsilon_1 + \eta \dot{\varepsilon}_2$$

or using equation (2.37)

$$\sigma = \xi \cdot \varepsilon + \eta \cdot \dot{\varepsilon} \tag{2.38}$$

This is the governing equation for the Kelvin (or Voigt) Model and it is interesting to consider its predictions for the common time dependent deformations.





INTRODUCTION

RHEOMETERS

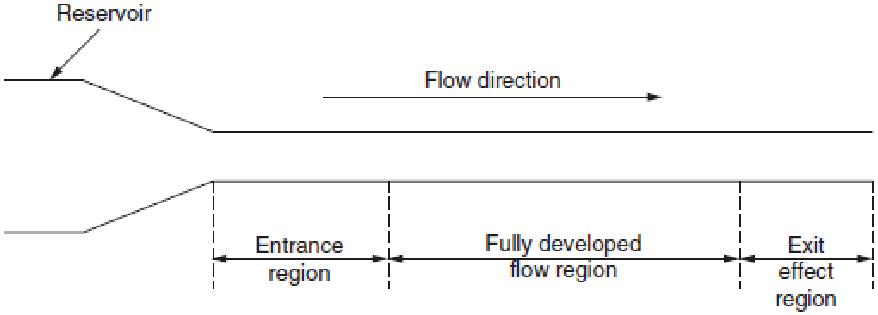
- A rheometer is a device used to measure the way in which a viscous fluid (a liquid, suspension or slurry) flows in response to applied forces.
- The word rheometer comes from the Greek, and means a device for measuring main flow.
- Rheometers: Capillary, Rotational, cone & plate.

- The fundamental methods can be classified under the specific geometry employed: capillary, Couette (concentric cylinder), and plate-and cone.

- 1. Capillary Flow:
- Capillary viscometers made of glass and operating under gravity are used mainly for Newtonian liquids. For non-Newtonian fluids, the design must allow operation over a wide range of flow rates, and the shear stress must be determined for fully developed flow conditions.
- The shear stress and shear rate at the wall can be determined from Equations (1) and (2), respectively (Brodkey, 1967):

$$\sigma_w = \frac{D\Delta P}{4L}$$

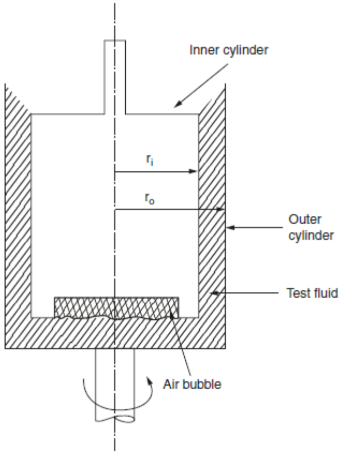
$$\left(\frac{dv}{dr}\right)_w = \frac{3}{4}\left(\frac{32Q}{\pi D^3}\right) + \frac{\sigma_w}{4}\frac{d\left(32Q/\pi D^3\right)}{d\tau_w}$$



- 1. Capillary Flow:
- Many foods such as applesauce, baby foods, and tomato puree are suspensions with relatively large particles.
- The flow behavior of a variety of food suspensions have been studied by using tubes having a diameter of 6–10 mm (Charm, 1960; Saravacos, 1968; Escardino et al., 1972; Rao et al., 1974; Scheve et al., 1974; Vitali and Rao, 1982).
- The pressure drop over a given length, required to compute the shear stress, has been measured by means of manometers and pressure transducers as well as the load cell of a universal testing machine (Blake and Moran, 1975).

- 2. Couette Flow Viscometers:
- A number of Couette (concentric cylinder) viscometers are available commercially.
- Corey and Creswick (1970) presented a design in which the revolutions per minute (rpm) of the rotating cylinder could be increased or decreased in a continuous manner.
- Either the outer or the inner cylinder can be rotated. However, when the outer cylinder is rotated, the transition to turbulent flow occurs at a higher speed than when the inner cylinder is rotated (Schlichting, 1960). For the case of the outer cylinder rotating and the inner cylinder being stationary, it can be shown that (Brodkey, 1967).

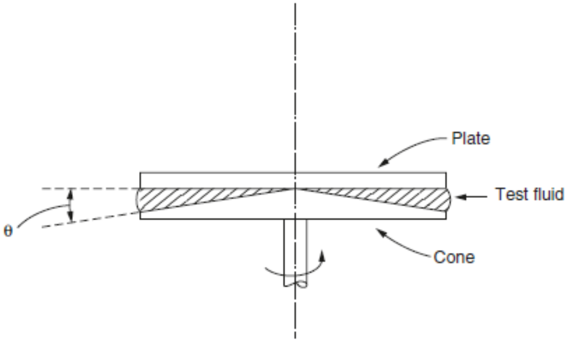
where Ω is the angular veloci $2\sigma_i \frac{d\Omega}{d\sigma_i} = \dot{\gamma}_i - \dot{\gamma}_o$ cylinder (radians/second),
·γ is the shear rate, and the subscripts
i and o denote the inner and outer cylinders, respectively.



- 3. Plate and Cone Viscometers:
- As the name indicates, a plate-and-cone viscometer consists of a circular flat plate and a cone.
- The cone angle is about 3° or less. When the angle is larger than 3°, edge effects can distort the flow field.
- For the case of a fixed plate and a rotating cone with a small angle, Brodkey (1967) showed that
- where σp is the shear stress at the plate,
- T is the torque per unit area, D is the plate diameter,
- Ω is the angular velocity, ·γ p is the shear rate at the plate,
- and θ is the cone angle in radians.

$$\sigma_p = \frac{3T}{D}$$

$$\dot{\gamma}_p = \frac{\Omega}{\theta}$$



INTRODUCTION

DIE SWELL

- Polymer melts can also exhibit elasticity.
- During flow they have the ability to store strain energy and when the stresses are removed, this strain is recoverable.
- A good example of elastic recovery is post extrusion swelling.
- After extrusion the dimensions of the extrudate are larger than those of the die, which may present problems if the dimensions of the extrudate are critical.
- In these circumstances some knowledge of the amount of swelling likely to occur is essential for die design.
- If the die is of a non-uniform section (tapered, for example) then there will be recoverable tensile and shear strains.
- If the die has a uniform cross-section and is long in relation to its transverse dimensions then any tensile stresses which were set up at the die entry for example, normally relax out so that only the shear component contributes to the swelling at the die exit.

INTRODUCTION

DIE SWELL

- If the die is very short (ideally of zero length) then no shear stresses will be set up and the swelling at the die exit will be the result of recoverable tensile strains only.
- In order to analyse the phenomenon of post extrusion swelling it is usual to define the swelling ratio, B, as

$$B = \frac{\text{dimension of extrudate}}{\text{dimension of die}}$$