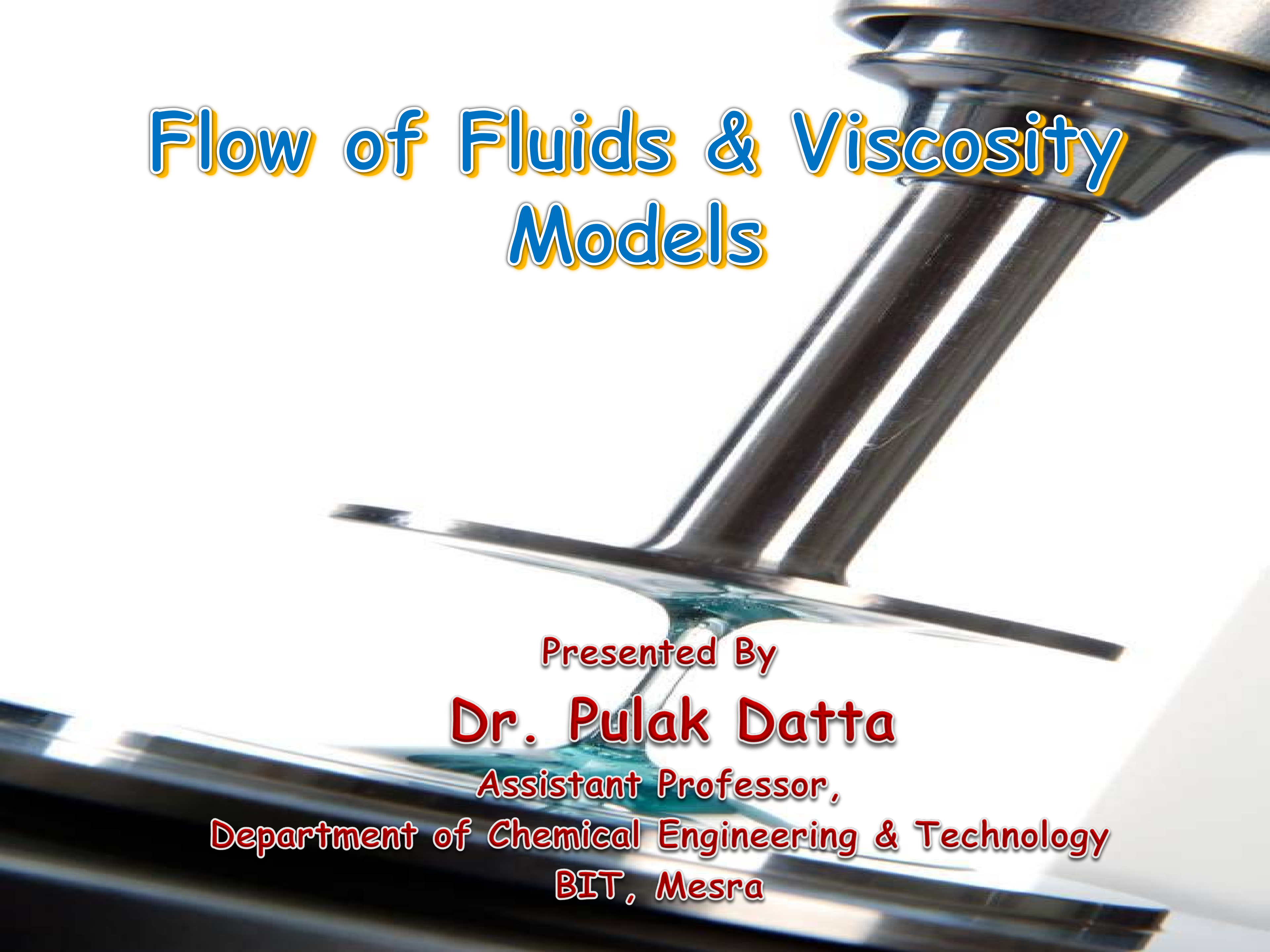
Flow of Fluids & Viscosity Models



Presented By

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Lecture Objectives:

Basic concepts of viscosity are introduced together with their analytical and experimental manifestations.

Lecture Contents:

1. Introduction and definitions of viscosity
2. Different types of fluid flow
3. Viscosity models to analyze viscosity

Lecture Outcome:

Upon successful completion of the course the student is able to solve and analyse problems involving different types of fluid flow.

FLOW OF FLUIDS

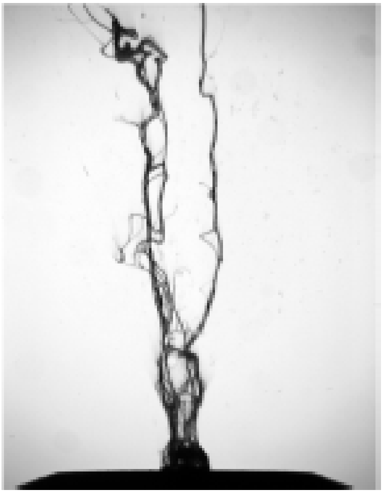
- ✓ Different fluids flow differently

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
- Applicable to a wide range of sample types, especially the bulk result of colloidal interactions



Using a simple illustrative picture:

„The Rheology Road“

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

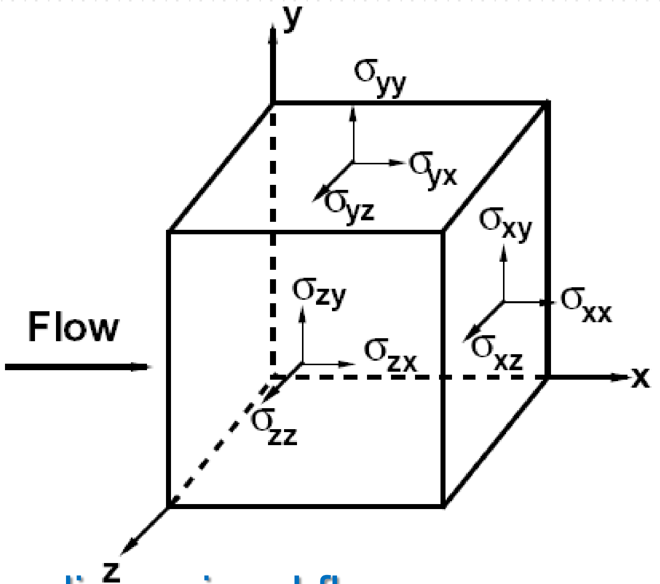
ideally viscous liquids
like water, oils
Law of Newton

viscoelastic liquids
like glues, shampoos

viscoelastic solids
like pastes, gels, rubbers

ideally elastic (rigid) *solids*
like stone, steel
Law of Hooke

Flow Behavior of Materials



Stress components in three dimensional flow

There are only 3 independent shear components and 2 normal stress differences. Thus, in Cartesian coordinates, these are

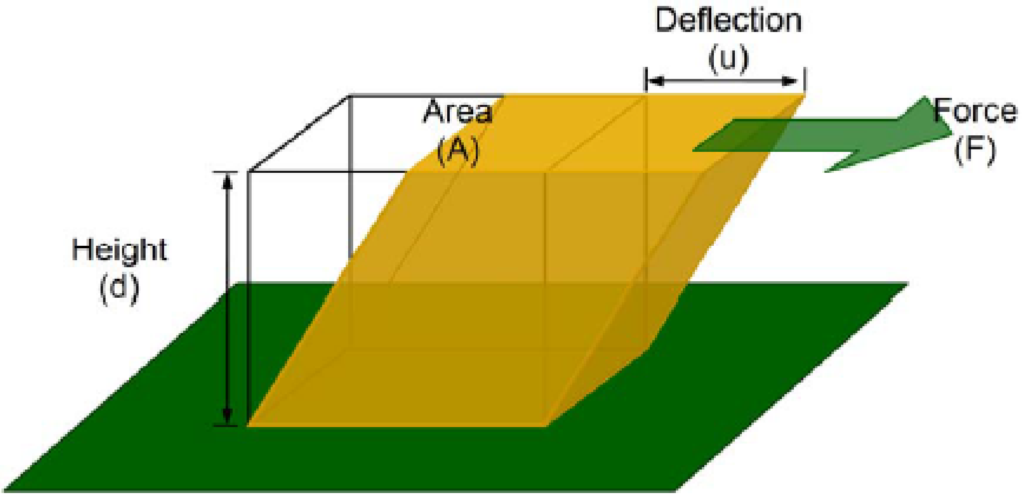
$$\sigma_{xy} (= \sigma_{yx})$$
$$\sigma_{xz} (= \sigma_{zx})$$
$$\sigma_{yz} (= \sigma_{zy})$$

and the two normal stress differences defined as

Primary normal stress difference, $N_1 = \sigma_{xx} - \sigma_{yy}$

Secondary normal stress difference $N_2 = \sigma_{zz} - \sigma_{yy}$

Rheology Definitions



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

Kinematic Viscosity:

It is the absolute viscosity divided by the density of liquid at a specified temperature. Kinematic viscosity $= \eta / \rho$; 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

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

Specific Viscosity

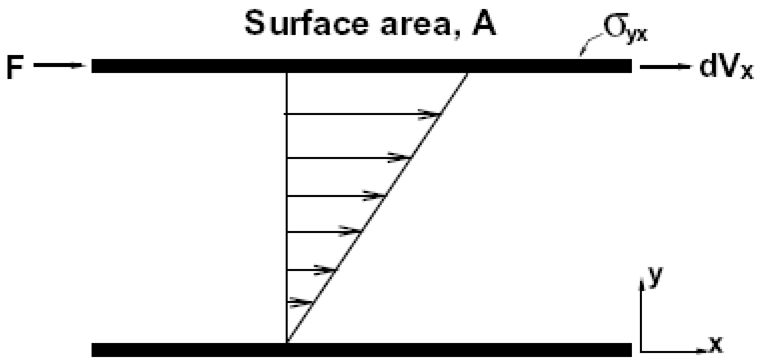
$$\eta_{sp} = (\eta_{rel} - 1)$$

Newtonian Flow of Fluids

NEWTONIAN FLOW

- Newton assumed that all materials have, at a given temperature, a viscosity that is independent of the shear rate.

$$\sigma_{yx} = \frac{F}{A} = \eta \dot{\gamma}_{yx}$$



- For Newtonian fluids, all the stress components are related linearly to the rate of deformation tensor components via the scalar viscosity. For instance the three stress components acting on the *x−face (oriented normal to the x−axis) are as follows*

$$\sigma_{xx} = -2\eta \frac{\partial V_x}{\partial x}$$

$$\sigma_{xy} = -\eta\left(\frac{\partial V_x}{\partial y} + \frac{\partial V_y}{\partial x}\right)$$

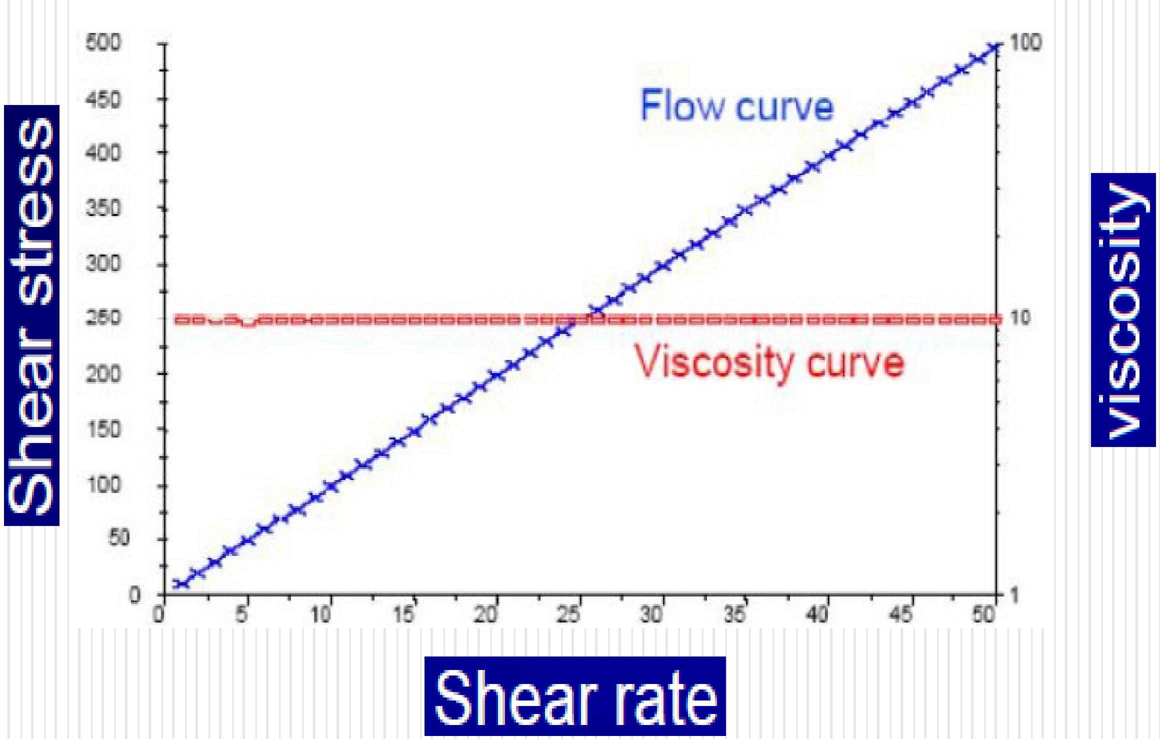
$$\sigma_{xz} = -\eta\left(\frac{\partial V_x}{\partial z} + \frac{\partial V_z}{\partial x}\right)$$

For a Newtonian fluid, in simple shear,

$$\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = 0$$

Because V_x only varies in the y−direction. Thus, Newtonian fluid requires it to satisfy the complete Navier-Stokes equations rather than simply exhibiting a constant value of shear viscosity.

NEWTONIAN FLOW



Non-Newtonian Flow of Fluids

NON-NEWTONIAN FLOW

The simplest possible deviation from the Newtonian fluid behavior occurs when

Time/ Kinematic History Independent

- The simple shear data $\sigma - \dot{\gamma}$ does not pass through the origin

  and/ or

- Result into a non-linear relationship between σ and $\dot{\gamma}$.

  - ✓ Conversely, the apparent viscosity, defined as $\sigma/\dot{\gamma}$, is not constant and is a function of σ or $\dot{\gamma}$.

$$\text{App. Viscosity}(\sigma/\dot{\gamma}) = f(\sigma, \dot{\gamma})$$

Time/ Kinematic History Dependent

- Indeed, under appropriate circumstances, the apparent viscosity of certain materials is not only a function of flow conditions (geometry, rate of shear, etc.), but it also depends on time, the kinematic history of the fluid elements under consideration.

NON-NEWTONIAN FLOW

Categories

1) Systems for which the value of $\dot{\gamma}$ at a point within the fluid is determined only by the current value of σ at that point; these substances are variously known as purely viscous, inelastic, time-independent or generalized Newtonian fluids (GNF). e.g. shear thinning, shear thickening behaviour, Bingham flow etc.

2) Systems for which the relation between σ and $\dot{\gamma}$. shows further dependence on the duration of shearing and kinematic history; these are called time-dependent fluids. E.g. thixotropy, rheopexy

3) Systems which exhibit a blend of viscous fluid behavior and of elastic solid-like behaviour. For instance, this class of materials shows partial elastic recovery, recoil, creep, etc. Accordingly, these are called *visco-elastic or elasto-viscous fluids.*

Time Independent Fluid Flow

(Generalized Newtonian Fluids)

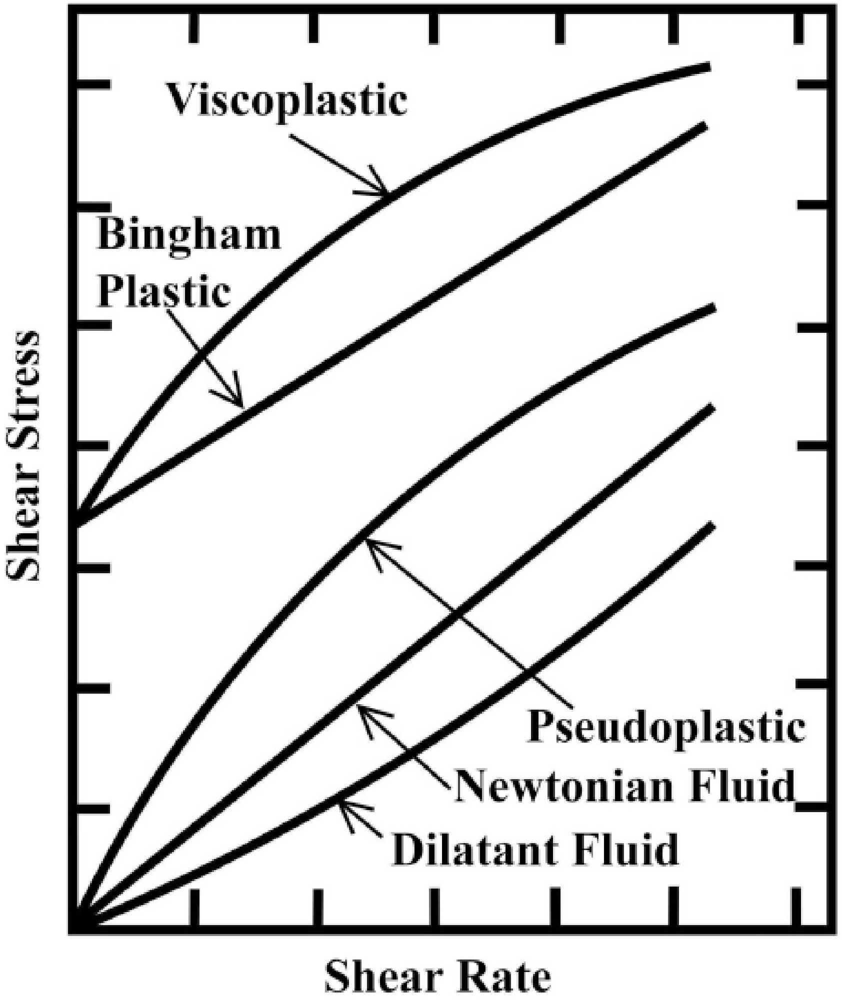
TIME-INDEPENDENT FLUID FLOW

The current value of the rate of shear at a point in the fluid is determined only by the corresponding current value of the shear stress and vice versa. Conversely, one can say that such fluids have no memory of their past kinematic history. Thus,

$$\dot{\gamma}_{yx} = f(\sigma_{yx})$$

Or, its inverse form,

$$\sigma_{yx} = f^{-1}(\dot{\gamma}_{yx})$$



Depending upon the above equation, three possibilities exist:

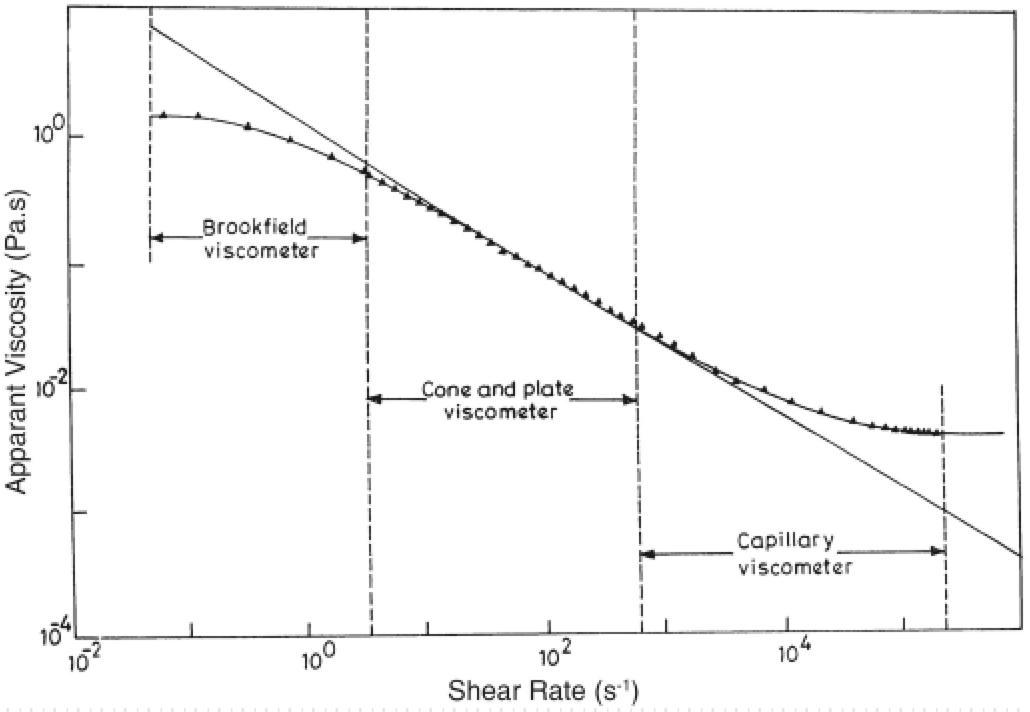
1) Shear- thinning or pseudoplastic behavior
2) Visco-plastic behavior with or without shear-thinning behavior
3) Shear- thickening or dilatant behavior.

Shear-Thinning Fluids

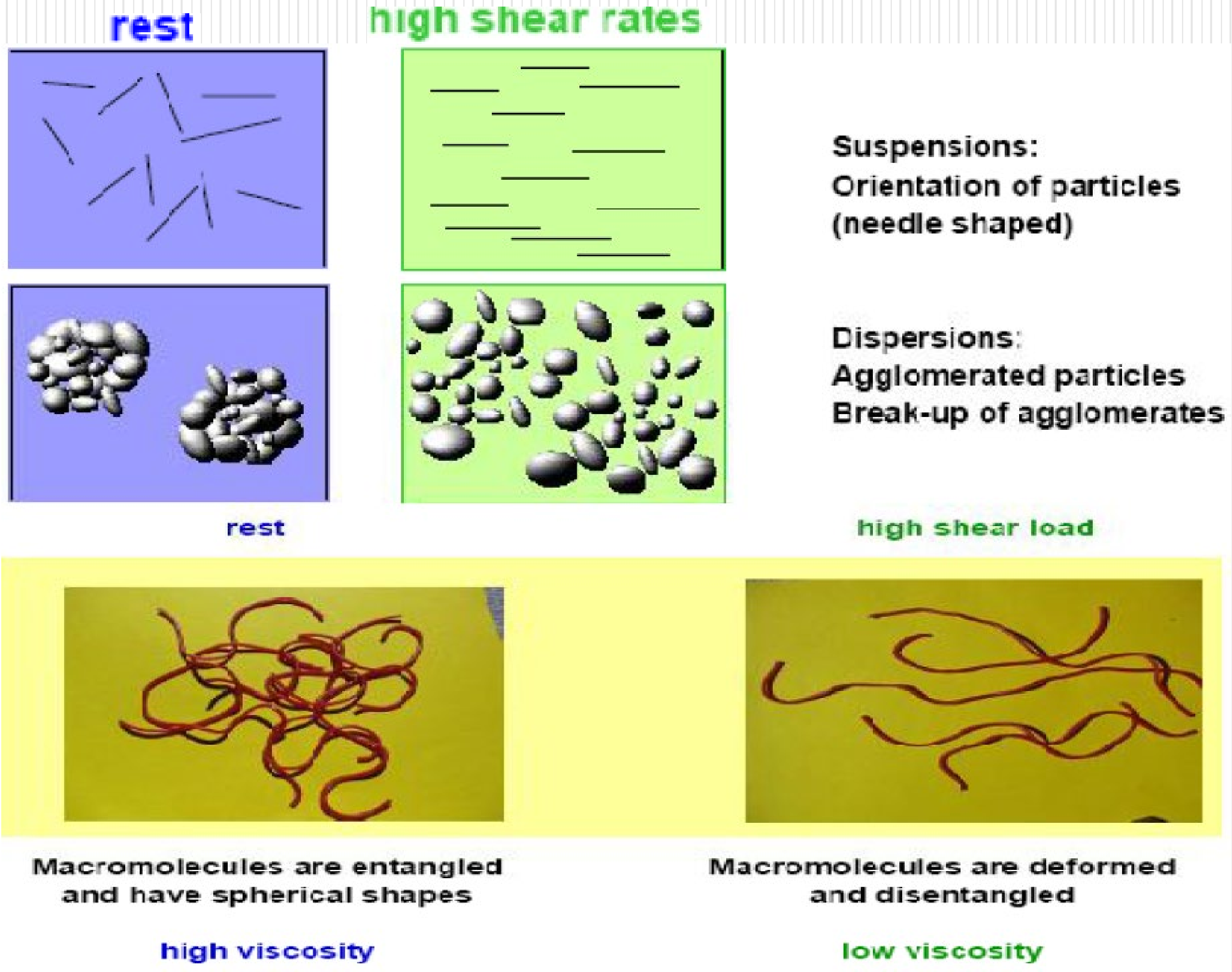
The most widely encountered type of time-independent non-Newtonian fluid behavior in engineering practice. It is characterized by an apparent viscosity which gradually decreases with increasing shear rate. In polymeric systems (melts and solutions), at low shear rates, the apparent viscosity approaches a Newtonian plateau where the viscosity is independent of shear rate (zero shear viscosity, η_0). Furthermore, only polymer solutions also exhibit a similar plateau at very high shear rates (infinite shear viscosity, η_∞), i.e.,

$$\lim_{\dot{\gamma}_{yx}\to 0} \frac{\sigma_{yx}}{\dot{\gamma}_{yx}} = \eta_0$$

$$\lim_{\dot{\gamma}_{yx}\to \infty} \frac{\sigma_{yx}}{\dot{\gamma}_{yx}} = \eta_\infty$$



Structural Reasons of Pseudo-plastic Flow Behaviour



Suspensions:
Orientation of particles
(needle shaped)

Dispersions:
Agglomerated particles
Break-up of agglomerates

Macromolecules are entangled
and have spherical shapes

high viscosity

Macromolecules are deformed
and disentangled

low viscosity

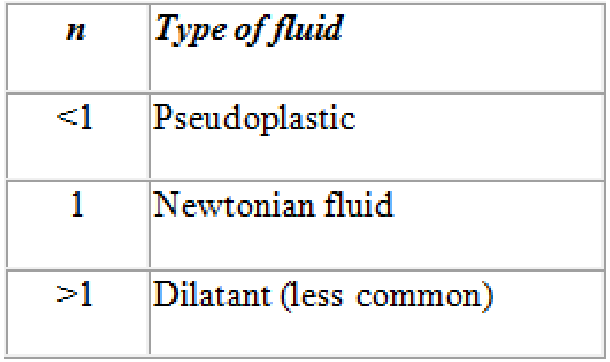
Power-law fluid/ Ostwald–de Waele power law (2 Parameters Model)

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 $\dot{\gamma} \to 0$ or $\dot{\gamma} \to \infty$

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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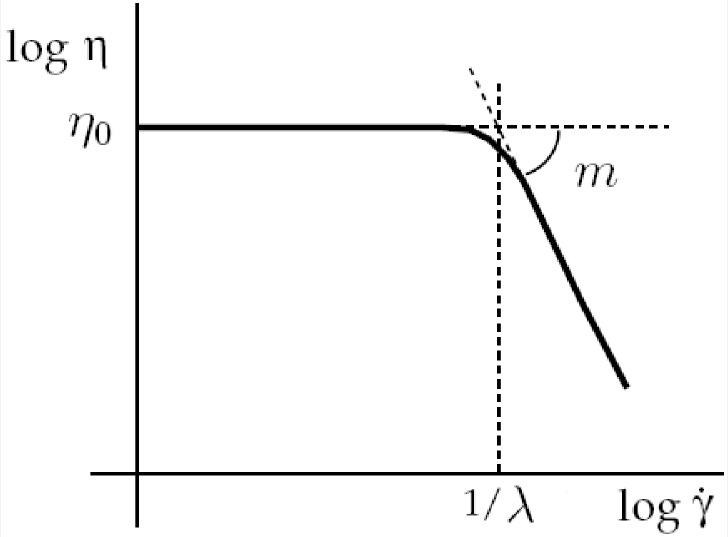


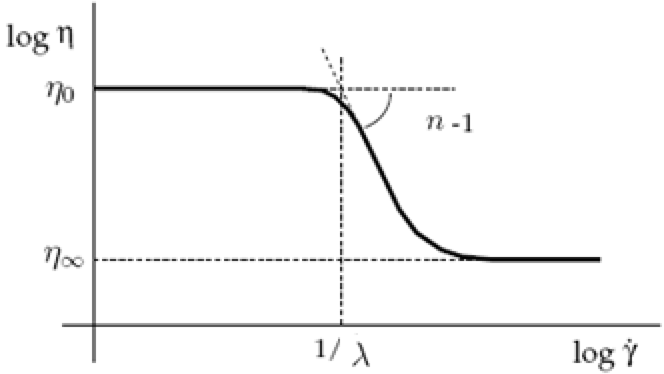
✓At low shear rate ($\dot{\gamma} \ll 1/\lambda$) cross fluids behave as Newtonian fluids
✓At high shear rate ($\dot{\gamma} \gg 1/\lambda$) as power-law fluids.

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

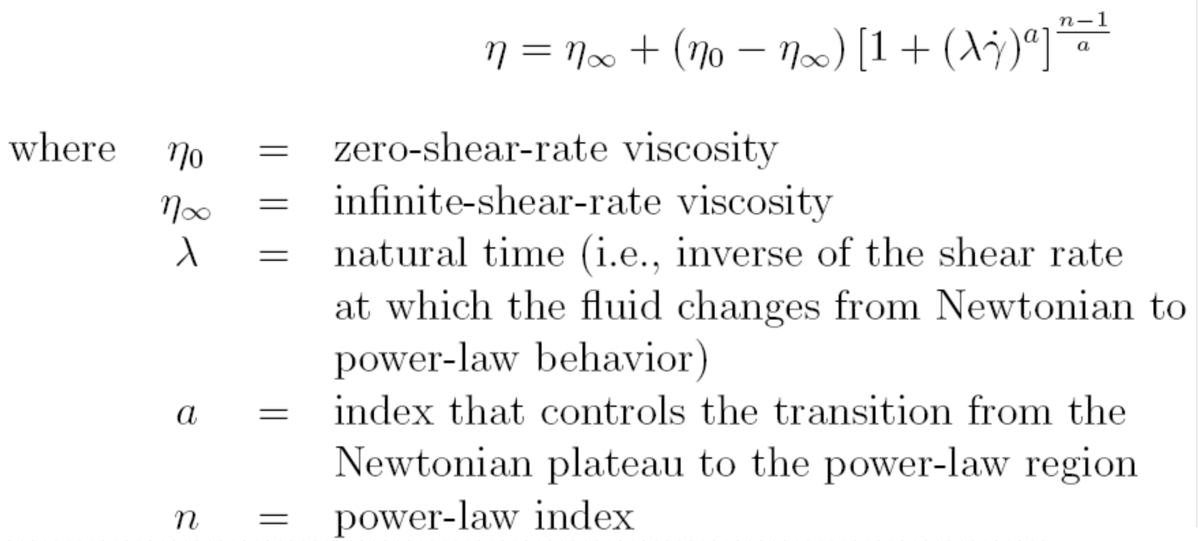


✓At low shear rate ($\dot{\gamma} \ll 1/\lambda$) Carreau fluid behaves as a Newtonian fluid
✓At high shear rate ($\dot{\gamma} \gg 1/\lambda$) Carreau fluid behaves as a power-law fluid.

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

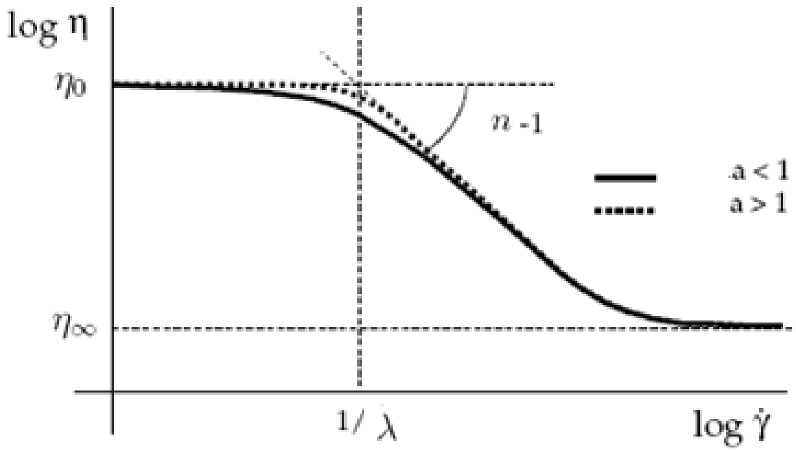
η_∞ = infinite-shear-rate viscosity

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

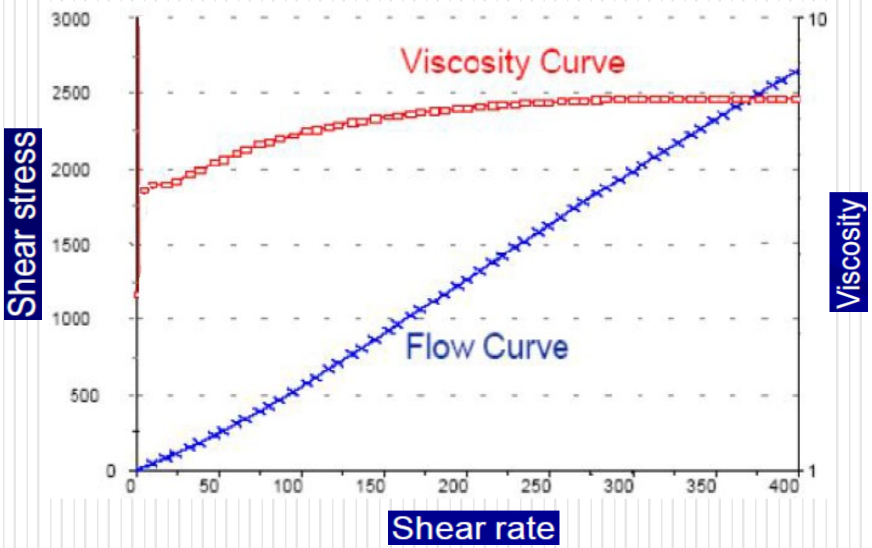
The Carreau-Yasuda law is a slight variation on the Bird-Carreau law. The addition of the exponent '*a*' allows for control of the transition from the Newtonian plateau to the power-law region.



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

Shear-thickening (Dilatant Flow)

- Certain suspensions with a high percentage (up to 50%) of deflocculated solids exhibit an increase in resistance to flow with increasing rate of shear.
- Systems actually increase in volume when sheared, hence also termed *dilatant.*
- When stress is removed, a dilatant system returns to its original state of fluidity. e.g. corn starch in water.



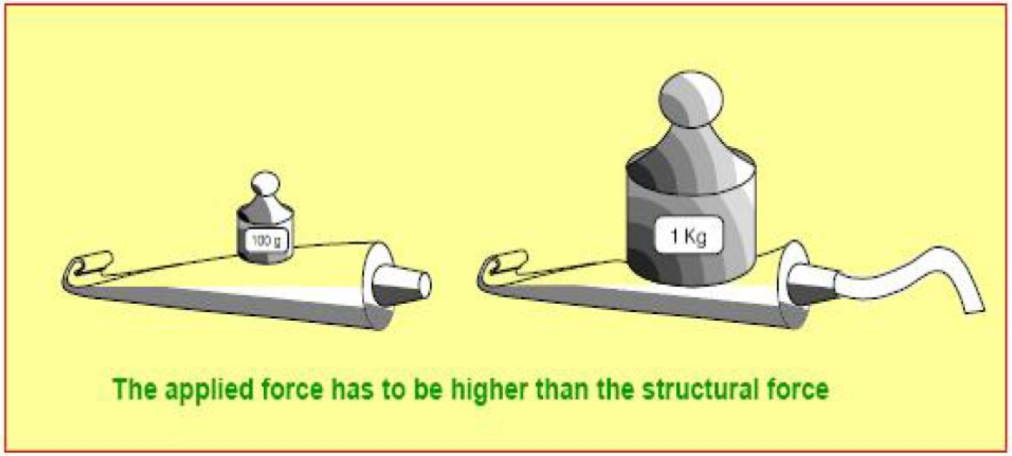
Reasons for Dilatancy

1. At rest particles are closely packed with minimal inter-particle volume (void), so the amount of vehicle is enough to fill in voids and permits particles to move at low rate of shear.
2. Increase shear stress, the bulk of the system expand (dilate), and the particles take an open form of packing.
3. The vehicle becomes insufficient to fill the voids between particles. Accordingly, particles are no longer completely wetted (lubricated) by the vehicle.
4. Finally, the suspension will set up as a firm paste.
5. This process is reversible.

Visco-Plastic Fluids

- This type of non-Newtonian fluid behavior is characterized by the existence of a threshold stress (called yield stress or apparent yield stress, σ_0) which must be exceeded for the fluid to deform (shear) or flow.

A certain shear stress has to be applied in order to let the sample flow



The applied force has to be higher than the structural force

Examples:

Pastes (tomato paste, chilli paste, tooth pastes)

- When the externally applied stress is less than the yield stress σ_0 .the substance will behave like an elastic solid (or flow like a rigid body)

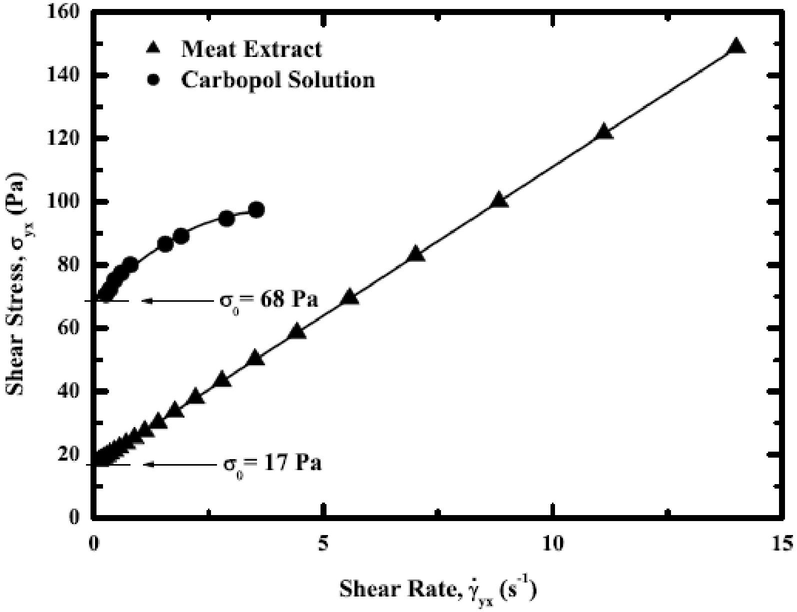
- When the external yield stress exceeds the value of σ_0 , the fluid may exhibit
  - ✓ Newtonian behaviour (constant value of η); known as Bingham bodies
  - ✓ Shear-thinning characteristics, i.e. $\eta(\dot{\gamma})$

Bingham Bodies

A fluid with a linear flow curve for $|\sigma| > |\sigma_0|$ is called a Bingham plastic fluid, and is characterized by a constant value of viscosity η_B

In one-dimensional shear, the Bingham model is written as:

$$
\begin{array}{ll}
\sigma_{yx} = \sigma_0^B + \eta_B \dot{\gamma}_{yx} & |\sigma_{yx}| > |\sigma_0^B| \\
\dot{\gamma}_{yx} = 0 & |\sigma_{yx}| < |\sigma_0^B|
\end{array}
$$

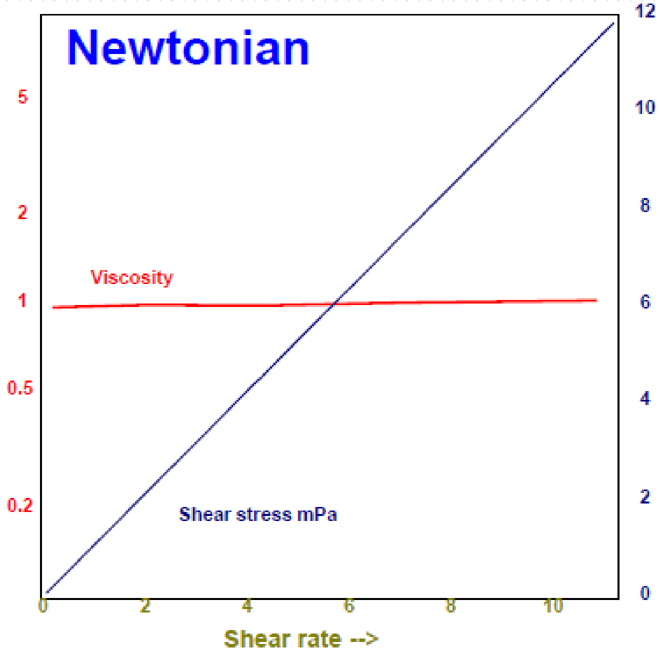


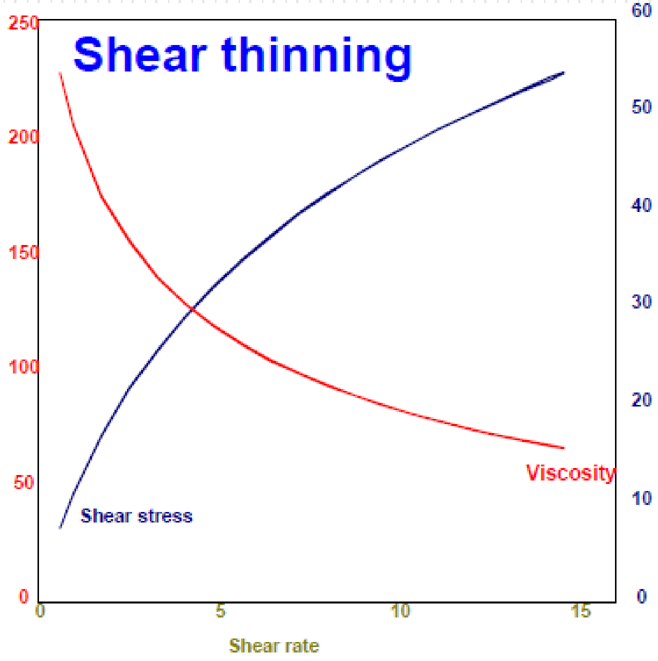
Examples; suspension of ZnO in mineral oil, certain paints, ointments

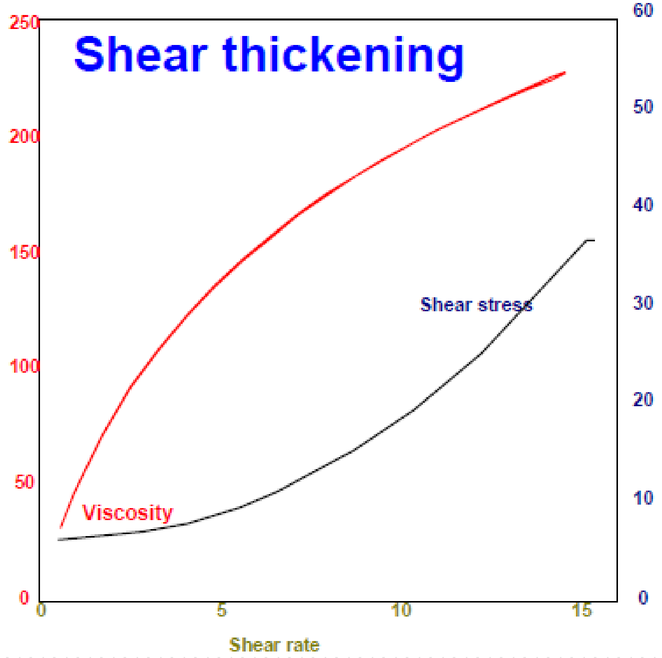
Herschel-Bulkley fluid

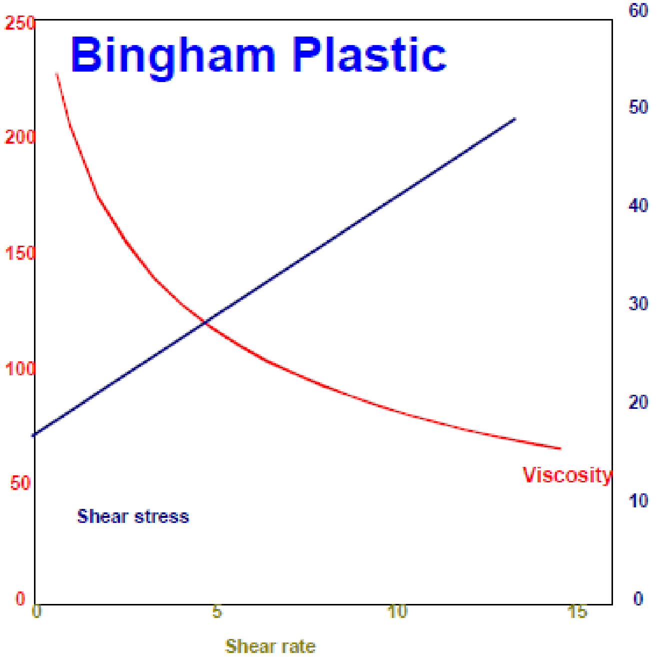
On the other hand, a visco-plastic material showing shear-thinning behavior at stress levels exceeding $|\sigma_0|$ is known as a yield-pseudoplastic fluid, and their behavior is frequently approximated by the so-called Herschel-Bulkley fluid model written for 1-D shear flow as follows:

$$
\begin{array}{ll}
\sigma_{yx} = \sigma_0^H + m(\dot{\gamma}_{yx})^n & |\sigma_{yx}| > |\sigma_0^H| \\
\dot{\gamma}_{yx} = 0 & |\sigma_{yx}| < |\sigma_0^H|
\end{array}
$$


Newtonian
Viscosity
Shear stress mPa
5
2
1
0.5
0.2
12
10
8
6
4
2
0
0
2
4
6
8
10
Shear rate -->


Shear thinning
Viscosity
Shear stress
250
200
150
100
50
0
60
50
40
30
20
10
0
0
5
10
15
Shear rate

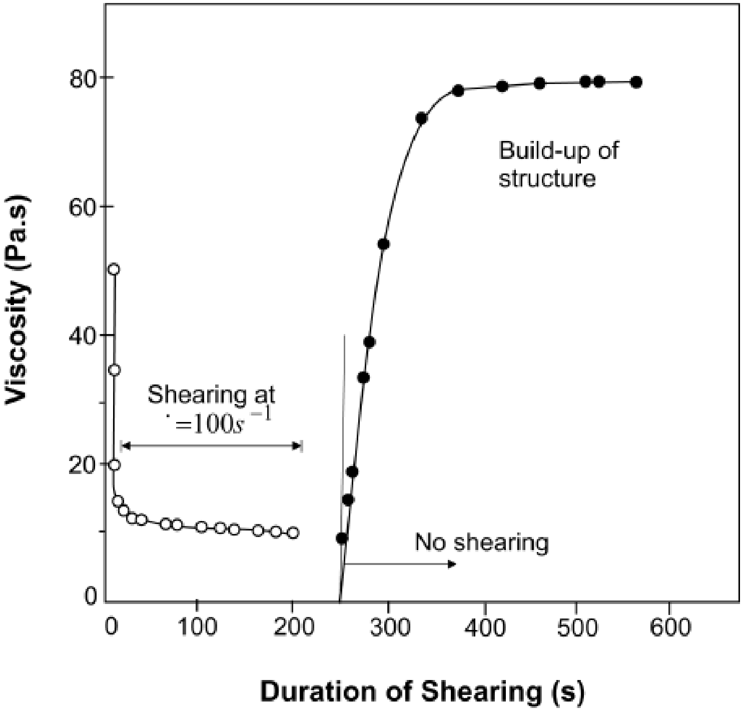

Shear thickening
Viscosity
Shear stress
250
200
150
100
50
0
60
50
40
30
20
10
0
0
5
10
15
Shear rate


Bingham Plastic
Viscosity
Shear stress
250
200
150
100
50
0
60
50
40
30
20
10
0
0
5
10
15
Shear rate

Time Dependent Fluid Flow

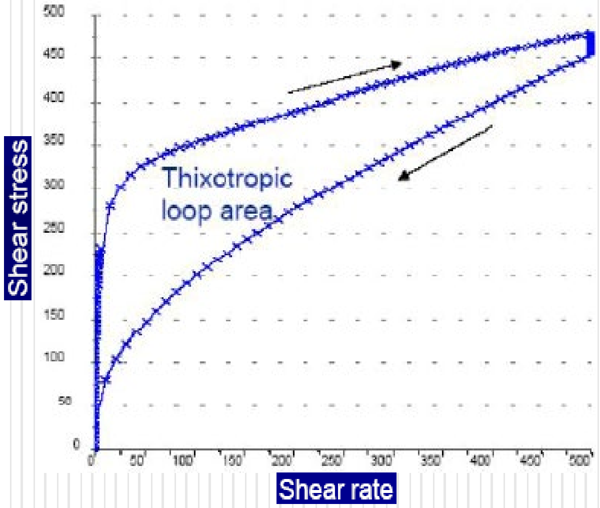
THIXOTROPY

- 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.



Hysteresis Loop

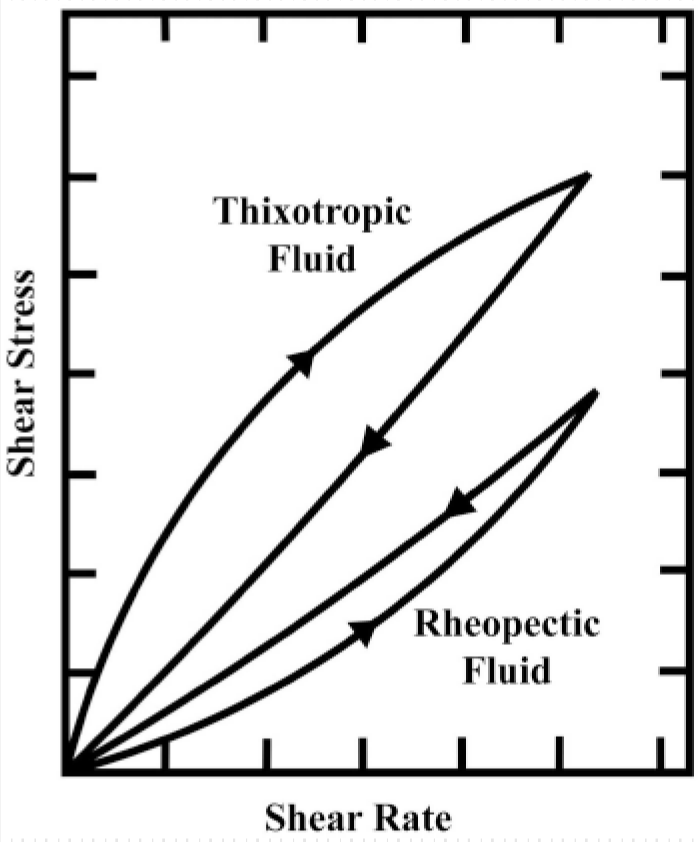
- In a single experiment, when the strain rate is increased at a constant rate from zero to some maximum value and then decreased at the same rate, a hysteresis loop is formed.
- The height, shape and the area of the loop depend on the rate of increase/decrease of shear rate, the maximum value of shear rate, and the past kinematic history of the sample.



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



Conclusions

- The discussion here is restricted primarily to the response of such structured fluids in unidirectional steady shearing motion which leads to the manifestation of shear-thinning, shear-thickening, visco-plastic, thixotropic, rheopectic, visco-elastic characteristics.

- This, in turn, provides some ideas on how to manipulate the microstructure of a system to realize desirable non-Newtonian features.

- The measurement and monitoring of viscosity, yield stress etc. is frequently used to control product quality in food and personal care product sectors, for instance.

THANK
YOU!

Effect of Temperature on Viscosity

Every polymer has a characteristic temperature, the "glass transition temperature" T_g, which determines the first condition. A brief discussion of the dependence of T_g on molecular structure is given in Appendix D. In the vicinity of the T_g the availability of space, i.e., free volume v_f, is the limiting factor; at higher temperatures, where there is no lack of free volume, the energy barriers become significant.

Both experimentally and theoretically it is found [14] that near T_g the dependence of viscosity upon free volume is described by the Doolittle equation:

$$\ln \eta = \ln A + B(v - v_f)/v_f \qquad (10\text{-}11)$$

It has been suggested that v_f increases approximately linearly with temperature above T_g:

$$v_f = v_f(T_g) + \alpha_f(T - T_g) \qquad (10\text{-}12)$$

Here α_f is the expansion coefficient of the free volume, approximately $(\alpha_L - \alpha_G)$, where α_L and α_G are the thermal expansion coefficients above and below T_g. Substituting v_f from Equation 10-12 into Equation 10-11, we arrive at the well-known WLF (Williams-Landel-Ferry) equation [14]:

$$\log \eta(T) = \log \eta(T_g) - \frac{(B/2.3f_o)(T - T_g)}{(f_o/\alpha_f) + T - T_g} \qquad (10\text{-}13)$$

In the WLF equation, f_o is the fractional free volume v_f/v_o at the T_g of the polymer.

The WLF equation describes the temperature dependence of viscosity well from T_g to about $T_g + 100$. Values of the parameters of the equation, expressed in slightly different form, are tabulated by Ferry [14, p. 316]. Ferry describes a graphical method for determining the WLF parameters from experimental data.

It is most helpful to note that Equation 10-13 can be expressed in a number of "universal" forms approximately applicable to all polymers. The most useful, although least accurate, form is Equation 2-129 with the parameters taken to be universal constants:

$$\log \eta(T) = \log \eta(T_g) - \frac{17.44(T - T_g)}{51.6 + T - T_g} \qquad (10\text{-}14)$$

It is not uncommon to express the viscosity in the familiar Arrhenius form, even though the activation energy E_a is not a constant in the region of applicability of the WLF Equation,

$$\eta = A \exp(E_a/RT) \qquad (10\text{-}15)$$

The activation energy E_a is then given by

$$E_a(\text{kcal/mol K}) = 4.13 \frac{T^2}{(51.6 + T - T_g)^2} \qquad (10\text{-}16)$$

From Equation 10-16 we see that E_a depends both on the absolute temperature T and upon the difference $T - T_g$. The activation energy increases, i.e., the viscosity becomes more temperature dependent, as one approaches T_g. This is illustrated in Figure 10-8, in which E_a calculated from Equation 10-16 is plotted for an assumed T_g of 373K (100°C).

Equation 10-16 can also be used to estimate the error in the temperature dependence resulting from the use of the "universal" form of the WLF Equation 10-14, instead of Equation 10-13, with experimentally measured parameters. For example, for polystyrene at 200°C the E_a from equation 10-13 is 40 kcal/mol K. From Equation 10-16 the calculated value is 31 kcal/mol K.

At temperatures appreciably higher than $T_g + 100$, the temperature dependence of viscosity is no longer affected as strongly by the increase of free volume. Instead, the energy barriers to motion become limiting. In that case the temperature dependence is given by Equation 10-15, with a constant E_a whose value depends upon the chemical structure of the polymer.

As was mentioned in Section 10.2, Van Krevelen and Hoftyzer [3] have proposed a more general viscosity-temperature relation and have tabulated data for a number of polymers. However, it is worth

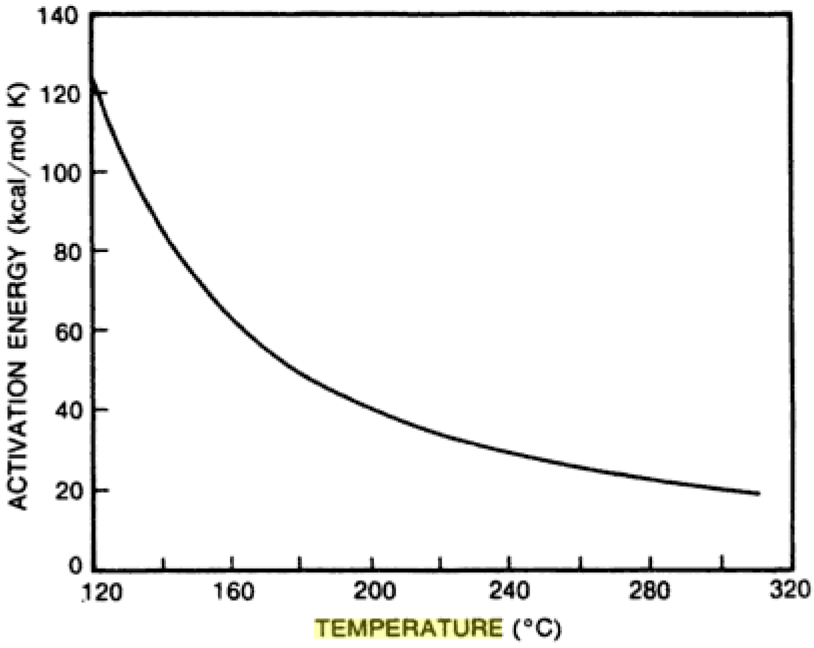


Figure 10-8. Arrhenius activation energy versus temperature for WLF temperature dependence of viscosity, calculated from Equation 10-18 with T_g taken to be 100°C (373 K).

noting that the WLF Equation 10-16 can give a reasonable estimate of E_a at high temperatures. For example, consider polyethylene terephthalate (PET), with a T_g of 70°C. At 285°C Equation 10-16 gives a value for E_a of 18 kcal/mol K. The experimental value is 13.5 [15], and Van Krevelen's calculated value [3] is 12 kcal/mol K. Similarly, for acetal copolymer the calculated value from the WLF Equation (assuming a T_g of -60°C) is 9.7, compared to a measured value of 7.1 kcal/mol K at 190°C. [8]. It appears that WLF overestimates E_a, but gives at least a reasonable first approximation.

In order to give a feel for the effect of the magnitude of E_a on the temperature dependence of viscosity, Figure 10-9 is a plot of the percentage increase of viscosity caused by a 1°C and a 10°C decrease of temperature at a melt temperature of 200°C.

2.4.4 Effects of Pressure and Dissolved Gas 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. This is shown as Eq. (2.17).

$$\ln\left[\frac{\eta_0(P)}{\eta_0(P_0)}\right] = \beta(P - P_0) \tag{2.17}$$

This implies that the pressure shift factor a_P is given by:

$$\ln\left[a_P(P)\right] = \beta(P - P_0) \tag{2.18}$$

Figure 2.6 shows the effect of pressure on the viscosity of a high-density polyethylene at 180 °C, and Fig. 2.7 is a maser curve based on the same data [14]. The horizontal shift factor is $a'_P(P)$, the prime indicating that the vertical shift factor was neglected, i.e., set equal to unity. The Barus Eq. (2.18) was found to fit the entire viscosity curve very well with b_P 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.

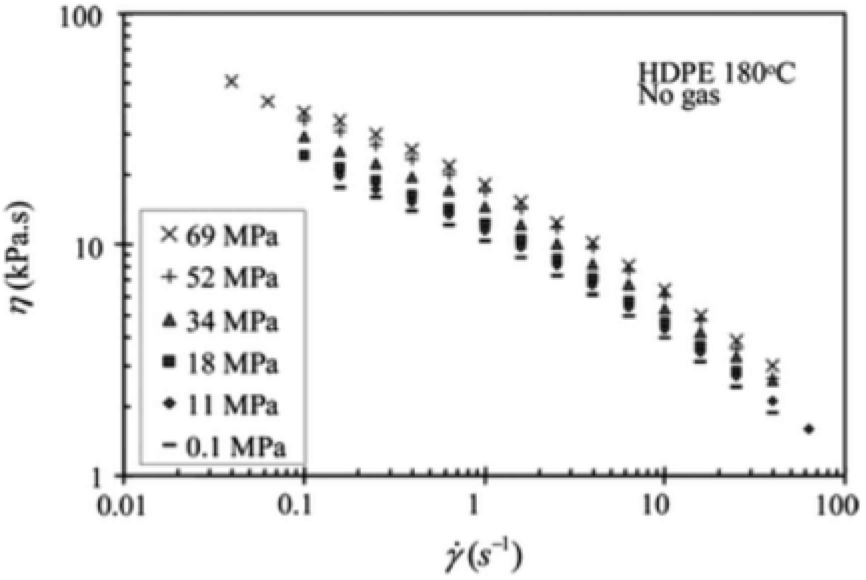


Fig. 2.6 Effect of pressure on the viscosity versus shear rate curve of HDPE. From Park and Dealy [14]

2.4.5 Effect of Molecular Weight on the Zero-Shear 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 η_0 with molecular weight becomes much stronger than linear. In the same range of rates, the viscosity depends increasingly on shear rate.

Plots of log(η_0) versus log(M) for several linear, monodisperse polymers are shown in Fig. 2.10 [16]. 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, η_0 starts to increase much more rapidly with M, and the viscosity starts to depend strongly on shear rate. Over a fairly narrow range of M, data on a log–log plot approach a line with a slope between 3.4 and 3.6. In other words for linear, monodisperse polymers having sufficiently high molecular weight the relationship between log(η_0) and log(M) is given by Eq. (2.20).

$$\eta_0 = KM^a \tag{2.20}$$

where α is usually the range of 3.5 ± 0.2

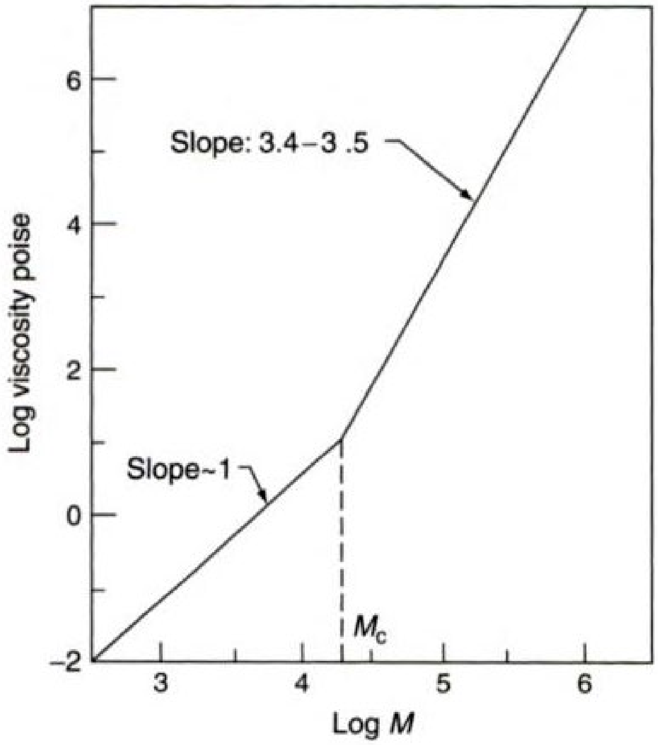


FIGURE Dependence of polymer (melt) viscosity on molecular weight (M): a typical plot of log viscosity against log M.

$$\eta = K_1 M_w \quad \text{for} \quad M_w < M_c$$

$$\eta = K_2 M_w^{3.5} \quad \text{for} \quad M_w > M_c$$

The value of M where the lines described by Eqs. (2.19) and (2.20) intersect for a given polymer, M_C, is called the *critical molecular weight for entanglement*. Values of M_C for a number of polymers are given in Appendix A. This is not to be confused with two other rheologically meaningful critical molecular weights M'_C and M_e, which will be introduced later.

For polydisperse materials, it is found that Eq. (2.20) continues to be valid if M is simply replaced by the weight-average molecular weight, as long as there are very few unentangled molecules present, i.e. those with $M < M_C$.

$$\eta_0 = K M_w^{\alpha} \tag{2.21}$$

This relationship leads directly to a blending law for viscosity. For example, in a binary blend of two monodisperse samples of the same polymer having molecular weights M_1 and M_2, the weight-average molecular weight of the blend is given by:

$$M_{wb} = w_1 M_1 + w_2 M_2 \tag{2.22}$$

where w_1, and w_2, are the weight fractions of the blend components.

Using Eqs. (2.20) and (2.21) to eliminate the molecular weights, we have:

$$\eta_{0,b} = K M_w^a = \left(w_1 \eta_{0,1}^{1/a} + w_2 \eta_{0,2}^{1/a} \right)^a \tag{2.23}$$

This equation has been tested for blends of monodisperse [17, 18] and polydisperse [19] materials.

2.4.6 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, although materials produced using metallocene catalysts can have polydispersities (M_w/M_n) as low as two. Figure 2.11 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. Chapter 7 describes methods for using viscosity data to infer the MWD of a linear polymer, although it is to be noted that this requires data of high accuracy. In the plastics industry it is often desired to estimate polydispersity from easily measured quantities. Shroff and Mavridis [20] have compared several empirical correlations that have been proposed to do this.

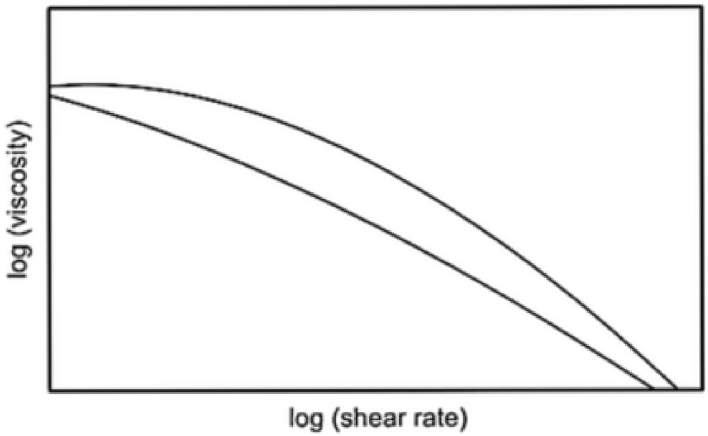


Fig. 2.11 Shapes of viscosity curves for two samples having the same M_w but with narrow (*upper curve*) and broad (*lower*) molecular weight distributions. The narrow MWD sample moves from a well-defined Newtonian region to power-law behavior over a narrower range of shear rates

The literature related to the physical testing of polymers is extensive. Several compilations are useful: the series edited by Schmitz (1965, 1966, 1968) and Brown (1969) and those volumes of methods of test and recommended practices dealing with plastics issued by the American Society for Testing and Materials (ASTM). There are also many pertinent articles in the *Encyclopedia of Polymer Science and Technology* (Mark 1964–1970). Beyond this listing, specific references have largely been omitted from this section.

Mechanical Properties

Stress–Strain Properties in Tension. One of the most informative mechanical experiments for any material is the determination of its *stress–strain curve in tension*. This is usually done by measuring continuously the force developed as the sample is elongated at constant rate of extension.

The generalized stress–strain curve for plastics shown in Fig. 9-7 serves to define several useful quantities, including *modulus* or *stiffness* (the slope of the curve), *yield stress,* and *strength* and *elongation at break*. This type of curve is typical of a plastic such as polyethylene. Figure 9-8 shows stress–strain curves typical of some other classes of polymeric materials. The properties of these polymer types are related to the characteristics of their stress–strain curves in Table 9-2.

Tensile properties are usually measured at rates of strain of 1–100%/min. At higher rates of strain—up to 10^6%/min—tensile strength and modulus usually increase severalfold, while elongation decreases. The interpretation of these results is complicated by large temperature rises in the test specimen.

In addition to tensile measurements, tests may also be performed in *shear, flexure, compression,* or *torsion*. For materials in film form, flexural tests are often

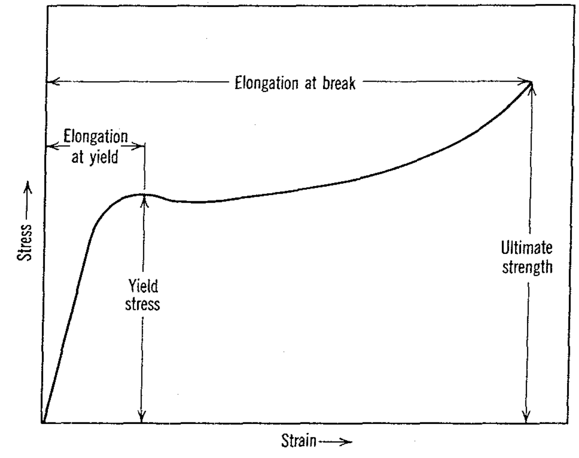


FIG. 9-7. Generalized tensile stress–strain curve for plastics (Winding 1961).

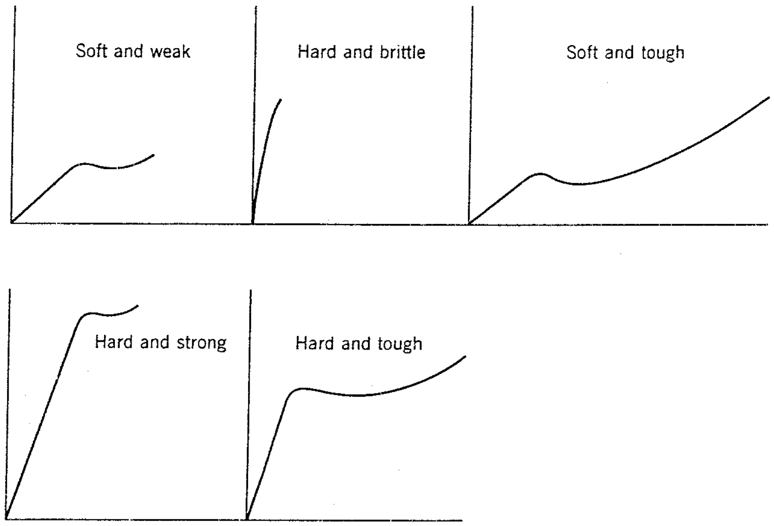


FIG. 9-8. Tensile stress–strain curves for several types of polymeric materials (Winding 1961).

used. These may include (for stiffer materials) measurement of *flexural modulus* or (for less stiff materials) *flexural* or *folding endurance* tests (see next pargraph).

Fatigue Tests. When subjected to cyclic mechanical stresses, most materials fail at a stress considerably lower than that required to cause rupture in a single stress cycle. This phenomenon is called *fatigue*. Various modes of fatigue testing in common use include alternating tensile and compressive stress and cyclic flexural stress. Results are reported as plots of stress versus number of cycles to fail. Many materials show a fatigue endurance limit, or a maximum stress below which fatigue failure never takes place.

TABLE 9-2. Characteristic Features of Stress–Strain Curves as Related to Polymer Properties[a]

	Characteristics of Stress–Strain Curve			
Description of Polymer	Modulus	Yield Stress	Ultimate Strength	Elongation at Break
Soft, weak	Low	Low	Low	Moderate
Soft, tough	Low	Low	Yield stress	High
Hard, brittle	High	None	Moderate	Low
Hard, strong	High	High	High	Moderate
Hard, tough	High	High	High	High

[a] Winding (1961).