RHEOLOGY

By,

Dr. Vaibhav G. Bhamare

Ph. D, M. Pharm, MBA

subscribe on you tube to

ONLINE PHARMA GURUKUL

RHEOLOGY AND VARIABLES

INTRODUCTION

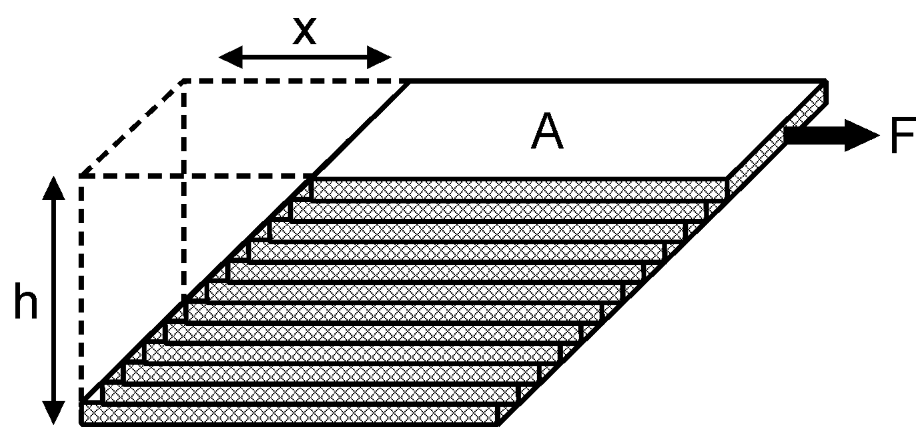
- Rheology can be defined as the branch of science that deals with deformation of a material under the influence of stress.

OR

- Rheology can be defined as the science which describes the flow of liquids and deformation of solids.
- The method used to analyze the rheological behaviour of a material is known as Rheometry.
- The term Rheology was suggested by Eugene C. Bingham and Crawford from the Greek words “rheo" means to flow and 'logos" means science.

- The objective of rheology is to determine the fluid flow that would be produced due to applied forces.
- The applied forces could be of different forms. Maybe because of pressure difference may be natural in origin such as gravitational force in falling fluid film.

VARIABLES



- **Viscosity (η):** Viscosity is the resistance to the flow of material.

  Unit: Poise or centipoises (0.01 poise)

- **Shear Stress (F)**: It is force applied per unit area required to bring about flow.

  Unit: dyne/cm^2

- **Rate of Shear (G):** It is the velocity gradient dv/dr between two planes of the body separated by an infinitesimally small distance.

  Unit: cm^{-1}

NEWTONS LAW OF FLOW

- **Statement:**

Newton's Law of Flow states that the higher the viscosity of liquid greater the shear stress required to produce a certain rate of shear.

$$\frac{F'}{A} = \eta \frac{dv}{dr}$$

where,

$\frac{F'}{A}$ = Shear Stress

η = Viscosity

$\frac{dv}{dr}$ = Rate of Shear

This law also gives us a quantitative definition of viscosity. Viscosity according to this law is the shear stress required to produce a unit rate of shear strain.

As per the above said quantitative definition, we can write

$$\eta = \frac{F}{G}$$

where

$$F = \frac{F'}{A}$$

$$G = \frac{dv}{dr}$$

NEWTONIAN and NONNEWTONIAN SYSTEMS

NEWTONIAN SYSTEMS

- Newtonian systems are the systems in which there is direct proportionality between shear stress and shear rate, i.e. these are the systems which follows Newton's law of flow.
- Newton's law of flow states that higher the viscosity of liquid higher the shearing stress.
- ∴ According to Newton's law of flow

$$\therefore \quad F \propto \frac{dv}{dr}$$

$$\therefore \quad F = \eta \frac{dv}{dr}$$

$$\therefore \quad F = \eta G$$

$$\therefore \quad \boxed{\eta = \frac{F}{G}}$$

Mathematically the viscosity of body is shear stress divided by shear rate.

- So all bodies that satisfy equation are called Newtonian systems/fluids.
- A representative flow curve or rheogram obtained by plotting rate of shear Vs. shear stress is

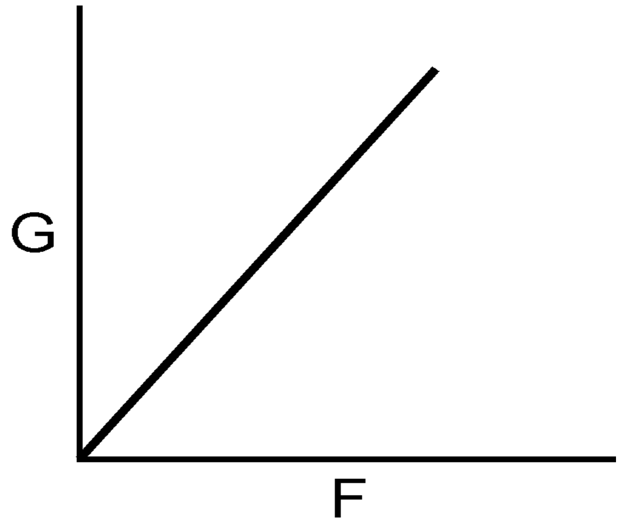
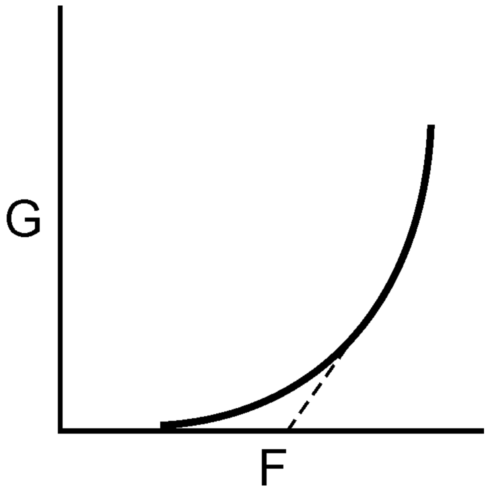
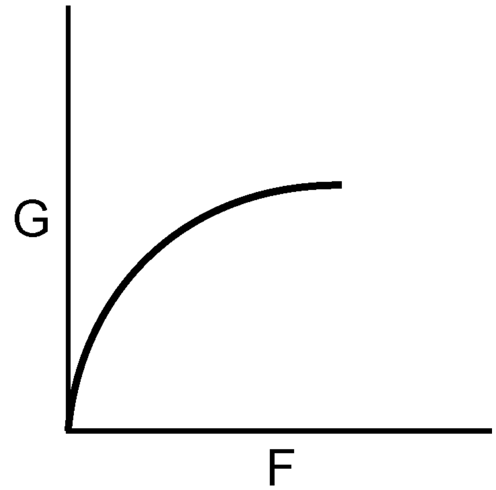


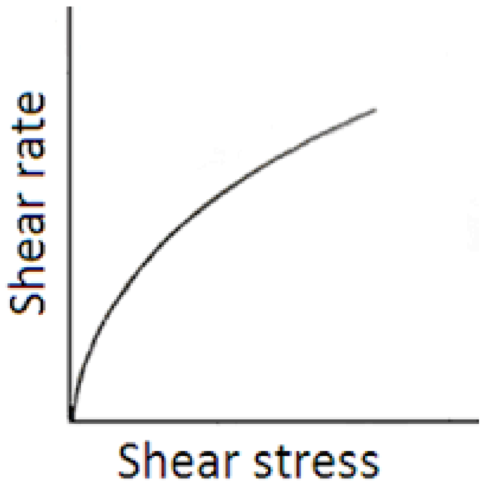
Fig: Newtonian System/Flow (Rheogram 1)

NON NEWTONIAN SYSTEMS

- Non-Newtonian systems are those substances that fail to follow Newton's Law of Flow.
- When the value of viscosity varies with a varying shear rate that does not obey equation no. 3, one needs to take into consideration the apparent viscosities of these bodies at particular shear rates.
- When non-Newtonian materials are analyzed and results are plotted, various consistency curves representing three classes of flow are recognized as plastic flow, pseudoplastic flow and dilatants flow.







Plastic Flow **Psuedoplastic Flow** **Dilatant Flow**

$$U = \frac{(F - f)}{G}$$

$$F^N = \eta^1 G$$

When,

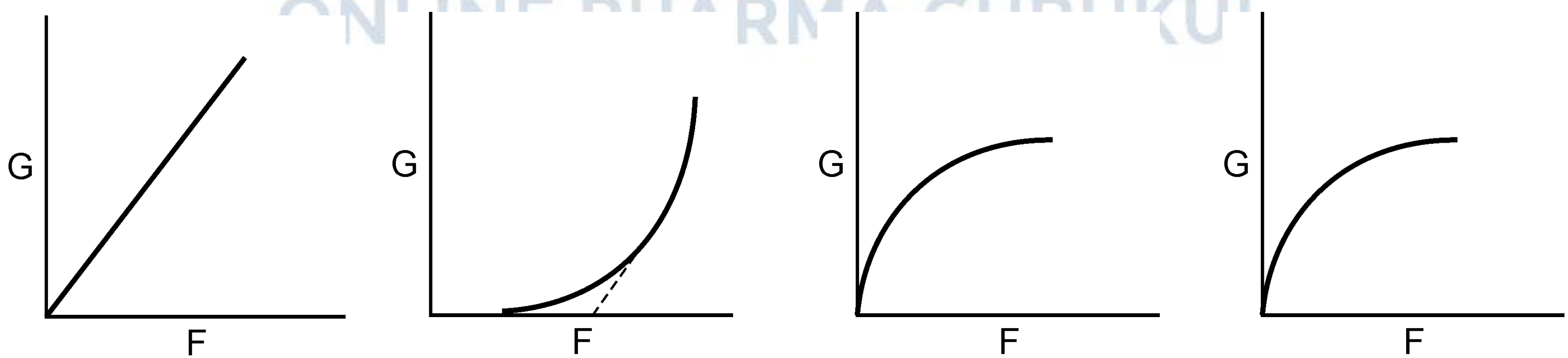
N = 1 Newtonian flow

N < 1 Pseudoplastic flow

N > 1 Dilatant flow.

THIXOTROPY

- Newtonian systems are the systems in which there is direct proportionality between shear stress and shear rate, i.e. these are the systems which follows Newton's law of flow.
- Non-Newtonian systems are those substances that fail to follow Newton's Law of Flow.
- In shear-thinning systems, viscosity decrease with increase in shear stress.
- In shear thickening system, viscosity increases with increasing shear stress.

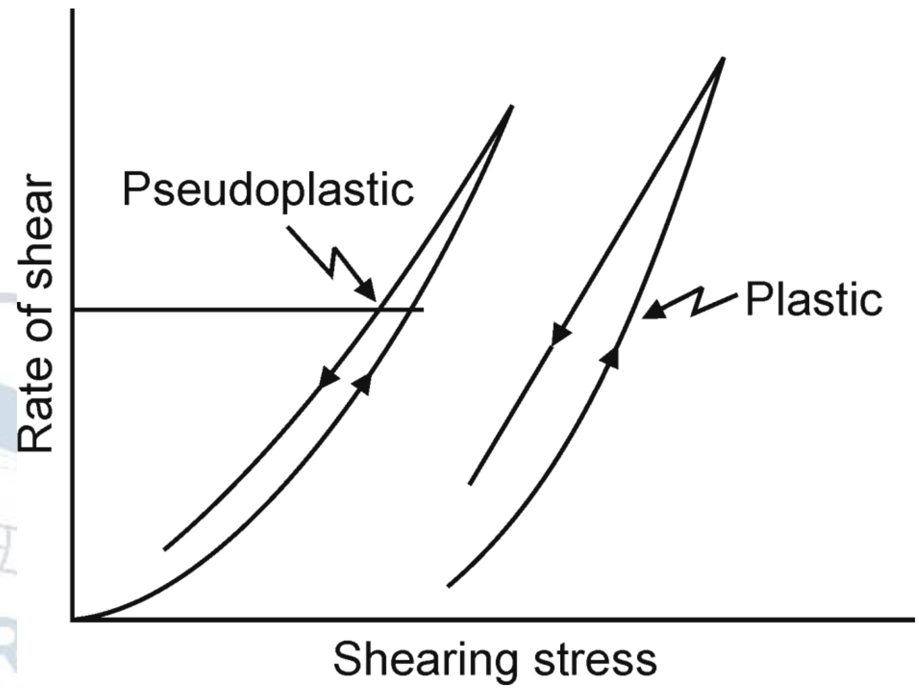


Newtonian Flow **Plastic Flow** **Psuedoplastic Flow** **Dilatant Flow**

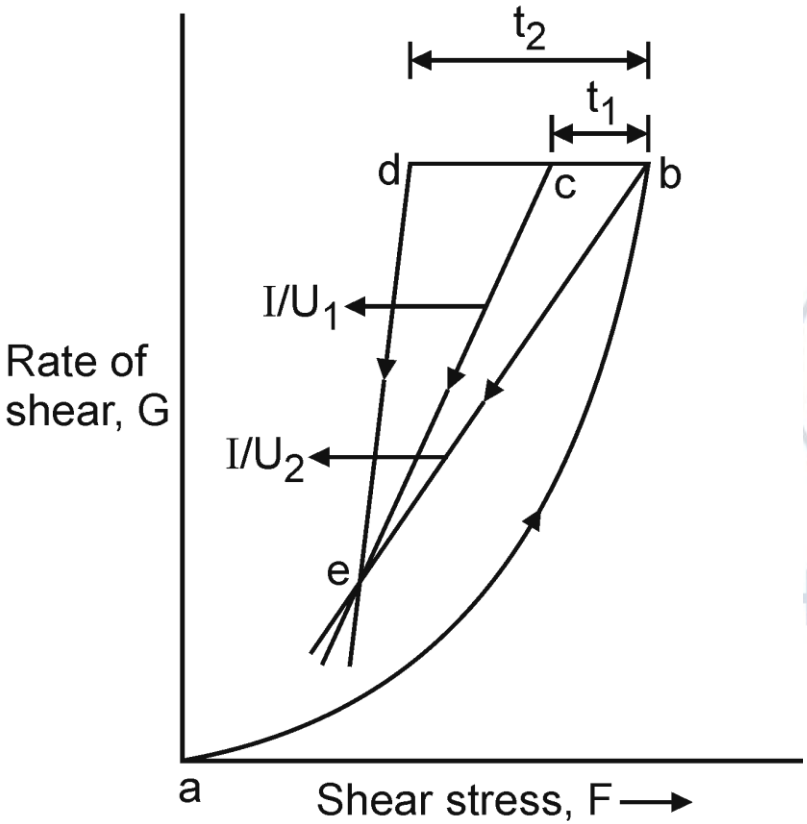
.... **Non Newtonian Flow** ....

THIXOTROPIC BEHAVIOUR

- In the Newtonian system, with change in shear stress, rate of shear will alter and the downward curve will be identical and superimposed to the upward curve.
- But in the case of non-Newtonian system, the downward curve can be displaced with the upward curve.
- With shear thinning systems, the down curve is frequently displaced to the left.
- The curves shown in the figure are called as thixotropic curve and the system exhibiting this type of curve are known as thixotropic systems.



- Thixotropy may be defined as isothermal and comparatively slow recovery, on the standing of a material of a consistency lost through shearing.



- Suppose that in rheogram the shear rate of bingham body is increased steadily from "a" to "b" and then decreased to "e" at the same rate. This will result in hysteresis loop "abe"
- If the shear rate is taken to point "b" and kept constant for t_1 seconds then shear stress and so consistency would decrease depending on the time of shear and it will give hysteresis loop "abce".
- If the sample had been held at the same shear rate for t_2 seconds, it will give loop "abde".

- These loops show that the rheogram for thixotropic material is not unique but it will depend on the rheological history of the sample.
- The curve obtained by thixotropic material is highly dependent on changes in the rate of shear and duration of time involved at a particular rate of shear.

MEASUREMENT OF THIXOTROPY

(1) Determination of structural breakdown at constant rate of shear:

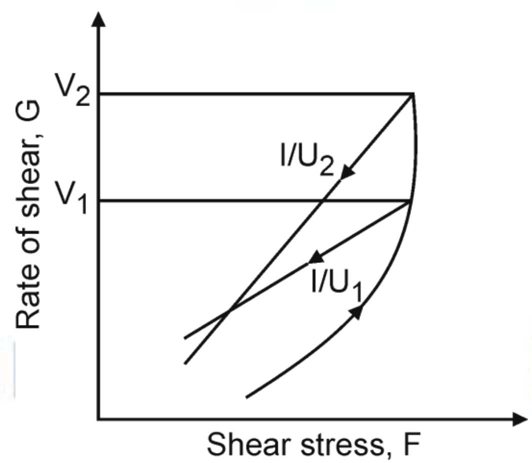
- As shown in figure, the sample is applied with a constant rate of shear t_1 and t_2 for seconds resulting in the formation of loop abce and abde respectively for t_1 and t_2 seconds.
- Based on such rheogram, a thixotropy coefficient B, the rate of breakdown with time at a constant shear rate is calculated as follows:

$$B = \frac{U_1 - U_2}{\ln \frac{t_2}{t_1}}$$

Where, U_1 and U_2 are plastic viscosities for t_1 and t_2 seconds

(2) Determination of structural breakdown due to increasing rate of shear:-

The principle involved in this approach is shown in figure in which two hysteresis loops are obtained having a different maximum rate of shear V_1 and V_2.



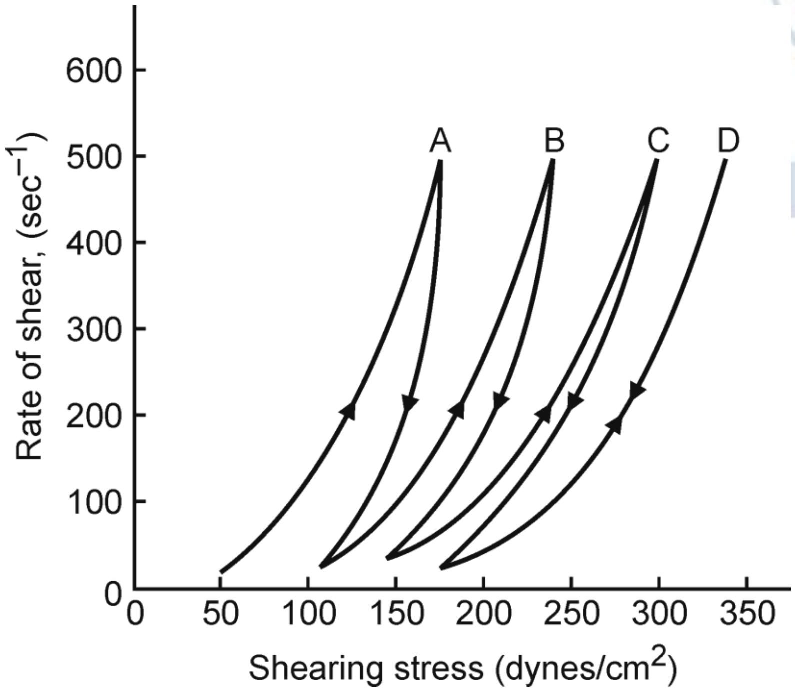
In this case, a thixotropic coefficient M in $dyne/cm^2$, the loss in shearing stress per unit increase in shear rate is obtained fro

$$M = \frac{2(U_1 - U_2)}{I_n\left(\frac{V_2}{V_1}\right)}$$

Where, U_1 and U_2 are plastic viscosities for two separate down curves having maximum shearing rates of V_1 and V_2 respectively.

NEGATIVE THIXOTROPY

- Generally, thixotropic systems are shear-thinning system i.e. decrease in consistency with down curves.
- Some thixotropic systems show an increase in consistency on the down curve and this phenomenon is called as negative thixotropy or anti-thixotropy.



- The down curve falls to the right of the up curve and it continuously thickened and finally reached equilibrium at which the up and down curve overlapped each other.
- After reaching the equilibrium the system was found to have a gel-like property and showed greater suspend ability.

VISCOSITY

- All liquids are composed of molecules. When put into motion, molecules and particles are forced to slide along each other. They develop a flow resistance caused by internal friction.
- Viscosity is the property of fluids that indicates resistance to flow.
- When a force is applied to the volume of material, then a displacement (deformation) occurs.
- The proportionality constant in Newton's Law of flow is known as the viscosity.
- Larger components present in a fluid are the reason for higher viscosity values.

UNIT

- The unit of viscosity is the poise which is defined as the shearing force required for producing a velocity of 1cm/sec between two parallel planes of liquid each 1 cm^2 in area and separated by a distance of 1 cm.
- Centipoise is the more convenient unit where 1 cp = 0.01 poise

TYPES OF VISCOSITY

Kinematic viscosity (ϑ)

- Kinematic viscosity is the measure of the inherent resistance of a fluid to flow when no external force is exerted, except gravity.
- The ratio of absolute viscosity (η) to the density (ρ) of the liquid at a definite temperature is known as kinematic viscosity.

$$\vartheta = \frac{\eta}{\rho}$$

- In the SI-system the theoretical unit of kinematic viscosity is m^2/s or the commonly used stoke (St) where 1St (stokes) = $10^{-4}\ m^2/s = 1\ cm^2/sec$
- Since the stoke is a large unit it is often divided by 100 into the smaller unit centistoke (cSt) where 1 St = 100 cSt

TYPES OF VISCOSITY

Relative viscosity (η_r) :

- It is the ratio of the viscosity of dispersion to the viscosity of the solvent.

$$\eta_r = \frac{\eta}{\eta_o}$$

Specific viscosity (η_{sp}) :

- Specific viscosity is obtained by subtracting one from relative viscosity.

$$\therefore \ \eta_{sp} = \frac{\eta}{\eta_o} - 1$$

$$\therefore \eta_{sp} = \frac{\eta - \eta_o}{\eta_o}$$

TYPES OF VISCOSITY

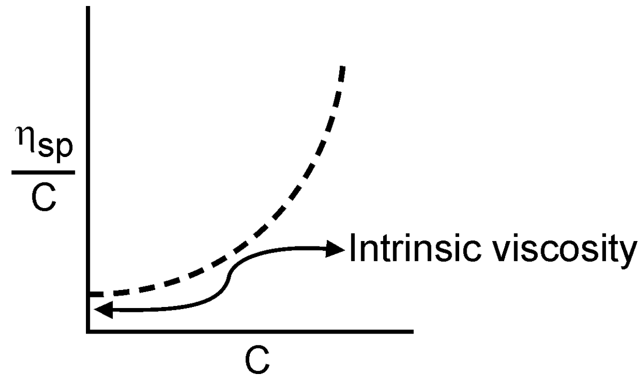
Reduced viscosity (η_{red}) :

- It is the ratio of specific viscosity to the concentration.

$$\therefore \eta_{red} = \frac{\eta_{sp}}{C}$$

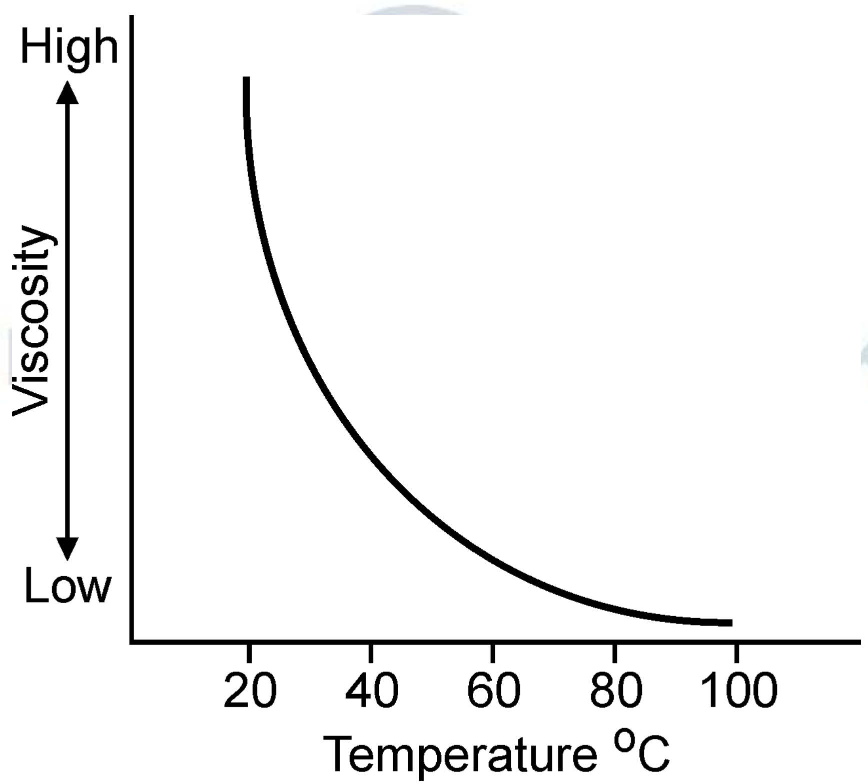
Intrinsic viscosity (η) :

- The Y-intercept obtained by extrapolating the curve obtained by taking reduced viscosity on the Y-axis and concentration on X-axis.



EFFECT OF TEMPERATURE

- Viscosity depends strongly on temperature. In liquids, it usually decreases with temperature, whereas in gases it increases.

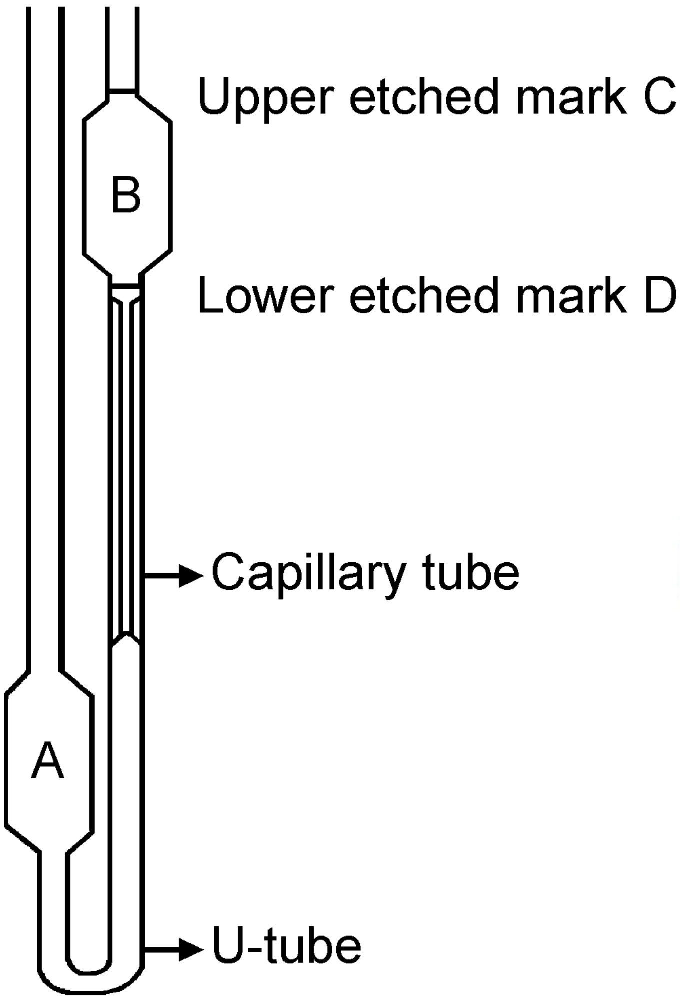


- With an increase in temperature, there is typically an increase in the molecular interchange as molecules move faster in higher temperatures.
- The gas viscosity will increase with temperature. According to the kinetic theory of gases, the viscosity should be proportional to the square root of the absolute temperature, in practice, it increases more rapidly.
- In a liquid, there will be molecular interchange similar to those developed in a gas, but there are additional substantial attractive, cohesive forces between the molecules of a liquid (which are much closer together than those of a gas). Both cohesion and molecular interchange contribute to liquid viscosity.
- The impact of increasing the temperature of a liquid is to reduce the cohesive forces while simultaneously increasing the rate of the molecular interchange.
- The former effect causes a decrease in shear stress while the latter causes it to increase.
- The result is that liquids show a reduction in viscosity with increasing temperature. With high temperatures, viscosity increases in gases and decreases in liquids, the drag force will do the same.

DETERMINATION OF VISCOSITY

- Looking to Newton's law of the flow, it is important to choose the correct instrumental method for Newtonian and Non Newtonian systems.
- One point instruments: As discussed with the Newtonian system it is important to choose an instrument that operates at a single rate of shear.
- Multipoint instrument: As discussed in the non-Newtonian system, it is important to choose instrument operating at a variety of rate of shear.
- A viscometer is an instrument used to measure the viscosity of a fluid. For liquids with viscosities which vary with flow conditions, an instrument called a rheometer is used. Thus a rheometer can be considered as a special type of viscometer.

Capillary Viscometer



- Capillary viscometers are the simplest form of viscometer available from which it is possible to obtain absolute values of viscosity for Newtonian fluids and to obtain limited information on power-law fluids.
- These devices are also known as Ubbelohde viscometer or Ostwald viscometers, named after Wilhelm Ostwald.
- The equation that governs the flow of liquid through a capillary is Poiseuille's equation

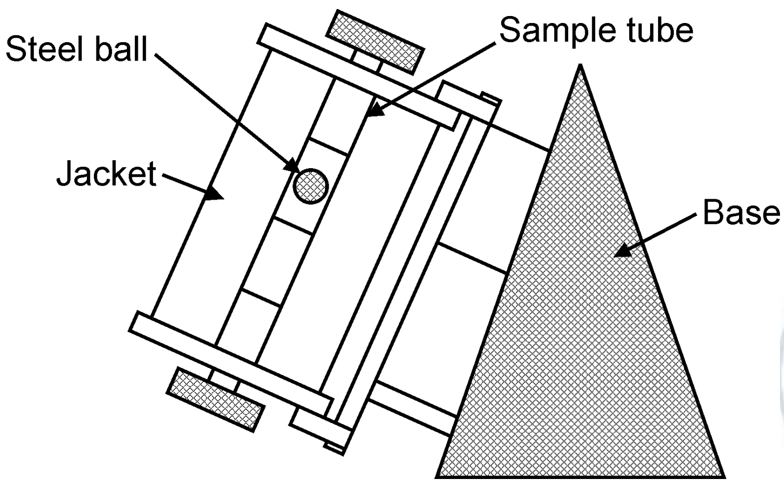
$$\eta = \frac{\pi r^4 t \Delta P}{8 l V}$$

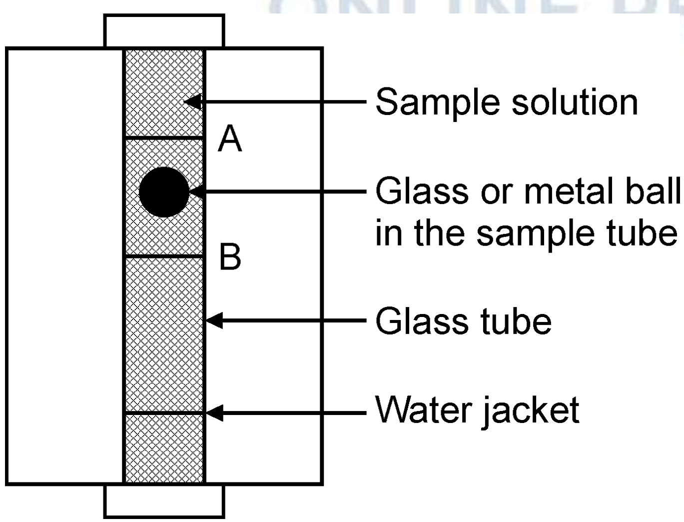
- As π, l, V and r are constant, equation can be written as

$$\eta_1 = K t_1 \rho_1 \qquad \eta_2 = K t_2 \rho_2$$

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}$$

Falling Sphere Viscometer





- The Falling Ball Viscometer uses the simple, but precise, Hoeppler principle to measure the viscosity of Newtonian fluids by measuring the time required for a ball to fall under gravity through a sample-filled tube that is inclined at an angle.
- The rolling and sliding movement of the ball through the sample liquid is at times in an inclined cylindrical measuring tube. The sample viscosity correlates with the time required by the ball to drop a specific distance and the test results are given as dynamic viscosity.
- The viscosity of a Newtonian liquid is then calculated from

$$\eta = t(S_b - S_f)\,B$$

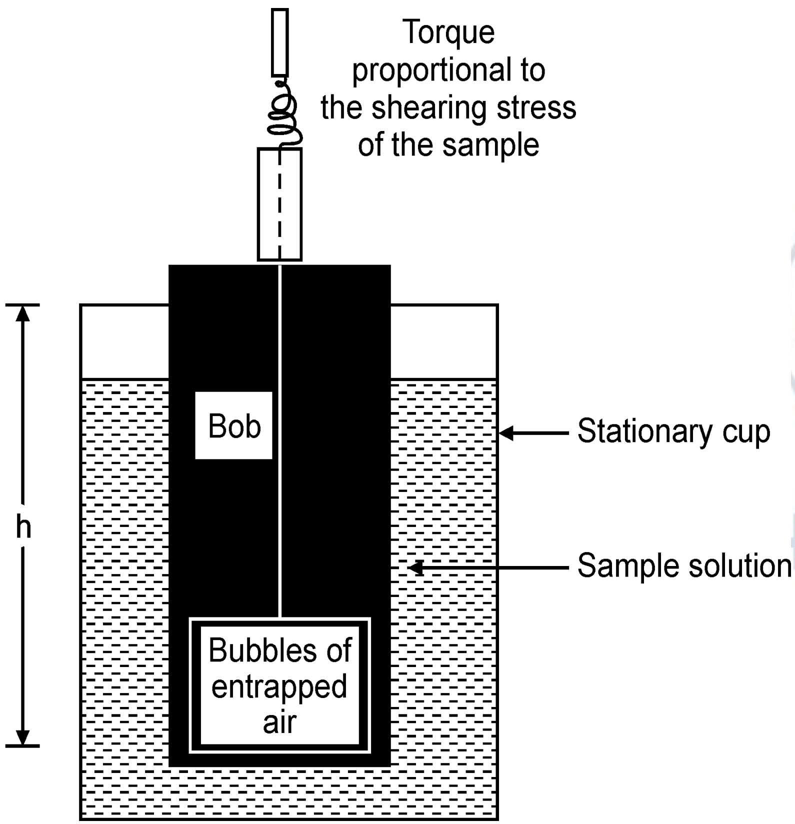
Rotational Viscometers

- Rotational viscometers use the idea that the torque required to turn an object in a fluid is a function of the viscosity of that fluid.
- Rotational viscometers works by getting the measurements of the torque on a vertical stand that moves the spindle in a rotational direction. The rotation of the spindle is usually proportional to viscosity of the sample.

    i) Cup and bob viscometer

    ii) Cone and plate viscometer

Cub and Bob Viscometer

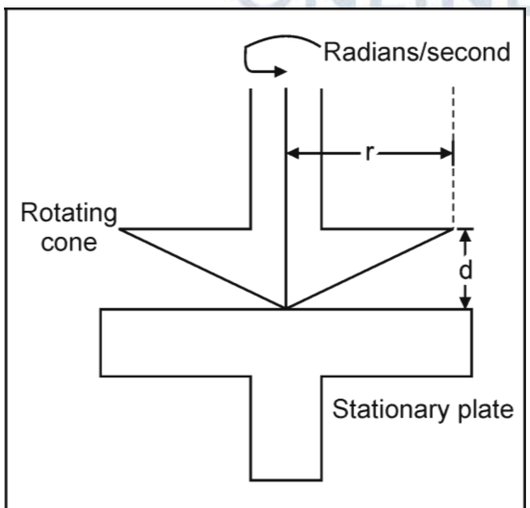


- "Cup and bob" viscometers work by defining the exact volume of a sample to be sheared within a test cell. The torque required to achieve a certain rotational speed is measured and plotted.
- There are two classical geometries in "cup and bob" viscometers, known as either the "Couette" or "Searle" systems, distinguished by whether the cup or bob rotates.
- The rotating cup is preferred in some cases because it reduces the onset of viscous fluid confined in the gap between two rotating cylinders at very high shear rates, but the rotating bob is more commonly used, as the instrument design can be more flexible for other geometries as well.
- The resultant torque is proportional to the viscosity of the sample.

$\eta = K_v \frac{W}{v}$ … equation for apparent viscosity for Pseudoplastic system

$U = K_v \left(\frac{w - w_f}{v} \right)$ … equation for plastic viscosity

Cone and Plate Viscometer



- "Cone and plate" viscometers use a narrow-angled cone near a flat plate.
- The mechanism involves two discs: one is cone-shaped and rotates at a certain angular velocity and the other is flat and stationary.
- The sample is placed between the two discs. Rotation of cone drags fluid layers, producing tangential friction or shear forces on the stationary disc.
- The flat disc is connected to a spring and turns at a small angle depending on the viscosity. Torque and distance of the spring's action are used to determine the viscosity of the sample.
- The viscosity can easily be calculated from shear stress (from the torque) and shear rate (from the angular velocity).

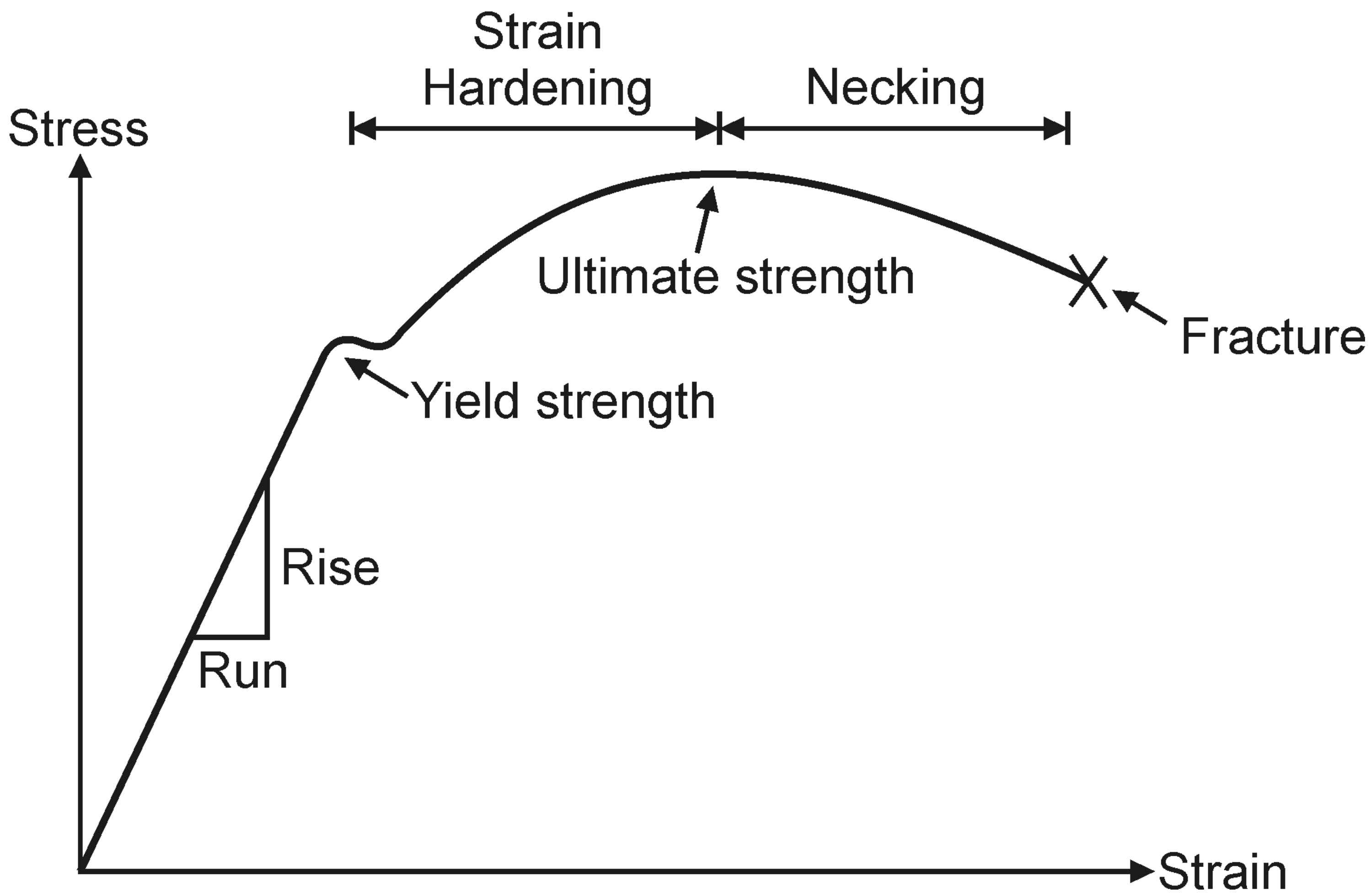
$\eta = C\frac{T}{V}$ … equation for viscosity for a Newtonian fluid

$U = C\frac{T - T_f}{V}$ … equation for plastic viscosity

DEFORMATION OF SOLID

- It is possible to change the shape and size of an object by the application of external forces.
- As deformation occurs internal intermolecular forces arise that oppose the applied force. If the applied force is not too great, these internal forces are sufficient to completely resist the applied force and allow the object to assume a new state of equilibrium and to return to its original state when the load is removed.
- A larger applied force may lead to permanent deformation of the object or even to its structural failure.
- Depending upon the type of material, size and geometry of the object and the force applied various deformation may result.

PLASTIC DEFORMATION



- Plastic deformation is the permanent distortion that occurs when a material is subjected to tensile compressive, bending or torsion stresses that exceed its yield strength and cause it to elongate, compress buckle, bend and twist.
- Plastic deformation slightly increases the electrical resistivity.
- Plastic deformation in a general sense can be defined as irreversible deformation. The structural effects of plastic deformation can be classified into three main categories:

  (i) Increased dislocation density

  (ii) Deformed grain morphology

  (iii) Modified grain-boundary character.

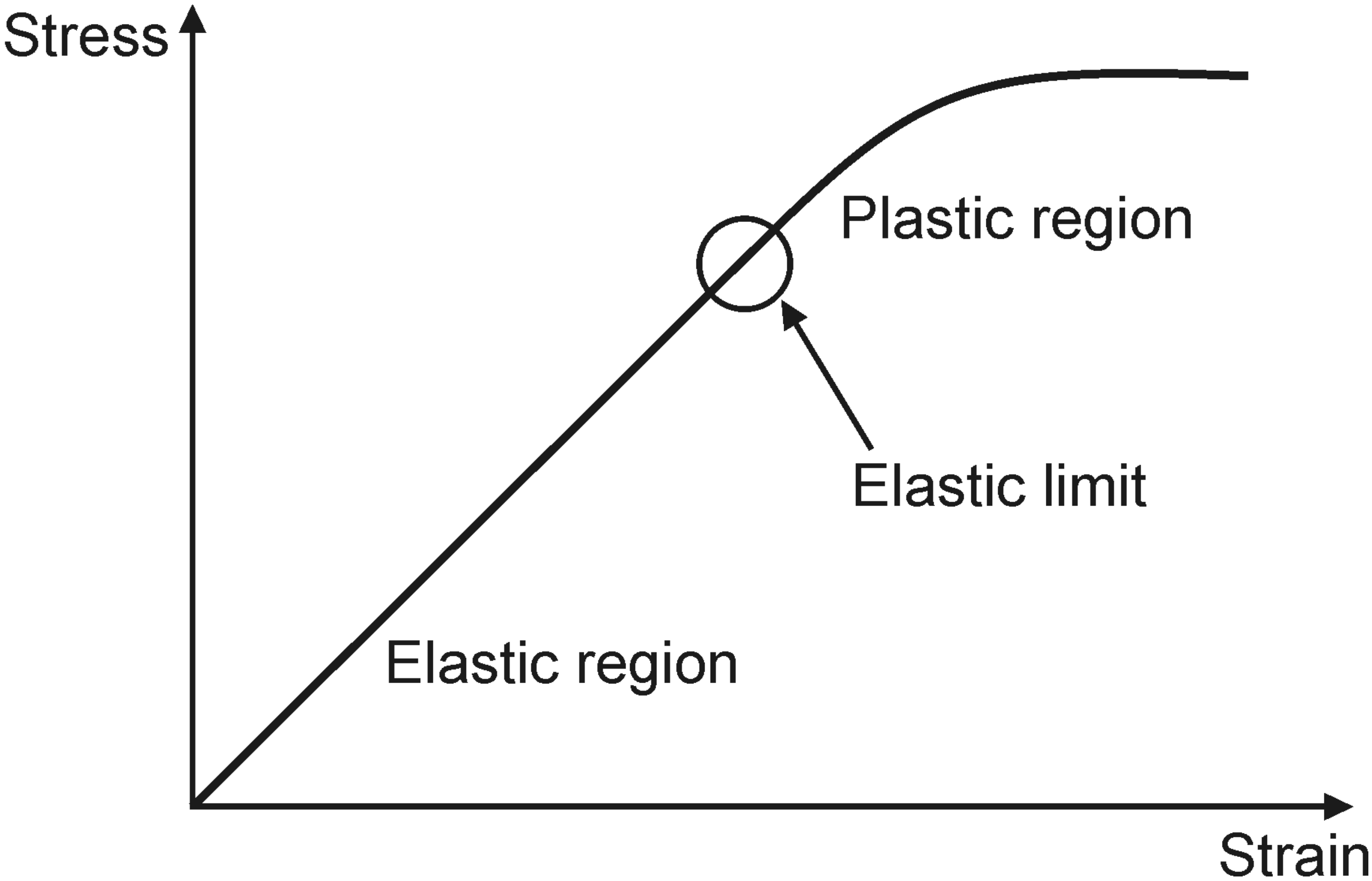
- Under the tensile stress plastic deformation is characterized as:

  (i) Strain hardening region: material becomes stronger through the movement of atomic dislocations.

  (ii) Necking region: reduction in cross-sectional area of the specimen. It begins after the ultimate strength is reached. The material can no longer withstand the maximum stress and strain in the specimen rapidly increases.

  (iii) Fracture: indicates the end of the plastic deformation

ELASTIC DEFORMATION



- A temporary shape change that is self-reversing after the force is removed, so that the object returns to its original shape, is called elastic deformation.

- This type of deformation involves stretching of the bonds, but the atoms do not slip past each other.

- Elastic deformation alters the shape of a material upon the application of a force within its elastic limit. This physical property ensures that elastic materials will regain their original dimensions following the release of the applied load. Here deformation is reversible and non-permanent.

- The elastic deformation of the material allows them to recover from stress and restore their normal functionality. But these properties degrade over time and in some conditions, the material can become brittle and lose their ductility.

- Materials become less pliable when cold or subjected to hardening chemicals that interfere with their elasticity.

- To retain or increase a material's elasticity, some softening materials are added to the mix. For example, special softening materials can be added to the polymer plastics mix to allow them to bend and give under pressure without permanently changing their shape.

Sr. No.	Plastic Deformation	Elastic Deformation
(1)	It is irreversible	It is reversible
(2)	It occurs when the bonds between atoms are broken and new ones are formed.	It occurs because atomic bonds are stretched when the load is applied.
(3)	It forces atoms to move and occupy microscopic defects in the metal, making it tougher.	It does not contribute to the strength of metals.
(4)	Plastic deformation begins beyond the elastic limit.	An object undergoes elastic deformation before plastic deformation.
(5)	Example: when a metal coat hanger is bent, it does not regain its original shape	Example: a stretched rubber band regains its shape after it is released.

ELASTIC MODULUS

- An elastic modulus is a quantity that measures an object or substance's resistance to being deformed elastically (i.e., non-permanently) when a stress is applied to it.
- An elastic modulus is also known as modulus of elasticity.
- The elastic modulus of an object is defined as the slope of its stress-strain curve in the elastic deformation region. A stiffer material will have a higher elastic modulus.
- Specifying how stress and strain are to be measured, including directions, allows for many types of elastic moduli to be defined. The three primary ones are:

  (i) Young's Modulus (E)

  (ii) Shear Modulus (G or μ)

  (iii) Bulk Modulus (K)

(i) Young's modulus (E) describes tensile elasticity or the tendency of an object to deform along an axis when opposing forces are applied along that axis; it is defined as the ratio of tensile stress to tensile strain. It is often referred to simply as the elastic modulus.

(ii) The shear modulus or modulus of rigidity (G or μ) describes an object's tendency to shear the deformation of shape at constant volume when acted upon by opposing forces; it is defined as shear stress over shear strain. The shear modulus is part of the derivation of viscosity.

(iii) The bulk modulus (K) describes volumetric elasticity or the tendency of an object to deform in all directions when uniformly loaded in all directions; it is defined as volumetric stress over volumetric strain and is the inverse of compressibility. The bulk modulus is an extension of Young's modulus to three dimensions.

Dr. VAIBHAV G. BHAMARE
(+91)7588176846
vaibhav.bhamre@gmail.com

subscribe on you tube to

ONLINE PHARMA GURUKUL