PHYSICAL PHARMACEUTICS-II

UNIT 2 NOTES

RHEOLOGY

- NEWTONIAN SYSTEM
- LAW OF FLOW
- KINEMATIC VISCOSITY
- EFFECT OF TEMPERATURE
- NON NEWTONIAN SYSTEM
- PSEUDOPLASTIC, DILATANT, PLASTIC FLOW
- THIXOTROPY
- DETERMINATION OF VISCOSITY
- VISCOMETERS
- DEFORMATION OF SOLIDS

IMPERFECT PHARMACY

RHEOLOGY

- Rheology is the science that deals with the flow and deformation of materials under applied forces.
- The term Rheology was coined by Eugene Bingham in 1920.
- It is derived from two greek words :
- Rheo means 'to flow'
- Logy means 'Study'.
- In Pharmacy, rheology is important for understanding the flow properties of :
- Liquids (syrups, emulsions)
- semi - solids (creams, gel, ointments)
- Solids (tablets etc.)

TYPES OF FLOW SYSTEM

There are basically two types of flow system

1. Newtonian System
2. Non- Newtonian System

① NEWTONIAN SYSTEM

- A Newtonian System (fluid) follows Newton's law of viscosity, which states :
  " The shear stress is directly proportional to the shear rate or deformation. "

$$\boxed{\text{Shear Stress} \propto \text{Shear Rate}}$$

- Mathematically, it can be written as :

$$\tau \propto du/dr$$

$$\boxed{\tau = \eta \frac{du}{dr}}$$

- Here
  - τ = Shear stress
  - η = viscosity (which is constant)
  - du/dr = rate of shear

- Rate of shear is defined as change in velocity (du) between two planes of liquid which is separated by distance (dr).

EXAMPLES

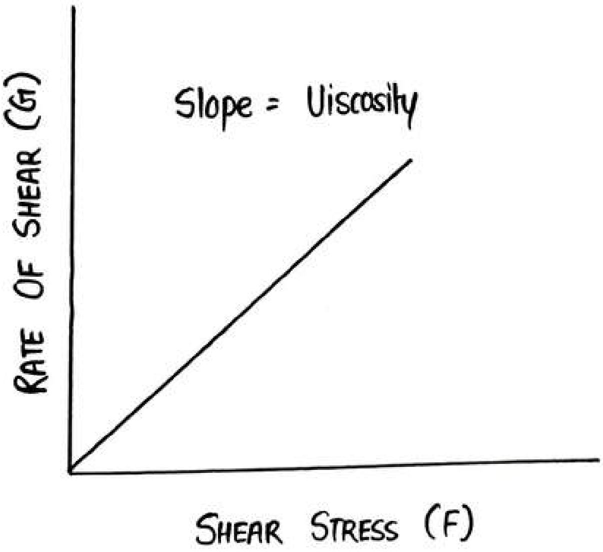
- Water
- Alcohol
- Chloroform
- Glycerin

Characteristics Of Newtonian Fluids

- Constant Viscosity : It does not change with shear rate or mixing
- Flow behaviour is linear - doubling the force doubles the flow.
- The begin to flow as soon as shear is applied.
- Viscosity only changes with temperature not with stress.

Graphical Representation

- A straight line is obtained when shear stress is plotted against shear rate.
- Slope = viscosity.



KINEMATIC VISCOSITY

- kinematic Viscosity is the ratio of fluid's dynamic viscosity to its density.

$$\boxed{\text{KINEMATIC VISCOSITY} = \frac{\text{Dynamic Viscosity } (\eta)}{\text{Density } (\rho)}}$$

- It describes how easily a fluid flows under gravity, without considering external force

UNITS

- SI UNIT : m^2/s
- Common Unit : Stokes or Centistokes

EFFECT OF TEMPERATURE ON VISCOSITY

- In case of liquids, viscosity is inversely related to temperature - as temperature increases, viscosity decreases for most liquids.
- When temperature increases :
- kinetic energy of molecules increases
- Molecules move freely & intermolecular forces weaken.
- As a result, resistance to flow decreases.
- Hence, viscosity drops.

IN GASES

- Viscosity increases with increase in temperature.
- Reason : More frequent collision b/w gas molecules at higher kinetic energy.

② Non- Newtonian System

- These fluids do not obey Newton's Law of Viscosity.
- Their viscosity is not constant - it changes with applied shear stress or shear rate.
- Flow behaviour is non- linear.

Characteristics Of Non- Newtonian System

- No fixed relationship between shear stress & shear ~~strain~~ rate.
- Viscosity may increase or decrease with applied force.
- They are found commonly in pharmaceutical & cosmetic formulations like suspensions, emulsions, creams, gels etc.

Types Of Non - Newtonian Flow

They are of mainly 3 types :

① Plastic flow
② Pseudo- Plastic flow
③ Dilatant Flow

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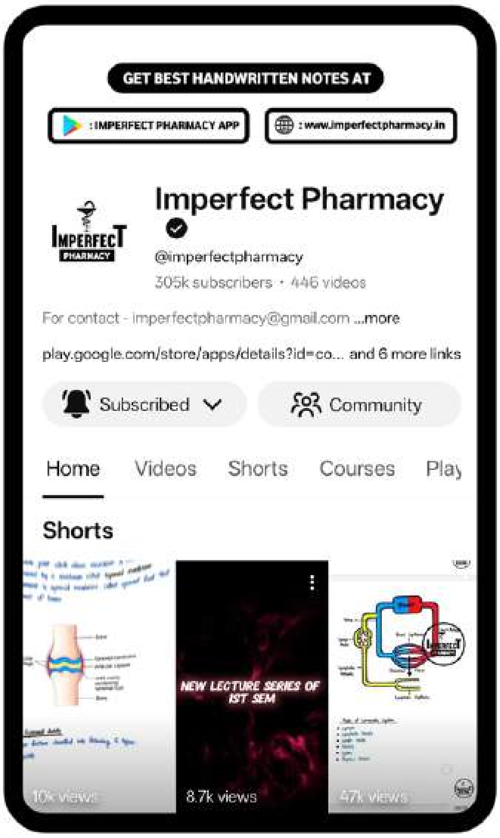

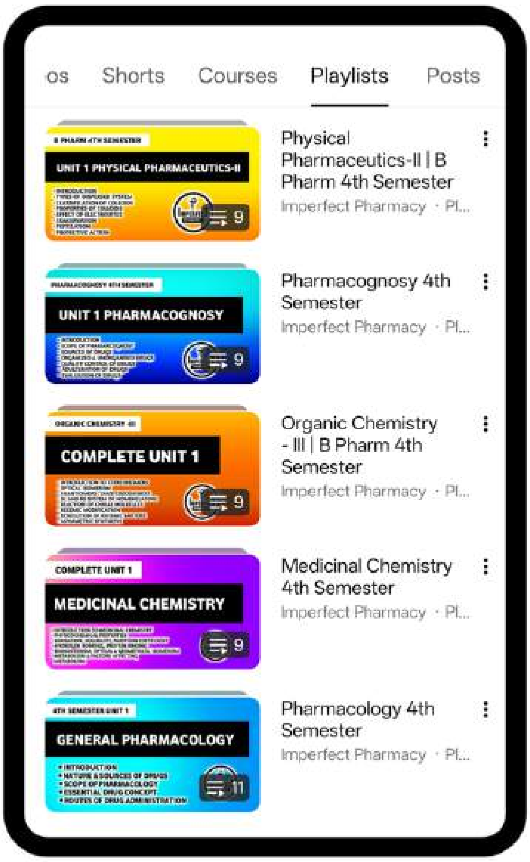

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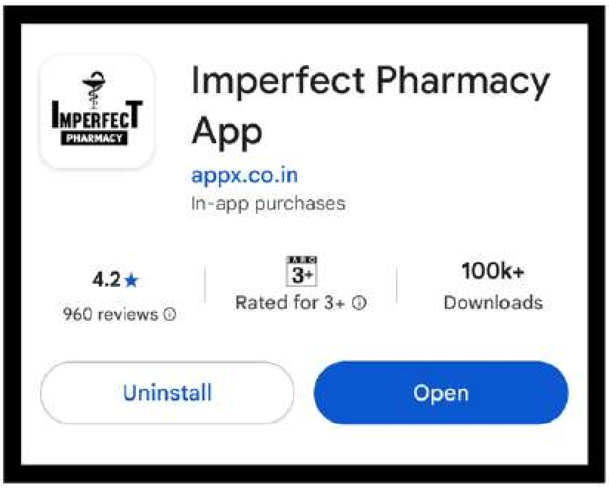


@ PLASTIC FLOW

- Plastic flow is a type of non-newtonian fluid behaviour where the fluid does not begin to flow until a certain minimum shear stress (called 'Yeild Stress') is applied.
- Below Yeild Stress : Fluid behaves like a solid
- Above Yeild Stress : Fluid starts to flow

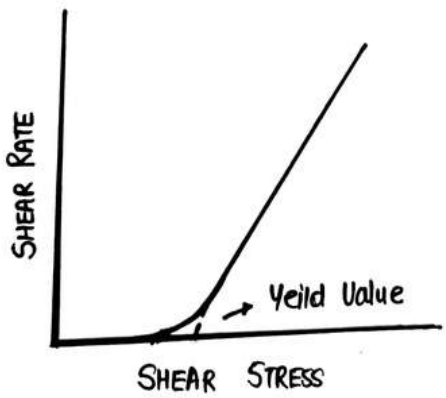
Yield Stress

- Yeild stress is the minimum force per unit area required to initiate flow in a plastic fluid.
- Once Yeild stress is overcome, the material flows like a fluid.

Graphical Representation

The Graph of plastic flow starts from yeild stress not origin

- Y - Axis : Shear Rate
- X - Axis : Shear Stress



Examples

- Toothpaste, Ointments, Gels etc.

(b) PSEUDOPLASTIC FLOW

- Pseudoplastic flow is a type of non-Newtonian fluid behaviour where the viscosity decreases as the shear rate increases.
- This behaviour is also known as Shear-Thining.

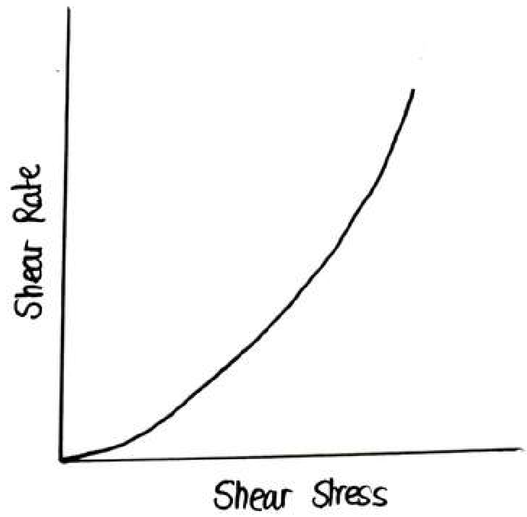
KEY CHARACTERISTICS

- No Yeild Stress : Flow starts as soon as force is applied.
- Viscosity decreases with more force : fluid becomes 'thinner' as you stir or pump it faster.
- The Graph of Pseudoplastic flow is non linear but passes through the origin

Example

- Blood, Yogurt, Shampoo, Paint etc.

Graphical Representation



© DILATANT FLOW

- Dilatant flow are those whose viscosity increases with an increase in shear rate.
- In simple words, the more force you apply, the thicker it becomes.

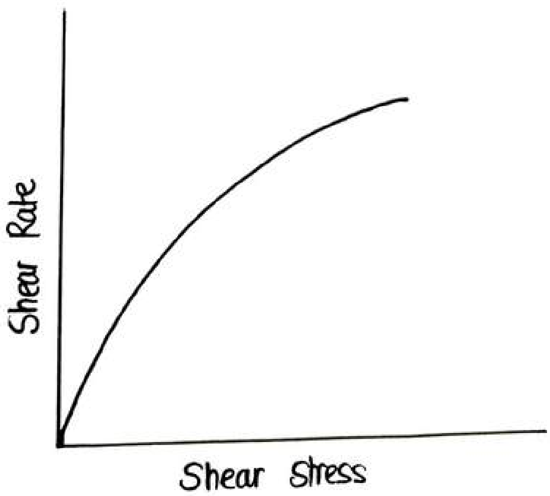
KEY FEATURES

- It is opposite of pseudoplastic flow
- With increase in shear stress it becomes more resistant to flow - behaves like a semi - solid or solid.
- There is non- linear relationship between shear stress and shear rate.

Example

- Cornstarch in water
- Wet sand
- Suspensions with high solid content.

Graphical Representation



THIXOTROPY

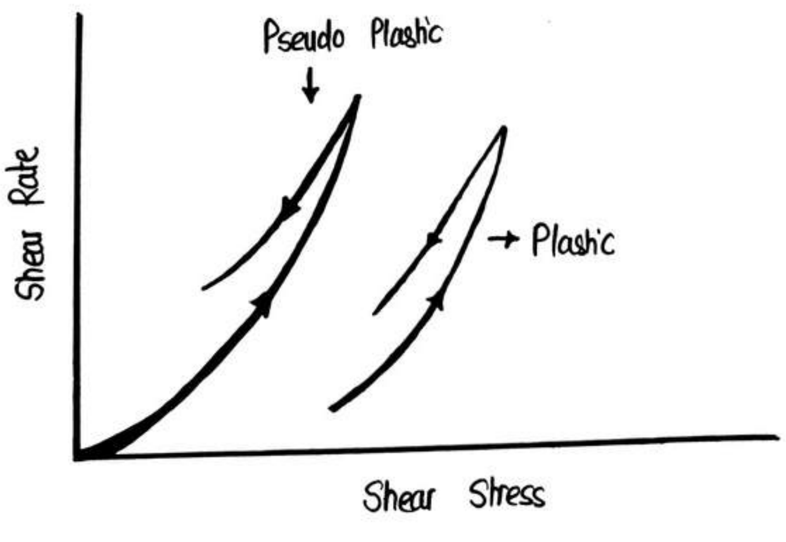
- Thixotropy is a time - dependent behaviour of Non- Newtonian fluids, where :
- Viscosity decreases over time when shear is applied.
- And viscosity gradually recovers when shear is removed.

- Thixotropy is mostly observed in pseudoplastic fluids but may also occur in plastic & dilatant systems.

THIXOTROPY IN PLASTIC & PSEUDOPLASTIC SYSTEMS

- In plastic & psudoplastic systems, increasing the shearing stress gradually decreases the viscosity of these systems.
- But when this shearing stress is removed, the systems regain their viscosity after a certain time lag. this phenomenon is known as thixotropy in plastic & pseudoplastic systems.

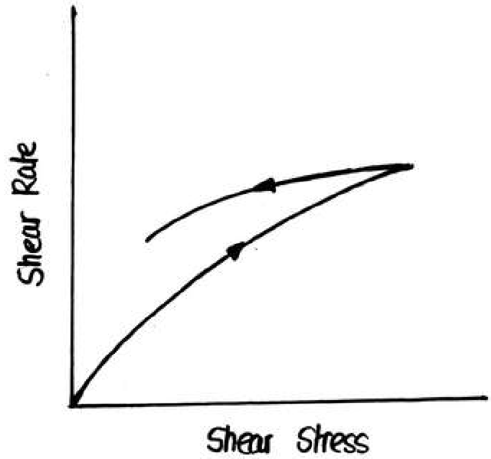
$$\text{Gel} \xrightarrow[\text{shear stress}]{\text{Application of}} \text{Sol} \xrightarrow[\text{Shear Stress}]{\text{Removal of}} \text{Gel}$$



Thixotropy in Dilatant System

In Dilatant System, with increase in shearing stress, viscosity also increases, However, the viscosity of the system decreases after a certain period of removing the shearing stress & This phenomenon is known as Thixotropy in dilatant system.

$$\text{Sol} \xrightarrow{\text{Application of Shear Stress}} \text{Gel} \xrightarrow{\text{Removal of Shear Stress}} \text{Sol}$$



THIXOTROPY IN FORMULATIONS

Thixotropy plays crucial role in various pharmaceutical formulations such as:

① Topical Preparations : Creams & gel spreads easily on skin due to low viscosity under shear stress & after application regain their viscosity so that they can stay.

② Suspensions : During shaking : thin & pourable
After shaking = thick enough so suspended particles do not settle.

③ Injections : Easier to inject under pressure.
Thickens once inside the body to prevent leakage.

DETERMINATION OF VISCOSITY

The Viscosity of a solution can be determined by using various Viscometers as follows:

① Capillary Viscometer
② Falling Sphere Viscometer
③ Rotational Viscometer

① CAPILLARY VISCOMETER

- A capillary viscometer is a device used to determine the viscosity of a liquid by measuring the time taken by a specific volume of liquid to flow through a narrow capillary tube under the influence of gravity.
- The most commonly used capillary viscometer is Ostwald's U-Tube Capillary Viscometer.

PRINCIPLE

The viscosity of desired sample is determined by comparing the flow time of the test liquid with the standard liquid.

PROCEDURE

- Fill the viscometer with the test liquid upto the mark.
- Use suction to draw the liquid above the upper timing mark.
- Release & start the stopwatch as the liquid passes the upper mark.
- Stop the watch as the liquid crosses the lower mark.

- Record the time (t_1)
- Repeat the same procedure with standard liquid (usually water)
- Use the formula to calculate viscosity.

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

Here, η_1 = viscosity of test liquid
η_2 = Viscosity of standard liquid
t_1 = Time required by test liquid
t_2 = Time required by standard liquid
ρ_1 = Density of test liquid
ρ_2 = Density of standard liquid.

APPLICATION

It is used in various pharmaceuticals for checking the viscosity of :

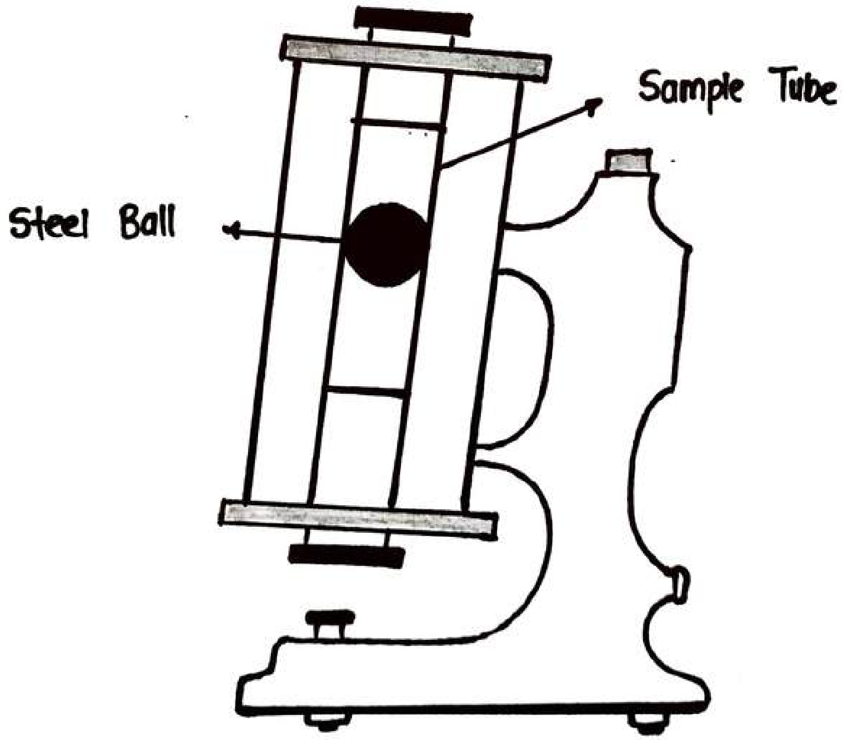
- Syrups
- Suspensions
- Emulsions
- Gels.

② FALLING SPHERE VISCOMETER

- It is known as Hoeppler falling Sphere Viscometer
- This viscometer is based on the principle of Stoke's Law.

METHOD

- Viscometer consist of a cylindrical glass tube filled by the liquid under investigation.
- The tube is enclosed by constant temperature jacket in which water is circulated around the tube.
- A glass or steel ball is allowed to fall down.
- The falling time is recorded.



- The viscosity of the test liquid can be calculated by using following formula :

$$\boxed{\eta = t\,(S_b - S_b)\,B}$$

Here ,
- η = viscosity of sample
- t = time travel in seconds for the ball to fall b/w two points.
- S_b = Specific gravity of the ball
- S_t = Specific gravity of fluid
- B = Constant for particular ball.

APPLICATION

- Less time - consuming .
- More accurate for Newtonian fluids .
- Often used in lubricant, oil or polymer industry .

③ Rotational Viscometer

- Rotational viscometers can be used for the accurate measurment of viscosity for both Newtonian & Non- Newtonian Fluids.
- The most commonly used ~~of~~ rotational viscometer is Cone and Plate Viscometer.

Principle

- In Rotational Viscometer, A cone is placed ~~at~~ over a flat plate with a small amount of test liquid in between
- The resistance to flow (torque) offered by the liquid is directly related to its viscosity.

Procedure

- Place a small volume of test liquid on the plate.
- Lower the cone onto the sample so it just touches the plate.
- Start rotation at desired rpm
- Measure the torque required to rotate
- Calculate the viscosity using given formula :

$$\boxed{n = k\,(T/v)}$$

Here,
- n = viscosity
- k = instrumental constant
- V = rpm
- T = torque reading.

DEFORMATION OF SOLIDS

- Deformation of Solids is defined as a process by which a solid material changes its shape, size or both when an external force or stress is applied.
- The internal structure of the solid resist the force, but if the force is strong enough, deformation occurs.
- It can be temporary (elastic) or permanent (plastic).

TYPES OF DEFORMATION

The deformation in solids can be categorized into two types:

1. Elastic Deformation
2. Plastic Deformation

TYPES OF FORCE INVOLVES IN DEFORMATION

There are following forces that are involved in deformation of Solids:

- Tensile force : Stretches Material
- Compressive Force : Compresses Material
- Shear Force : Causes sliding b/w layers
- Torsional force : Twisting Force

① ELASTIC DEFORMATION

- Elastic Deformation is a type of deformation in which a material temporarily changes its shape or size under an applied force, but return to its original shape once the force is removed.
- It is a reversible process
- It follows Hook's Law
- Occurs within the elastic limit of the material.

CHARACTERISTICS

- Reversible : No permanent change occurs.
- Instantaneous : Happens as soon as force is applied or removed.
- Follows Hooke's Law

HOOKE'S LAW

- Within the elastic limit, the stress applied on a body is directly proportional to the strain produced in it.

$$\text{Stress} \propto \text{Strain}$$

or

$$\text{Stress} = E \cdot \text{Strain}$$

$$E = \frac{\text{Stress}}{\text{Strain}}$$

- Here, E = Young's Modulus = Measure of stiffness.
  - High E = Less Elastic
  - Low E = More Elastic

ELASTIC LIMIT

- It is defined as maximum amount of stress that a material can withstand without permanent deformation.
- Beyond this limit, plastic deformation begins.

Examples

- Rubber
- Human Skin
- Pharmaceutical Polymers

② PLASTIC DEFORMATION

- Plastic Deformation is defined as permanent change in the shape or size of solid material when a stress beyond the elastic limit is applied.
- The material does not return to its original shape in plastic deformation even after the force is removed.
- It is an irreversible process.
- It occurs when atomic or molecular structure slips or repositions permanently.

CHARACTERISTICS

- Irreversible.
- Does not follow Hooke's law
- Involved dislocation movement in atomic structure.
- Occurs at higher stress levels.

EXAMPLES

- Bending an Aluminium Rod
- Denting a car body.

HECKEL'S EQUATION

- Heckel's equation is used to analyze the compressibility of powders during tablet compression.
- It relates applied pressure to the density of the material as it gets compressed into tablet.

$$\boxed{\ln\left(\frac{1}{1-D}\right) = kP + A}$$

- Here D = Relative density of powder
  k = Slope of the curve (related to plasticity)
  P = Applied Pressure
  A = Constant related to particle re-arrangement.

APPLICATION

- Tells how a powder behaves under compression.
- Useful for selecting binders & excipients.
- Optimize tablet formulation.
- Adjust compression force in tablet machines.

STRESS

- Stress is the force per unit area that applies to an object to deform it.

$$\text{Stress} = \frac{\text{Force}}{\text{Area}}$$

- It's unit is N/m^2 or Pascal
- It is represented by σ.

TYPES OF STRESS

There can be following type of Stress :

① Tensile Stress : When force pulls the object → stretches it.

② Compressive Stress : When force pushes the object → compress it

③ Shear Stress : When force acts parallel to surface

STRAIN

- It is change is shape or size of a material (deformation) when stress is applied

$$\text{Strain} = \frac{\text{Change in dimension}}{\text{Original dimension}}$$

- It doesn't have a unit.
- It is represented by ε

TYPES OF STRAIN

There can be following types of strain :

1. Tensile Strain : Due to increase in length.
2. Compressive strain : Due to decrease in length.
3. Shear Strain : Due to angular deformation (change in shape)

ELASTIC MODULUS

- Elastic Modulus is a measure of material's stiffness - it tells us how much a material resist deformation when stress is applied within elastic limit.

$$\text{Elastic Modulus} = \frac{\text{Stress}}{\text{Strain}}$$

- High E = Material is stiff
- Low E = Material is flexible

TYPES	APPLIED FORCE	CHANGE IN
① Young's Modulus :	Tensile / Compressive	Length
② Shear Modulus :	Shear force	Shape
③ Bulk Modulus :	Uniform Pressure	Volume

Example

- Stell has high Young's Modulus ∵ Very Stiff
- Rubber has low Young's Modulus : Flexible.

THANK YOU

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