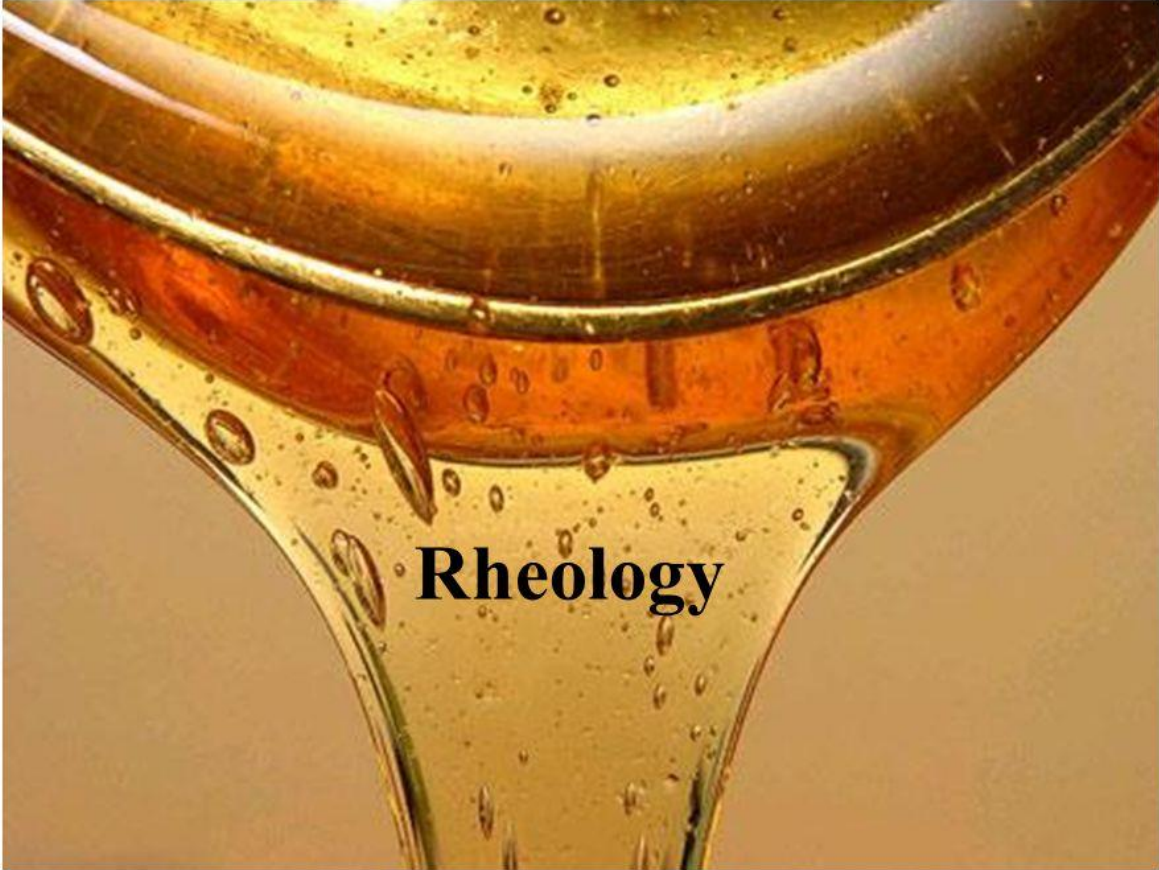# Rheology

By

Lecturer

Ghaidaa S. Hameed

Rheology

Rheology

- Rheo – to flow
- logos – science
- ology – the study of
- **Rheology** is the science concerned with the deformation of matter under the influence of a stress.
- **Viscosity** is an expression of the resistance of a fluid to flow, the higher the viscosity, the greater the resistance.

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Application in pharmacy

- Formulation of emulsion, paste, suppository and tablet coating.

- Mixing and flow of the material during packaging into container and removal prior usage. Such pouring from a bottle, extrusion from tube, passage through needle.

- Patient acceptance

- Physical stability

- Biological availability (absorption rate from GIT)

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Types of Flow

- **Newtonian (Newtonian Law of Flow)**

- **Non Newtonian**

1. Newtonian system

- The higher the viscosity of a liquid, the greater is the force per unit area (shearing stress) required to produce a certain rate of shear"

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shearing force

- A shearing force is applied to the top of the rectangle while the bottom is held in place. The resulting shear stress, F, deforms the rectangle into a parallelogram. The area involved would be the top of the parallelogram.
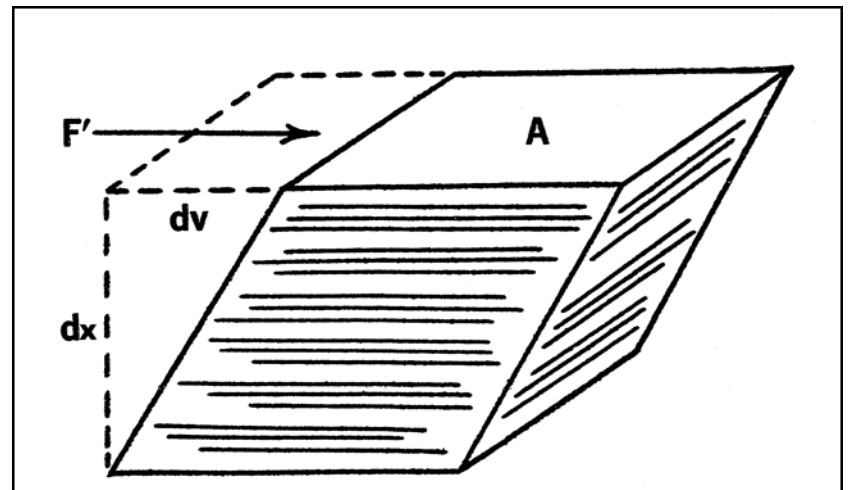
- The difference in the velocity gradient *(dv)* between two plan of liquid separated by distance *(dx)* is the *rate of shear (dv/dx)* and it symbol is *G.*
- The force per unit area required to bring about flow is called the *shearing stress* ant its given a symbol *F*

- F α G $\longrightarrow$ F = η . G

η is the viscosity of the liquid

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

- Increased viscosity = increased shear force or shear stress required to produce a certain rate of shear (Rate of shear should be directly proportional to the shearing stress)

- A certain shear stress with produce a certain rate of shear

Newtonian rheogram
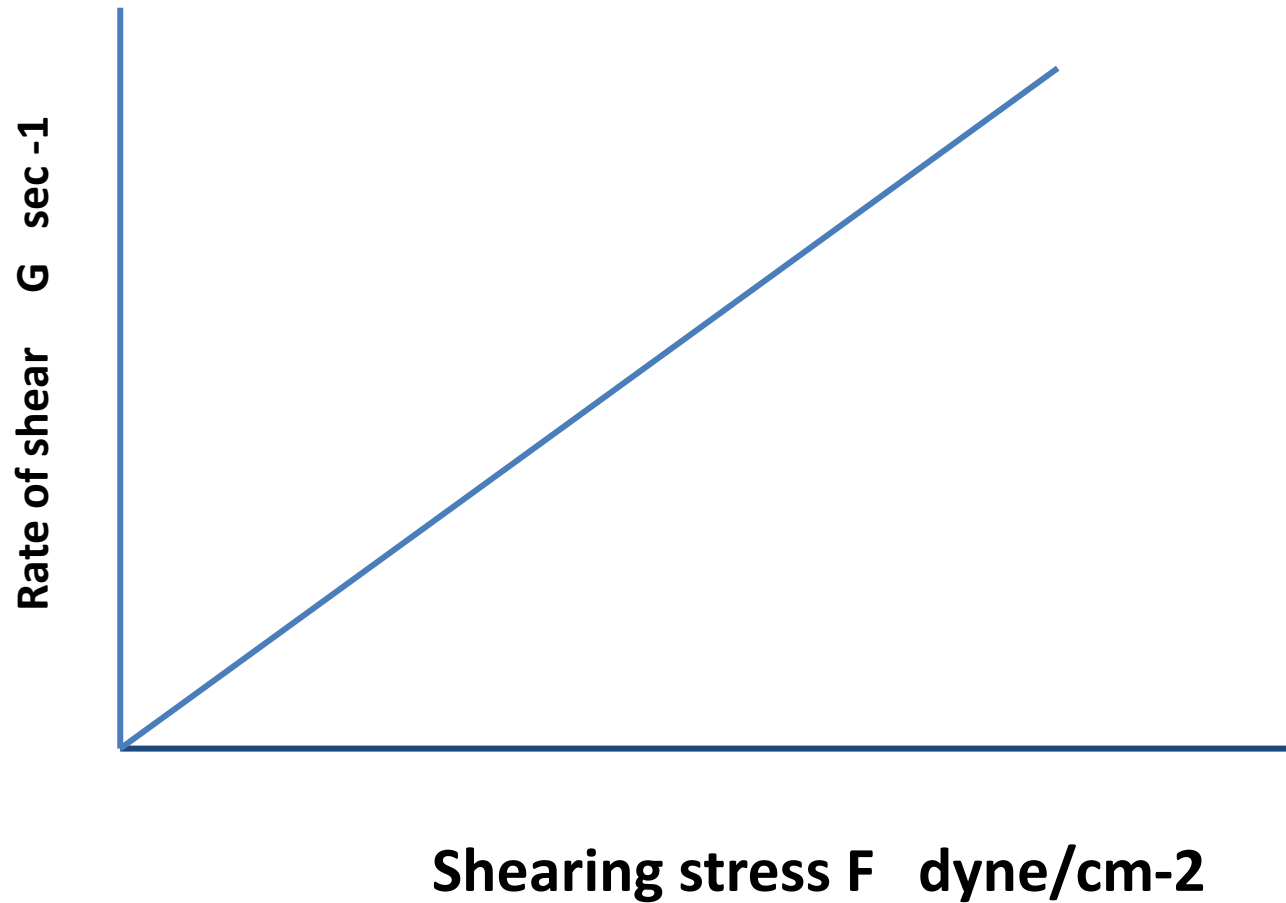
- In common terms, this means the fluid continues to flow, regardless of the forces acting on it. For example, water is ***Newtonian***, because it continues to exemplify fluid properties no matter how fast it is stirred or mixed.

- For a Newtonian fluid, the viscosity, by definition, depends only on ***temperature*** and ***pressure*** (and also the ***chemical composition*** of the fluid if the fluid is not a pure substance), not on the forces acting upon it.

- **VISCOSITIES OF SOME FLUIDS OF PHARMACEUTICAL INTEREST**

―――――――――――――――――――――――――――――

Fluid	Dynamic viscosity at 20°C (mPa s)
Chloroform	0.58
Water	1.002
Ethanol	1.20
Glyceryl trinitrate	36.0
Olive oil	84.0
Castor oil	986.0
Glycerol	1490

―――――――――――――――――――――――――――――

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NON-NEWTONIAN SYSTEMS

- A non-Newtonian fluid is a fluid whose flow properties are not described by a single constant value of viscosity.

- Many polymer solutions and molten polymers are non-Newtonian fluids, as are many commonly found substances such as ketchup, starch suspensions, paint, blood and shampoo.

- Most pharmaceutical fluids do not follow Newton's equation: because the viscosity of fluid varies with the rate of shear. therefore a single determination of viscosity at any one rate of shear cannot yield the entire rheological profile.

i. Plastic or Bingham flow

ii. Pseudoplastic flow

iii. Dilatant flow

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- A In a **non-Newtonian fluid**, the relation between the **shear stress** and the **strain rate** is nonlinear, and can even be time-dependent. Therefore a constant coefficient of viscosity cannot be defined.

- A ratio between shear stress and rate of strain (or shear-dependent viscosity) can be defined, this concept being more useful for fluids without time-dependent behavior.

Bingham plastics

- Clay suspensions, drilling mud, toothpaste, mayonnaise, chocolate, and mustard. The classic case is ketchup which will not come out of the bottle until you stress it by shaking.

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Plastic flow

The substance that exhibits plastic flow are known as **Bingham bodies.**

Plastic flow curves do not pass through the origin, but intersect the shearing stress axis at a particular point referred to as the **yield value**.

The Bingham bodies does not begin to flow until a shearing stress exceed the yield value .

At a stress below the yield value the substance act as an elastic material.

Rate of shear

Slop = mobility

f = yield value

Shearing stress

Plastic flow
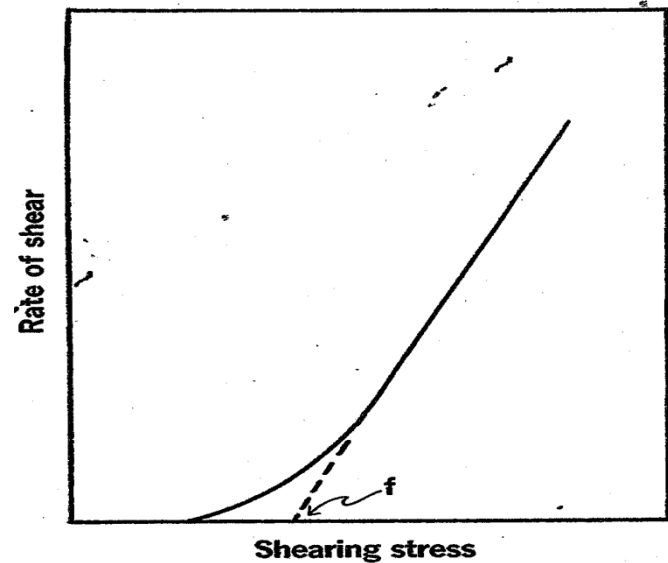
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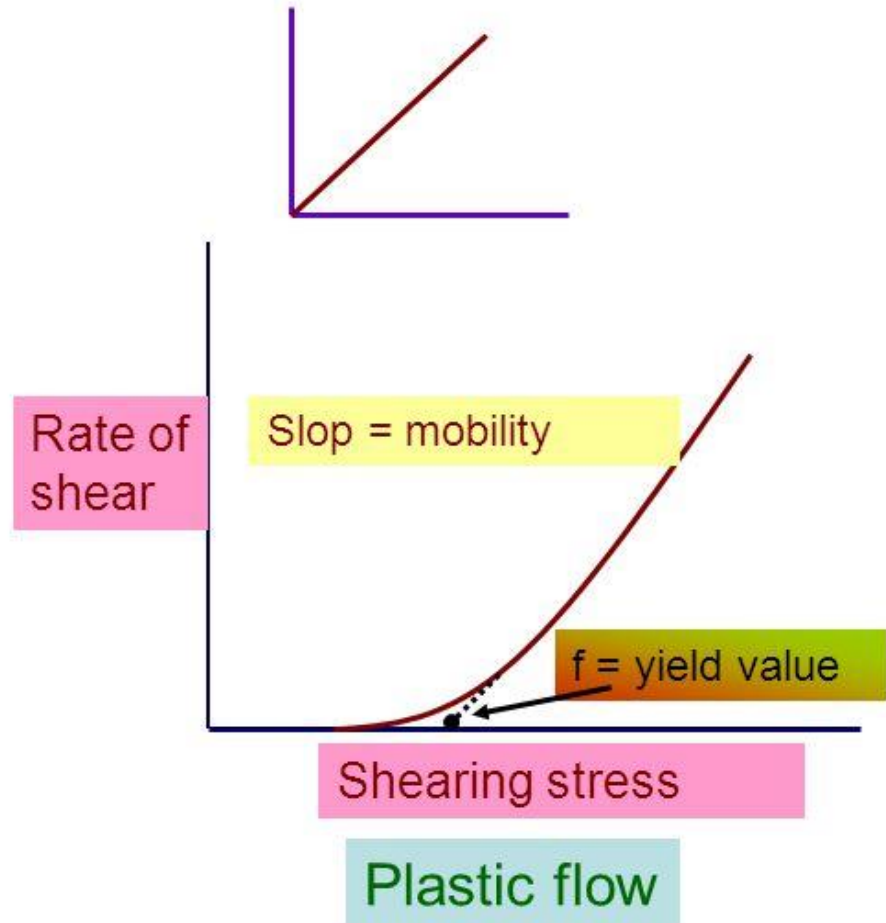
- A Bingham body does not begin to flow until a shearing stress, corresponding to the yield value, is exceeded.

- If stress is less than the yield value, the system behaves like a solid and exerts elastic deformations that are reversible.

- The quantitative behaviour of these bodies is best described by the Bingham Equation where f_B is the Bingham yield value:

Newtonian $F = \eta \cdot G$

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

Non-Newtonian $\eta_{pl} = \dfrac{F - f_B}{G}$ (dyne/cm2)
(plastic viscosity)

(b) Simple plastic flow

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- In practice, **deformation and flow** usually occurs at a **lower shear stress** value and this accounts for the **curved portion** of the curve.

- The **viscosity decreases initially** and then remains **constant**.

- In a **highly flocculated system**, there is interaction between flocs which results in a **structured system** and **plastic flow** is associated with these systems *e.g highly flocculated suspensions.*

- The yield value is present because of the **contacts between adjacent particles** (caused by van der Waals forces which may be capable of withstanding weak stresses) which must be **broken down before flow** can occur.

- Consequently, the **yield v**alue is an indication of the **degree of flocculation**; the more flocculated the suspension, the higher will be the yield value.

- This type of behaviour is also exhibited by *creams and ointments.*

Pseudoplastic flow

• Many pharmaceutical products exhibit **pseudoplastic flow** include natural and synthetic gums e.g. liquid dispersions of tragacanth, sodium alginate, methylcellulose, sodium carboxymethylcellulose,.

• As a general rule: Pseudoplastic flow is exhibited by polymers in solution

Plastic systems are composed of flocculated particles

Shearing stress

(c) Simple pseudoplastic flow

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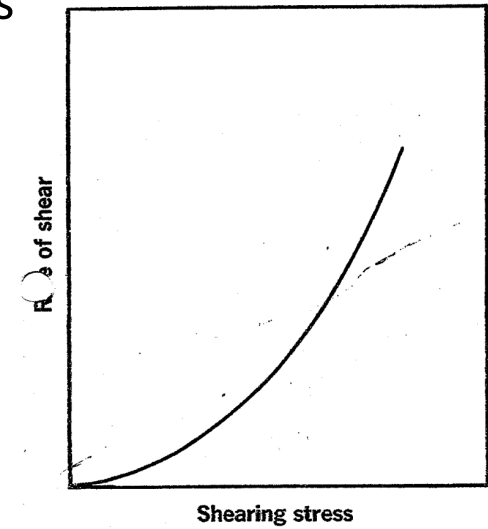
- The curve commences at the origin and there is no yield value.

- No part of the curve is linear, so viscosity cannot be expressed by any single value.

- The apparent viscosity may be obtained at any rate of shear from the slope of the tangent to the curve at the specified point.

- The viscosity decreases with an increasing rate of shear (shear-thinning systems).

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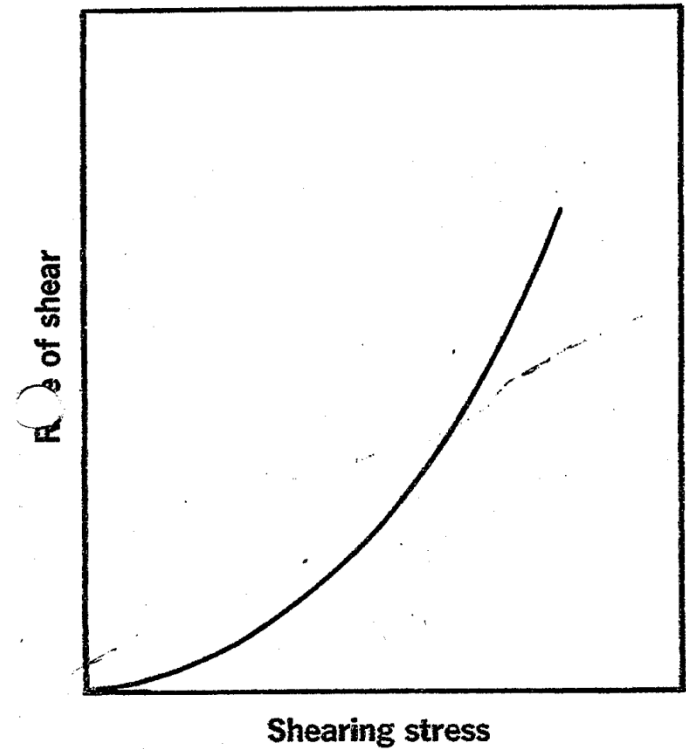
- Pseudoplastic flow cannot be satisfactorily expressed by fundamental equations.

- The following empirical equation correlates most closely with experimentally observed flow not involving stress over vast ranges:

$$\eta' = \frac{F^N}{G}$$

η' is a apparent coefficient.

- The exponent **N** rises as the flow becomes increasingly non-Newtonian.

- When $n = 1$, this equation reverts to the classic Newton equation and the flow is Newtonian.

1/η = gradient (changes with S)

R_ _ e of shear

Shearing stress

(c) Simple pseudoplastic flow

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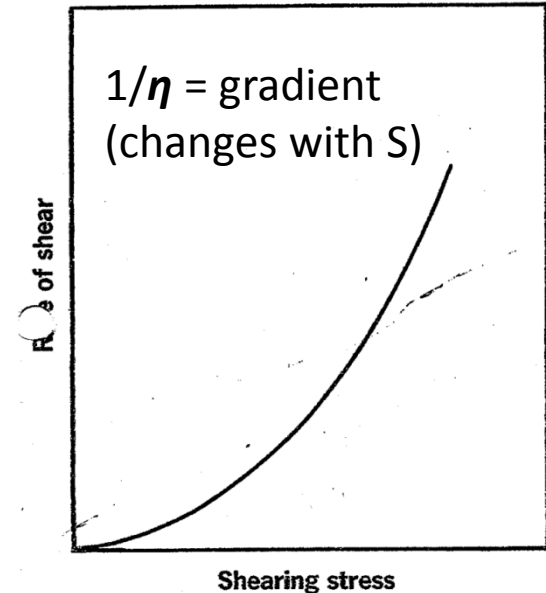
At the Particulate level:

- The curved rheogram for pseudoplastic materials results from a shearing action on the long-chain molecules which become entangled and associated with immobilized solvent.

- As the shearing stress is increased, the randomly arranged particles tend to become disentangled and align their long axes in the direction of flow.

- This orientation reduces the internal resistance of the material and offers less resistance to flow. Some of the entrapped water will also be released.

- Both of these account for the lower viscosity. Once stress is removed, the structures reform spontaneously.

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Dilatant flow

- Dilatant flow - usually ***suspensions containing a high concentration (>50%) of small, deflocculated particles***.

- Exhibit an increase in resistance to flow with increasing rates of shear.

- Systems increase in volume when sheared - termed ***dilatant***.

- The reverse of pseudoplastic systems.

- Pseudoplastic systems – ***shear-thinning systems***, Dilatant materials - ***shear-thickening systems***.
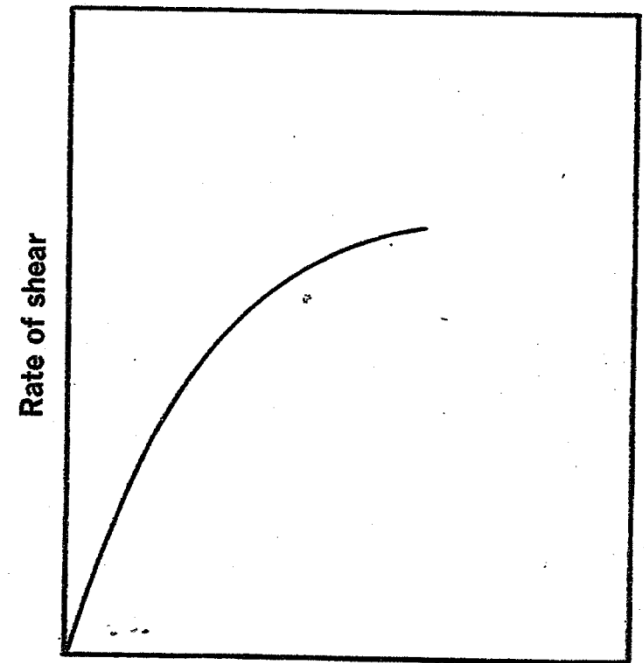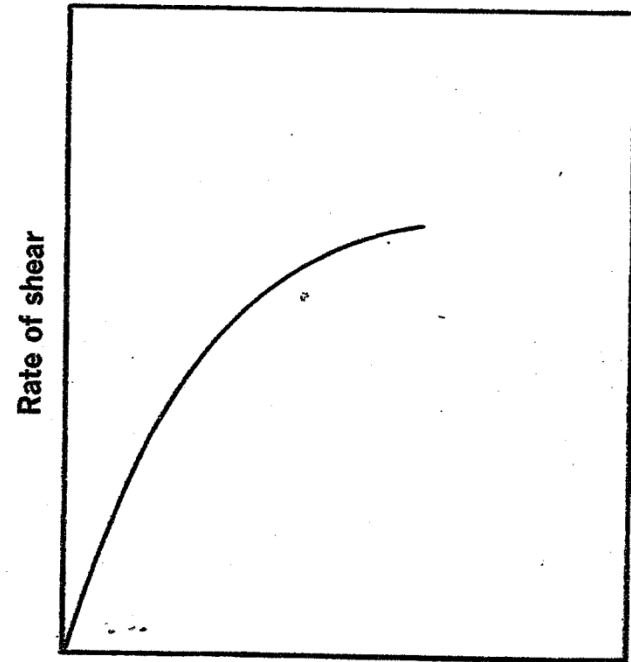

Shearing stress

(d) Dilatant flow

Rate of shear (y-axis label)

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- The same equation can be used to describe dilatancy in quantitative terms:

$$\eta' = \frac{F^N}{G}$$

N < 1

- *N* is always less than 1

- Decreases as the degree of dilatancy increases.

- As *N* approaches 1, the system becomes increasingly Newtonian in behaviour.

(d) Dilatant flow

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At the particulate level:

- At rest:
  - particles closely packed
  - voids at a minimum.

increasing
rates of shear

close packed particles;
minimum void volume;
sufficient vehicle;
relatively low consistency

open packed (dilated) particles;
increased void volume;
insufficient vehicle;
relatively high consistency

- Vehicle:
  - sufficient to fill this volume
  - allows the particles to move relative to one another at low rates of shear.

- Can pour a dilatant suspension from a bottle without shaking as it is relatively fluid without shear stress applied.

- If the shear stress is increased by shaking, the bulk expands or dilates as the particles move quickly past each other and take an open form of packing.

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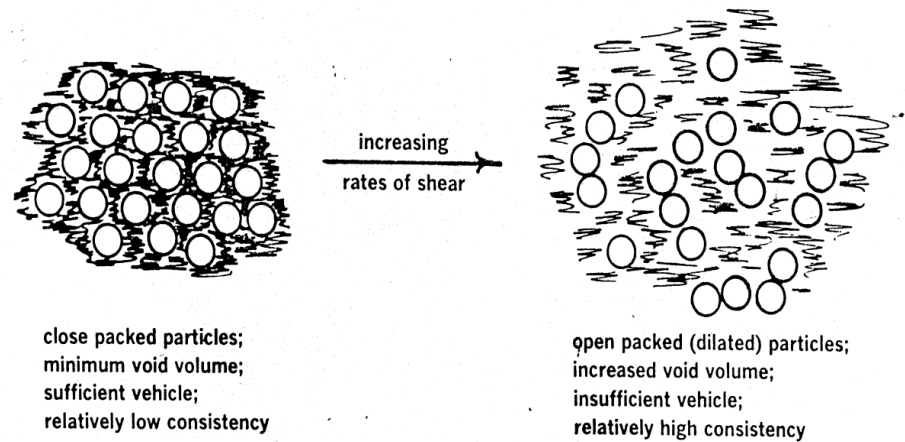
- Such an arrangement results in a significant increase in the void volume, with the vehicle now being insufficient to fill the voids between the particles.

- The resistance to flow increases since the particles are no longer completely wetted or lubricated by the vehicle and eventually the suspension will set up as a firm paste.

- Caution must be taken in processing dilatant materials.
  - Usually, the processing of dispersions containing solid particles is facilitated by the use of high speed mixers, blenders or mills.

  - Dilatant materials may solidify under these conditions of high shear, thereby overloading and damaging the processing equipment.
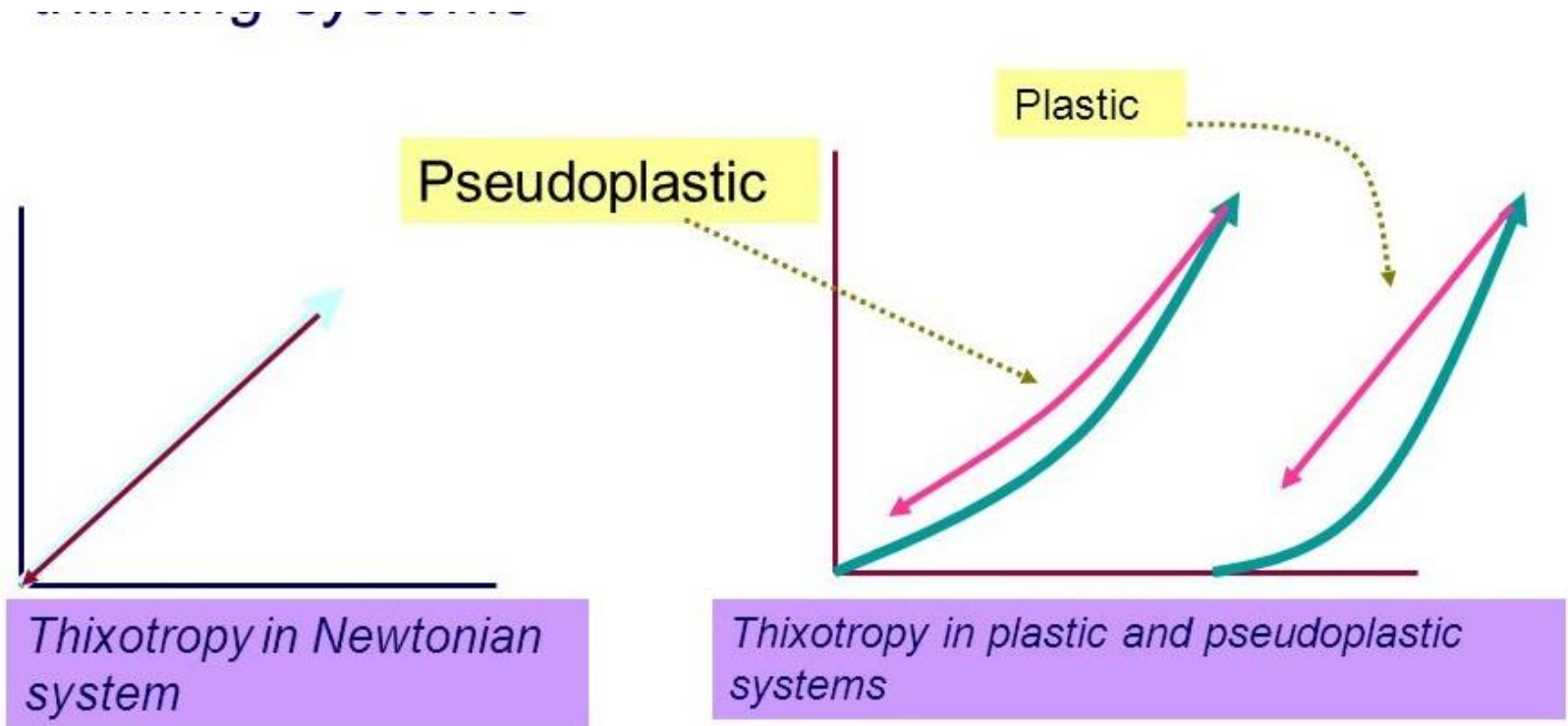
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Fig. 19-2. Representative flow curves for various materials.
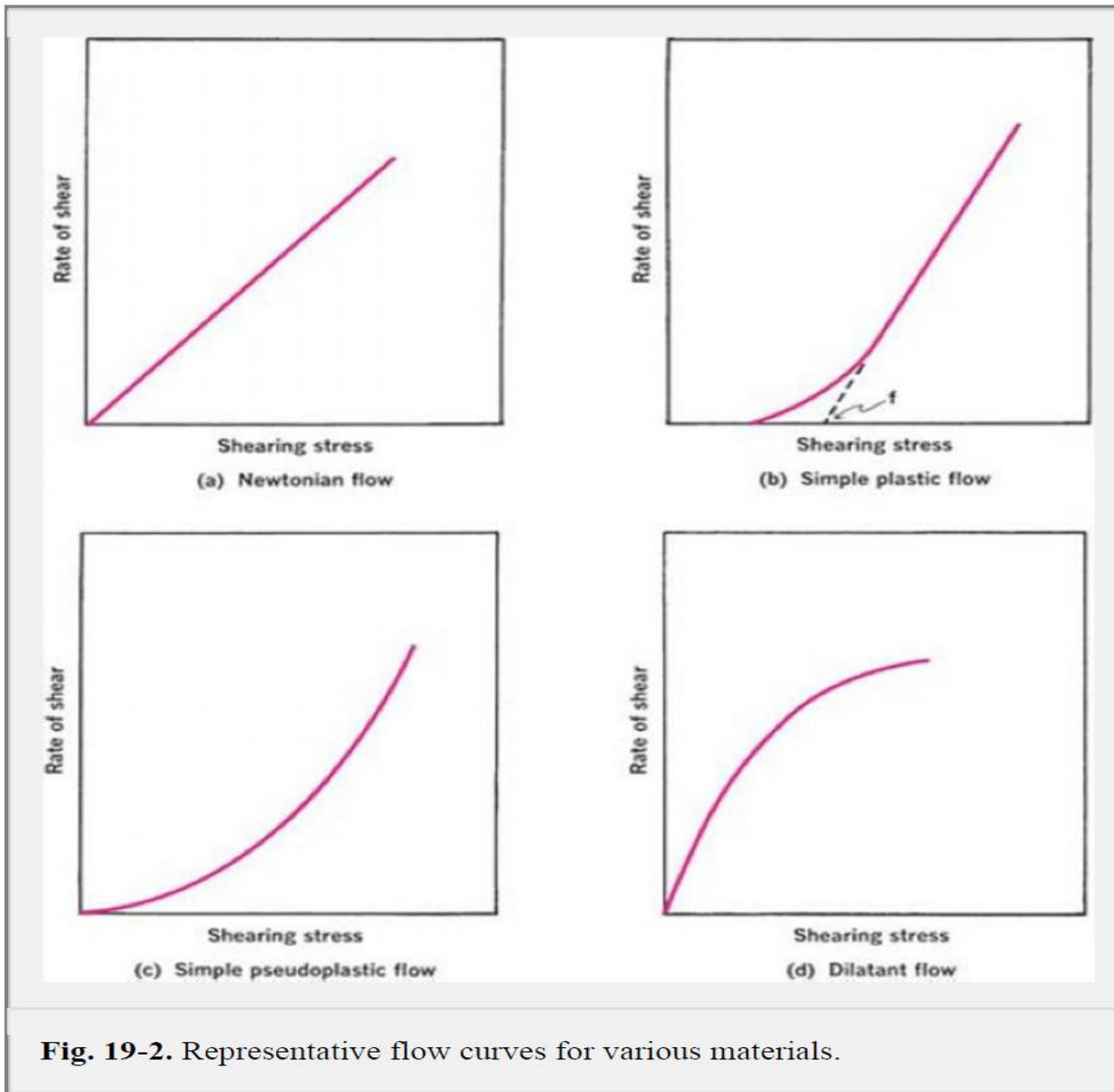
THIXOTROPY

Description

- So far for Newtonian and non-Newtonian behaviour:

  - observed behaviour when the rate of shear was progressively increased and plotted against the resultant shear stress.

- Assumed that if the rate of shear was reduced, the down-curve would be identical with and superimposed on the up-curve.

- This is so with -   Newtonian systems

                    -        some non-Newtonian materials.

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THIXOTROPY

Thixotropy in Newtonian system

Thixotropy in plastic and pseudoplastic systems

- For most non-Newtonian systems:
- The flowing elements, whether particles or macromolecules, may not adapt immediately to the new shearing conditions.
- When subjected to a particular shear rate, the shear stress and consequently the viscosity, will decrease with time.
- Therefore the down-curve can be displaced with regard to the up-curve.

- **Thixotropic systems** usually contain **asymmetric particles** and through numerous points of contact, these particles set up a loose **3-D network** throughout the sample.

- **At rest**, this structure confers **some degree of rigidity** on the system, and it resembles a **gel**.

- **As shear is applied** and flow starts, this **structure begins to break down** as the points of contact are disrupted and the particles become aligned in the general direction of flow.

- The **material undergoes a gel to sol transformation** and exhibits **shear thinning**.

- Upon **removal of the stress**, the structure starts to **reform**. This is not instantaneous, but is a **progressive restoration** of consistency as the asymmetric particles come into contact with each other by undergoing random Brownian movement.

Shear-thinning systems (plastic and pseudoplastic)

- down-curve is frequently displaced to the left of the up-curve rheogram exhibits a hysteresis loop.
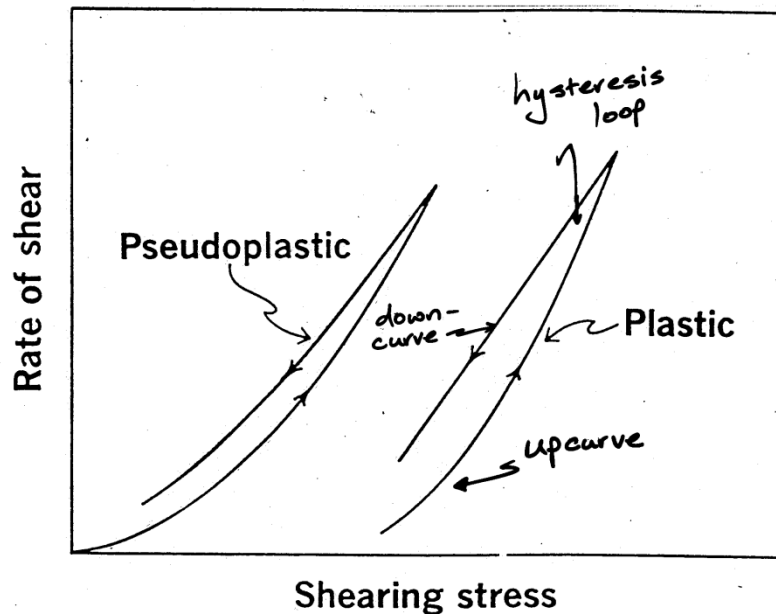

FIG. 19-4. Thixotropy in plastic and pseudoplastic flow systems.

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- i.e. the material has a lower consistency at any one rate of shear on the down-curve than it had on the up-curve.

- Indicates a breakdown of structure that does not reform immediately when the stress is removed.

- This phenomenon is known as thixotropy and may be defined as:

- "A**n isothermal and comparatively slow recovery, on standing of a material whose consistency is lost through shearing**".

- According to this definition, thixotropy can **only** be applied to shear-thinning systems.

The rheograms obtained with thixotropic materials are:

- highly dependent on the **rate** at **which shear is increased or decreased**

- **the length of time** a sample is subjected to any one rate of shear.

Measurement of thixotropy

- Main characteristic of a thixotropic system is the hysteresis loop.

- The area of hysteresis has been proposed as a measure of thixotropic breakdown.

- Two approaches:

  - determine the structural breakdown with time at a constant rate of shear.
  - determine the structural breakdown due to increasing shear rate.

- Limitations:
  - Does not taken into account the shape of the up- and down-curves. So
  - Two different materials may produce loops of similar area but which have completely different shapes representing totally different flow behaviour.

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- **Rheogram of white soft paraffin**

- This is typical of a loop obtained with some samples of white **soft paraffin** where the up-curve exhibits a number of bulges.

- *Lower shear rates*
  - the bulges are thought to be associated with the initial loss of 3-D structure.

- *Higher shear rates*
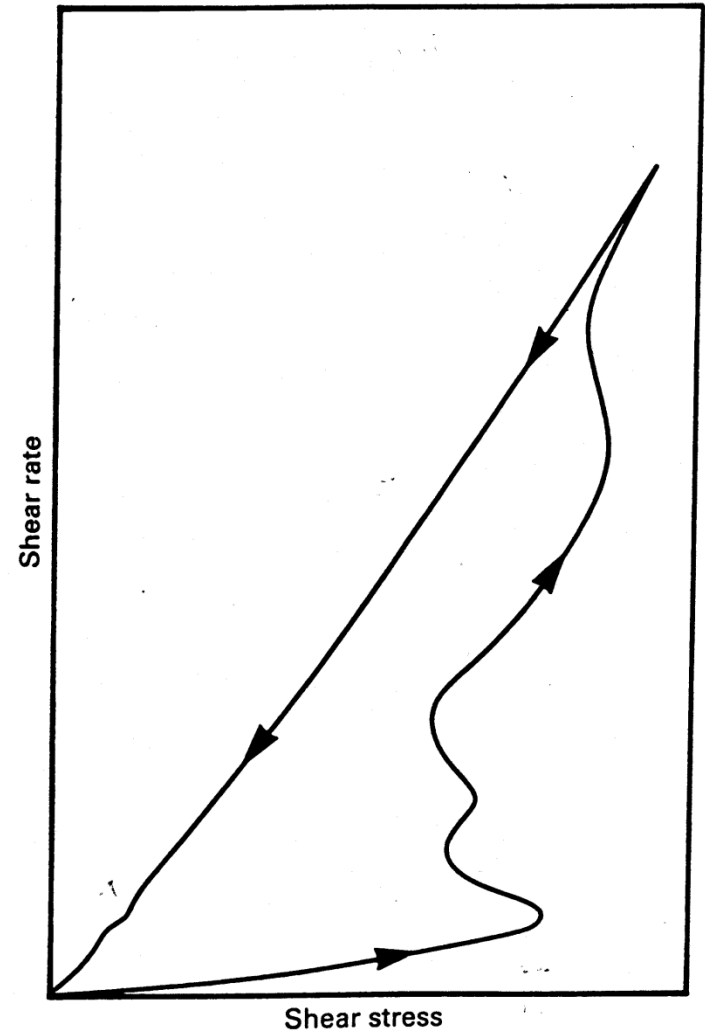 - the smoother deviations here are associated with molecular reorientation.

Fig. 2.12 Complex rheogram produced by a pharmaceutical gel

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Rheopexy

- This is a characteristic exhibited by **some thixotropic systems**.

- A phenomenon where a **sol forms a gel** more readily **when gently shaken** than when allowed to form the gel while the material is kept at rest.

- The rocking motion provides a mild turbulence which aids in returning de-randomised particles to a random orientation.

- The **gel** is the **equilibrium form**.

Thixotropy in formulation

- **Thixotropy is a desirable property** in liquid pharmaceutical systems that ideally should have:

- **A high consistency** in the container **yet pour or spread easily**.

- e.g.

   -a well formulated suspension will not settle out readily in the container

   -will become fluid on shaking and will remain so long enough for a dose to be dispensed.

   -will regain consistency rapidly enough so as to maintain the particles in a suspended state.

- Also desirable with emulsions, lotions, creams, ointments and parenteral suspensions to be used for intramuscular depot therapy.

DETERMINATION OF RHEOLOGIC PROPERTIES

Why measure viscosity?

-Formulation development
  - -Quantities of ingredients
  - -Grades of ingredients
  - -Formulation requirements
  - -Production Methods - mixing rate
      - temperature
  - -Setting limits for production

- Production
  - -Quality Assurance / Batch-to-batch
      uniformity
  - -Production methods - variability
  - -Adjustments to formulation - thicken
  - - Quality of ingredients – natural
      products vary

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- Other rheologic properties:
	- stickiness
	- "spreadability"

Pharmaceutical Considerations and Applications

- **Problems in establishing meaningful shear rates**
  Viscosity requirements often **emperical**, however, researchers have attempted to establish shear rates relating to the use of pharmaceuticals e.g.

  - topical application - 120 sec^{-1}
  - nasal spray in a plastic squeeze bottle - 1000 sec^{-1}
  - pouring from a bottle - below 100 sec^{-1}.

- However, think about the shear rate resulting from rubbing a cream into the skin. This can range from 100 to 10 000 sec^{-1} depending on the degree of rubbing. The shear rate for individual use by a process therefore varies greatly.

- Another example is squeezing a product from a collapsible container - the shear rate depends on the squeezing force that the subject can exert easily.

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- **Visual perception**

  The importance of viscosity in visual perception must be considered
  e.g.   cream to hold its shape in a jar

             a lotion to pour

             a toothpaste to retain its ribbon shape on a brush.

  Here shear rate is determined by subjectively evaluating an acceptable rate of deformation or flow under the constant stress of gravity.

- ***Ease of use***

  e.g. Toothpaste.
  - After applying a rate of shear in squeezing the tube, the toothpaste must flow onto the bristles.
  - It must then recover its viscosity sufficiently to maintain its   ribbon shape on the brush.
  - With shear, it must thin rapidly for ease in brushing.

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- **Topical preparations must meet certain criteria for:**

  - Desirable pharmaceutical properties feel, spreadability, colour, odour

  - Desirable pharmacological properties – drug release

- **Other psychologic and sensory characteristics e.g.**

  - Sensations in the mouth

  - Between the fingers

  - On the skin

  are important considerations for manufacturers of cosmetic products and dermatologic products.