University of Kerbala

Physical Pharmacy

Lecture 7

Rheology

Hamid Alghurabi
Assistant Lecturer
in Pharmaceutics

Overview

Types of flow

- Newtonian systems
- Non-Newtonian systems

Thixotropy

- Definition
- Applications in formulations

Determination of rheological properties

Learning Objectives

1. Define rheology, and describe its application in the pharmaceutical sciences and practice of pharmacy.
2. Understand and define the following concepts: shear rate, shear stress, viscosity, kinematic viscosity, fluidity, plasticity, yield point, pseudoplasticity, shear thinning, dilatancy, shear thickening, thixotropy.
3. Define and understand Newton's law of flow.
4. Differentiate flow properties and rheograms between Newtonian and non-Newtonian materials.
5. Appreciate the fundamentals of the practical determination of rheologic properties.

Rheology
Definition

The term “rheology” (from the Greek *rheo-* “to flow” and *-logy* “science”) is used to describe the flow of liquids and the deformation of solids.

Viscosity is an expression for the resistance of a fluid to flow; the higher the viscosity, the greater is the resistance.

Simple liquids can be described in terms of absolute viscosity (single value).

Heterogeneous dispersions are more complex and cannot be expressed by a single value.

Rheology
Pharmaceutical Applications

Rheology is involved in:

1. Mixing and flow of materials, their packaging into containers, and their removal prior to use (pouring from a bottle, extrusion from a tube, or passage through a syringe needle).
2. Selection of processing equipment used in the manufacture of pharmaceutical systems.
3. Influencing patient acceptability to a particular product, physical stability, and even biologic availability.

University of Kerbala

Types of flow

Newtonian Systems
Non-Newtonian Systems

Types of flow

Materials are classified according to the type of flow and deformation, into two categories:

1. Newtonian systems.
2. Non-Newtonian systems.

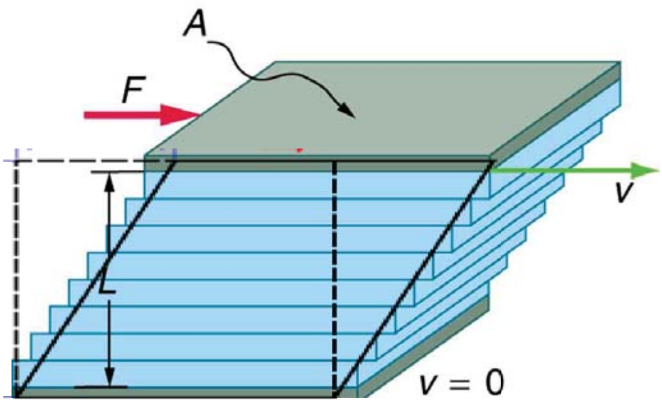
Newtonian Systems

Newton's Law of Flow

Consider a block of liquid consisting of parallel plates of molecules, in which the bottom layer is fixed and the top plane of liquid is moved at a constant velocity.

The difference in velocity (dv) between two planes of liquid separated by the distance (dr) is the ***rate of shear*** (dv/dr) and is given the symbol G.

The force per unit area (F/A) required to bring about flow is called the ***shearing stress*** and is given the symbol F.



Newtonian Systems
Newton's Law of Flow

Shearing stress is directly proportional to rate of shear:

$$\boldsymbol{F} \,\alpha\, \boldsymbol{G} \quad \Longrightarrow \quad \boldsymbol{F} = \eta \times \boldsymbol{G}$$

where η is the ***viscosity***.

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

The higher the viscosity of a liquid, the greater is the shearing stress required to produce a certain rate of shear.

Materials that obey Newton's law of flow are known as ***Newtonian systems***

Newtonian Systems
Viscosity Units

The unit of viscosity is the *poise* $(\boldsymbol{p})$ which is defined as the shearing force required to produce a rate of shear equal to 1 cm S^{-1}

Centipoise $(\boldsymbol{cp})$ is equal to 0.01 poise and is more conveniently used for most work.

The CGS units for poise are dyne sec cm^{-2}

Fluidity $(\boldsymbol{\varphi})$ is defined as the reciprocal of viscosity:

$$\varphi = \frac{1}{\eta}$$

Newtonian Systems
Kinematic Viscosity

Kinematic viscosity is the absolute viscosity divided by the density of the liquid at a specific temperature:

$$\boldsymbol{Kinematic\ viscosity} = \frac{\eta}{\boldsymbol{p}}$$

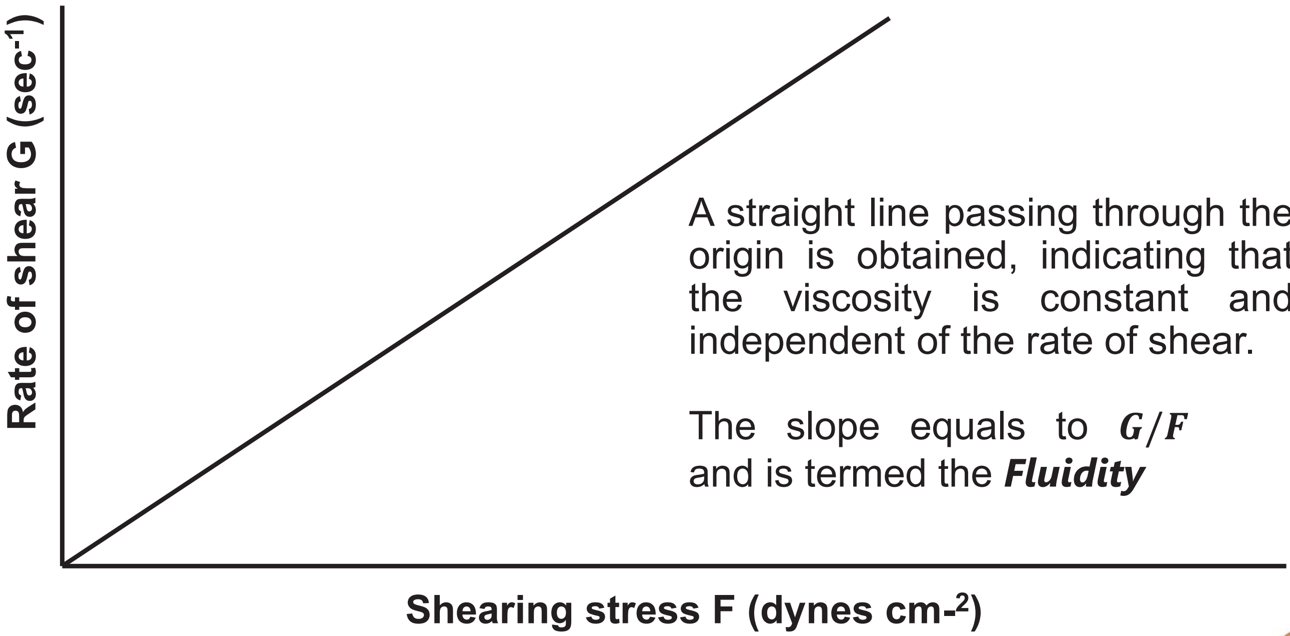
The units of kinematic viscosity are the *stoke* ($\boldsymbol{s}$) and the *centistoke* ($\boldsymbol{cs}$).

Absolute viscosities of some liquids commonly used in pharmacy:

Liquid	Viscosity (cp)
Castor oil	1000
Olive oil	100
Water	1.0019

Newtonian Systems
Rheogram

A representative flow curve (*rheogram*) for a Newtonian system (obtained by plotting $\boldsymbol{F}$ versus $\boldsymbol{G}$)



Non-Newtonian Systems

The majority of fluid pharmaceutical products are not simple liquids and do not follow Newton's law of flow.

These systems are referred to as ***non-Newtonian***.

Non-Newtonian behavior is generally exhibited by liquid and solid heterogeneous dispersions (e.g. colloids, emulsions, suspensions, and ointments).

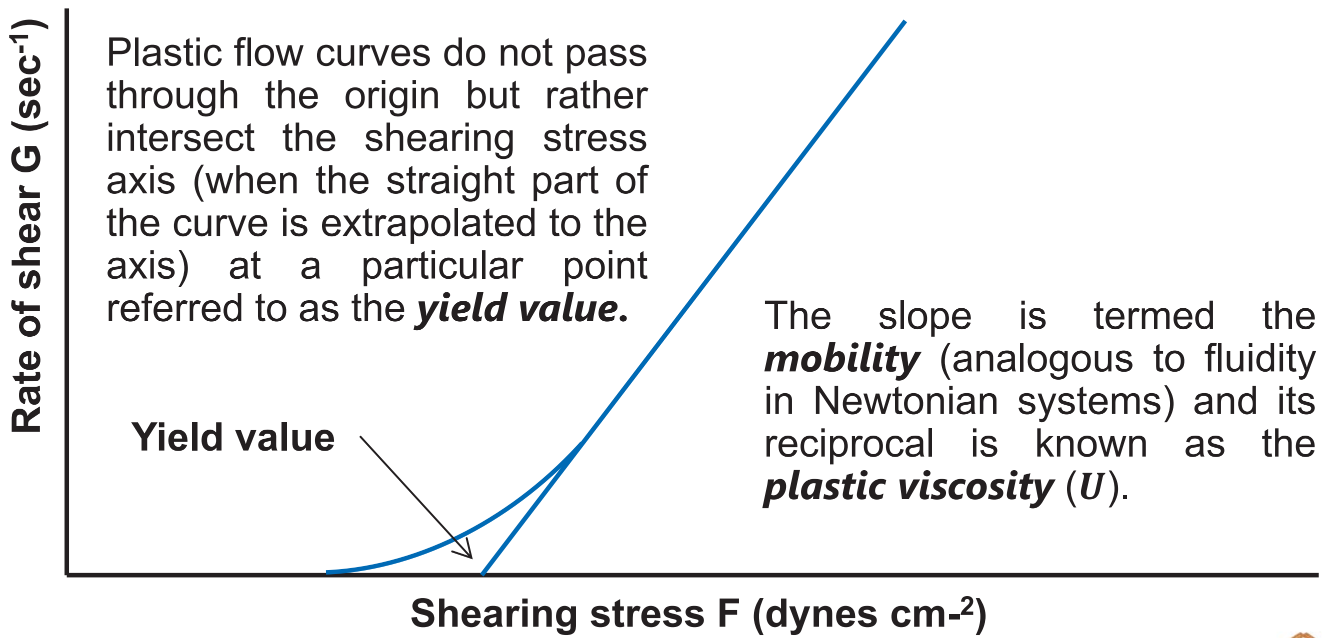
According to the rheograms of non-Newtonian materials, three classes of flow are recognized:

1. ***Plastic Flow*** (or ***Bingham Flow***)
2. ***Pseudoplastic Flow***
3. ***Dilatant Flow***

Non-Newtonian Systems

Plastic Flow

The curve represents a material that exhibits plastic flow:



Non-Newtonian Systems
Plastic Flow

The equation describing plastic flow is

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

f: yield value (dynes/cm^2)

A plastic (Bingham) body does not begin to flow until a shearing stress exceeds the yield value.

At stresses below the yield value, the substance acts as an elastic material.

Non-Newtonian Systems
Plastic Flow

Plastic flow is associated with the presence of flocculated particles in concentrated suspensions.

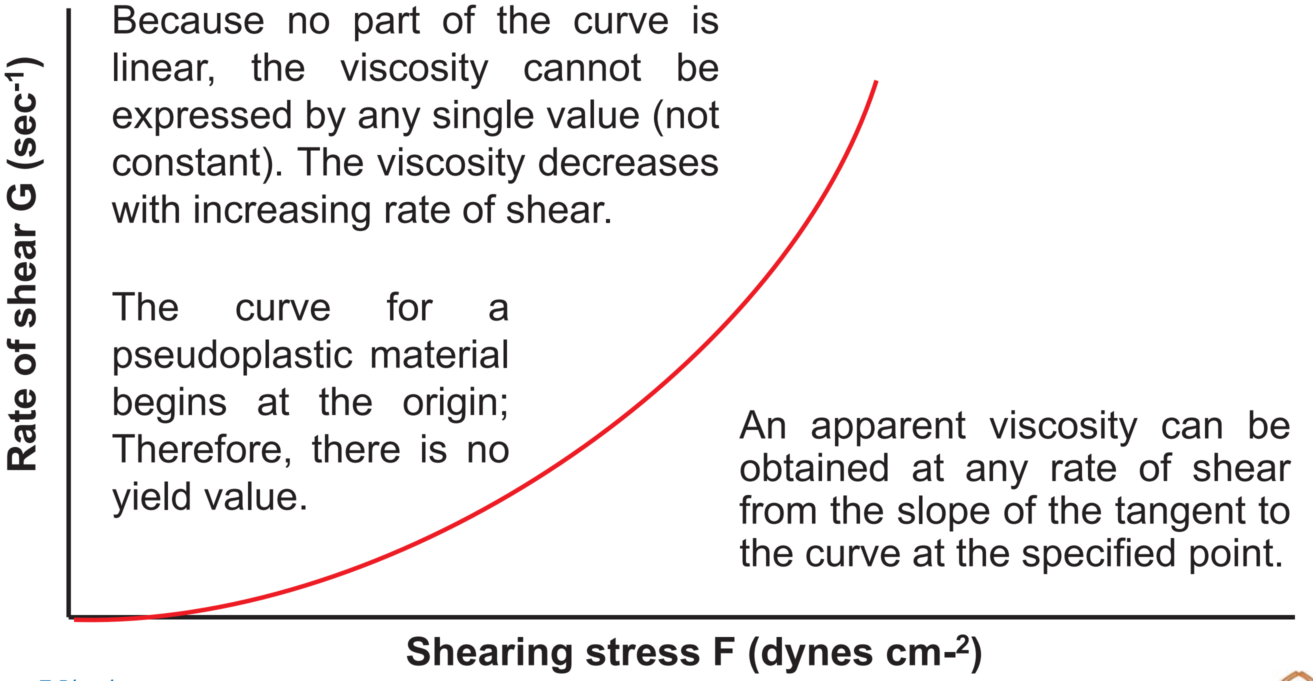
A yield value exists because of the contacts between adjacent particles (via van der Waals forces), which must be broken before flow can occur.

The more flocculated the suspension, the higher will be the yield value.

Non-Newtonian Systems

Pseudoplastic Flow (Shear-Thinning Systems)

Many pharmaceutical products, exhibit pseudoplastic flow:



Because no part of the curve is linear, the viscosity cannot be expressed by any single value (not constant). The viscosity decreases with increasing rate of shear.

The curve for a pseudoplastic material begins at the origin; Therefore, there is no yield value.

An apparent viscosity can be obtained at any rate of shear from the slope of the tangent to the curve at the specified point.

Non-Newtonian Systems

Pseudoplastic Flow (Shear-Thinning Systems)

The pseudoplastic viscosity is expressed by the exponential formula:

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

η': apparent viscosity.

The exponent N rises as flow becomes increasingly non-Newtonian. When $N = 1$, the equation reduces to:

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

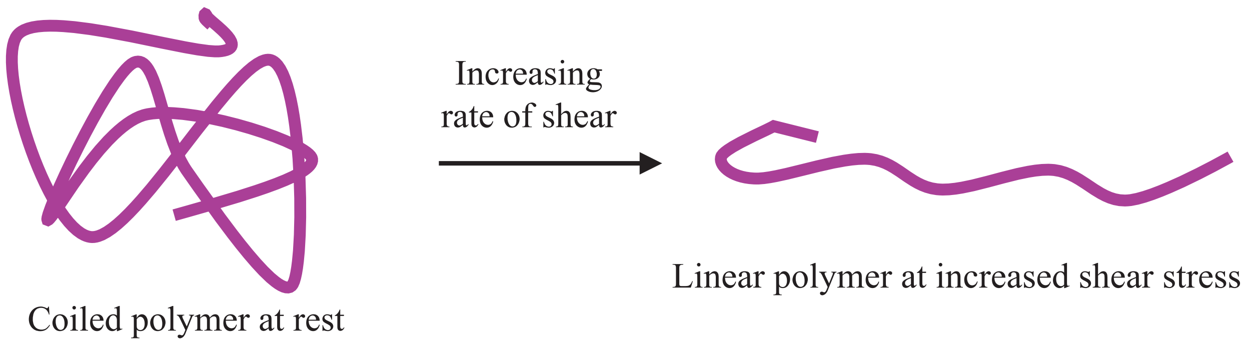
and flow is Newtonian.

Non-Newtonian Systems

Pseudoplastic Flow (Shear-Thinning Systems)

The pseudoplastic flow is associated with the presence of materials with long-chain molecules (e.g. linear polymers).

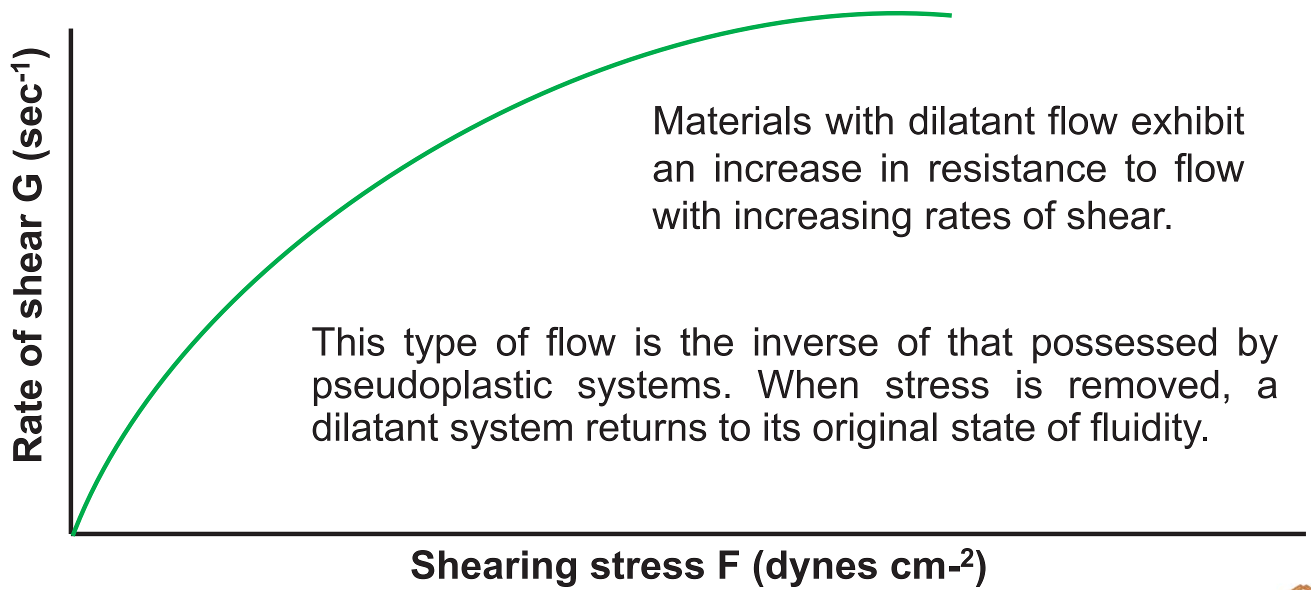
As shearing stress is increased, normally disarranged molecules begin to align in the direction of flow, reducing internal resistance of the material, and allowing a greater rate of shear.



Non-Newtonian Systems

Dilatant Flow (Shear-Thickening Systems)

Certain suspensions exhibit dilatant flow:



Non-Newtonian Systems
Dilatant Flow

The equation $\eta' = \frac{F^N}{G}$ can be used to describe dilatancy in quantitative terms.

In this case, *N* is always less than 1 and decreases as degree of dilatancy increases. As *N* approaches 1, the system becomes increasingly Newtonian in behavior.

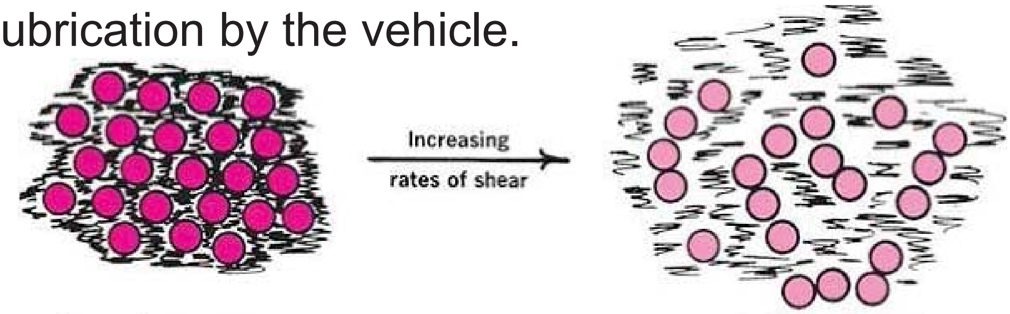
Substances possessing dilatant flow properties are usually suspensions containing a high concentration (about 50% or greater) of small, deflocculated particles.

These suspensions increase in volume when sheared and are hence termed *dilatant*.

Non-Newtonian Systems
Dilatant Flow

At low rates of shear, particles are closely packed with minimal voids, allowing the vehicle to fill the voids and permits particles to move relative to one another

As shear stress is increased, the system dilates; making the vehicle insufficient to fill the increased voids between particles. Accordingly, resistance to flow increases due to poor lubrication by the vehicle.



Close-packed particles; minimum voids; sufficient vehicle; low consistency

Dilated particles; increased void volume; insufficient vehicle; high consistency

Thixotropy

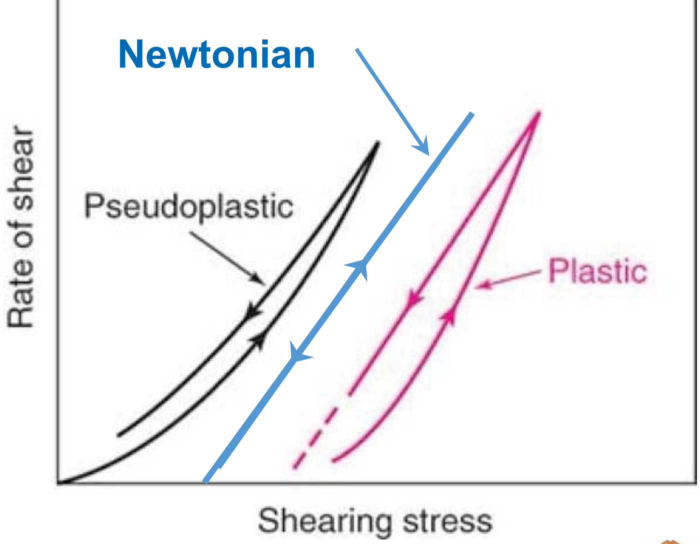
Definition

Applications in Formulations

Definition

In Newtonian systems, if the rate of shear were reduced once the desired maximum had been reached, the downcurve would be identical with, and superimposable on, the upcurve.

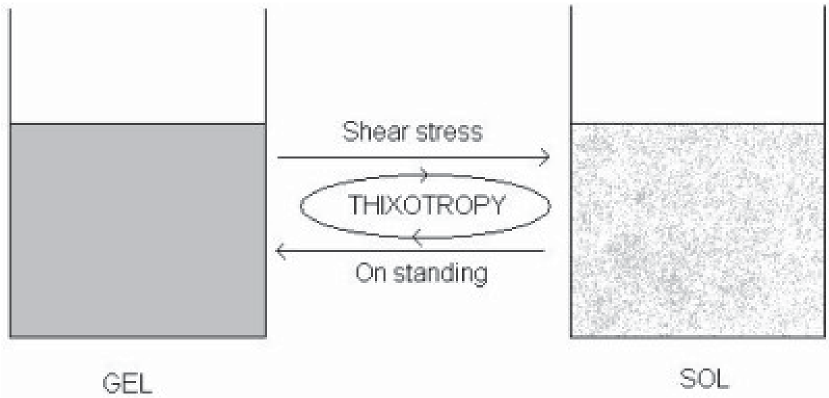
With shear thinning systems (i.e., pseudoplastic), the downcurve is displaced to the left of the upcurve; showing that the material has a lower consistency on the downcurve than on the upcurve.



Definition

The lower consistency of a material on the downcurve indicates a breakdown of structure that does not reform immediately when stress is removed.

This is known as ***thixotropy***, which can be defined as "an isothermal and relatively slow recovery (on standing) of a material consistency, lost through shearing."



Applications in Formulations

Creams and Ointments

Formulation should spread easily on the skin and retains its original form on removal of stress in order to adhere at the site of application

Injections (e.g. Procaine Penicillin)

Transform from gel to sol when passing through hypodermic needle then revert to gel at the site of intramuscular injection where the drug is slowly released in the body

Suspensions

The suspension exist as a gel in resting state. Upon shaking, the gel will convert into a solution, then reverts back to a gel upon storage.

Determination of Rheological Properties

Determination of Rheological Properties

Because shear rate in a Newtonian system is directly proportional to shearing stress (the rheogram is a straight line), a complete rheogram can be obtained form a single point determination. Therefore instruments that operate at a single shear rate can be used.

In non-Newtonian systems, multiple point determination is required to obtain a complete rheogram (a single-point determination is useless). Therefore, instruments that can operate at a variety of shear rates are used.

Determination of Rheological Properties

4 instruments are used for determining rheological properties:

Capillary Viscometer

Falling-Sphere Viscometer

Cup-and-Bob Viscometer

Cone-and-Plate Viscometer

The first two (single–shear-rate instruments) are used only with Newtonian materials, whereas the latter two (multipoint, rotational instruments) are used with both Newtonian and non-Newtonian systems.

References

Attwood, D. & Florence, A. T. 2008. *Physical pharmacy,* London. Chicago, Pharmaceutical Press.

Sinko, P. J. M. A. N. 2006. *Martin's physical pharmacy and pharmaceutical sciences: physical chemical and biopharmaceutical principles in the pharmaceutical sciences,* Philadelphia, Lippincott Williams & Wilkins.