Lesson 1.

Rheological Properties of Foods

1.1. INTRODUCTION

Rheology is the science of flow and deformation of matter and describes the interrelation between force, deformation and time. It is the study of the manner in which materials respond to applied stress or strain. The term comes from Greek ‘rheos’ meaning to flow. The science of rheology is only about 76 years of age. It was founded by two scientists meeting in the late ‘20s and finding out having the same need for describing fluid flow properties.

The scientists were Professor Marcus Reiner and Professor Eugene Bingham.

Sensory evaluation as a scientific discipline represents a very unique technique that harnesses human behavioral instincts of perception, learning, cognition, psychophysics and psychometric for the evaluation of foods. The textural properties of a food are that group of physical characteristics that are sensed by the feeling of touch, are related to the deformation, disintegration and flow of food under application of force. Textural characteristics are an important factor in the overall quality of many food products. Unless these quality attributes meet the standards which the consumer expects, the product will be rejected regardless of its nutritional value.

1.3. IMPORTANCE OF RHEOLOGY

Study of rheological properties is important in food science due to its utility in food processing operations and sensory characteristics. It gives information about the microstructure of a food. Rheology properties are manifestation of the rate and nature of the deformation that occurs when a material is stressed. These parameters can be used to predict how the fluid will behave in a process and in determining the energy requirement for transporting the fluid from one point to another in processing plant. Rheologyical parameters are also useful in defining the quality attribute of food products.

1.3.1. Rheology is very important in the following area in the food industry

(i) Mixing-Two or more material are blended manually or mechanically.

(ii) Flow Control-Flowablity of material varies from very thin to highly viscous.

(iii) Dispensing- Material comes out easily or with difficulty.

(iv) Settling/ Floating – Material with different specific gravity either settle or float depending on viscosity of the material.

(v) Pumping- Liquids or semi-solids are forced through the pipe

(vi) Coating- Spreading of one material as thin layer over other.

(vii) Cleaning – Soil removal from the surface of the equipments and pipeline.

(viii) Control of processing parameters- velocity, magnitude of pressure drop, piping design, pumping requirement for fluid transport system, power requirement of agitation, power requirement of mixing and blending, amount of heat generated during extrusion etc.

(ix) Influence on unit operations – Heat transfer, Mass transfer, mixing, grinding, sedimentation, separation, filtration, evaporation and drying etc.

(x) Study of rheology helps to select proper method of harvesting and sorting of raw materials

(xi) Study of rheology helps to select proper ingredients to manufacture processed foods.

(xii) Study of rheology helps to select proper technology/equipment to manufacture processed foods with desirable sensory and rheological properties.

(xiii) Study of rheology helps in newer product development (e.g. dietetic ice cream, paneer, low fat mozzarella cheese etc.)

(xiv) Study of rheology helps in designing processing equipment, packaging machines, transportation system etc.

(xv) Study of rheology helps to improve sensory quality of the products

(xvi) Study of rheology helps in marketing the products.

2.2. EXAMPLES OF APPLICATION OF RHEOLOGICAL STUDY IN THE FOOD INDUSTRY

· **Meat products** : To evaluate type of breed; its growth rate (tenderness); to evaluate effect of pickling, chilling, aging, preservation, etc. on rheological property of meat; for measurement of toughness and compactness of meat and meat products; establishment of quality grade for marketing and export.

Fruits and vegetables : To evaluate variety of crop; for predicting the effect of storage and ripening period on process; prediction of storage and ripening period; in prediction of stage of harvesting and stage of maturing; used for sorting; measurement of\ textural variation, gives us an idea about growing practice; method of harvesting.

Jams and jellies : helps to decide variety of blending ingredients, esp. pectin; deciding jelling quality of pectin as well as integrity of gel structure, helps in deciding ingredients.

Snack foods : To evaluate formula for dough making and paste, particularly for extrusion; for measurement and adjustment of solids content; for measurement of textural properties like crispiness, hardness, softness and other properties to decide packaging and packing material; helps in predicting shelf-life of product under given storage conditions and history of product (method of harvesting, storage conditions, pre-treatments and processing unit operations).

Confectioneries : To evaluate the quality of raw material; to optimize the processing parameters; to decide the ingredient varieties to be used; for measuring properties like thickness of coating, chewiness, elasticity, brittleness and shelf life of product.

Paste : (Tomato paste, spreads, relishes, puddings, gels, jams, jellies, etc.) – used to evaluate consistency of mixture used for measured viscometric parameters at different stages of processing; deciding the pectin retention and prediction of consistency of final products.

Bakery : To evaluate dough consistency; to estimate floor time and rise time; effect of additives; prediction of shelf life.

Dairy products : To evaluate the effect of ingredients i.e. creaming in fat-free dairy products, fat mimic products by using micro-fluidization of whey protein concentrate, desired quality of mozzarella.

Rheological Properties of Fluid Foods

5.1. INTRODUCTION

It is necessary to study properties of fluid food products for designing and lay-outing of transport system (piping and pumping layout). For the fluid food products, the design of transport system mainly depends on the type and description of flow characteristics of the product. Some of the properties are interdependent and some are dependent on the fluid food composition and therefore it is necessary to measure dependant properties and we can predict its rheological properties.

Most important dependant fluid food property is viscosity i.e. resistance against flow, generally indicated by μ i.e. dynamic viscosity / ή kinematic viscosity ($ή = \mu / \rho$). In food industry μ is broadly used to describe a single parameter known as 'consistency'. But this approach may lead to confusion in many cases due to non-Newtonian behaviour of many fluid food products. The rheological classification of food is given in Fig-5.1. The stress and rate of shear diagram indicate varieties of food products classified under different categories, which is considered to be non-Newtonian as shown in the figure 5.2.

5.2. CLASSIFICATION

The fluids can be classified into following categories depending on the response to the applied shear force.

5.2.1. Newtonian Fluids:

Newtonian fluids are fluids which exhibit a linear increase in the shear stress with the rate of shear. These fluids exhibit a linear relationship between the shear stress and the rate of shear. The slope ' μ ' is constant therefore; the viscosity of a Newtonian fluid is independent of the rate of shear. These fluids exhibit a pure viscous flow i.e. the product begins to flow with the slightest force and the rate of flow is proportional to the magnitude of force applied. The examples of Newtonian fluids are milk, clear fruit juices, sucrose solution, most types of honey, corn syrup etc. The equation for characterizing Newtonian fluid is

$T = \mu (-dv/dx)$ ----- (Eq-1)

Where, T = shear stress, μ = dynamic viscosity ($\eta = \mu/\rho$) , -dv/dx = velocity gradient

5.2.2. Non-Newtonian Fluids:

A non-Newtonian fluid is broadly defined as one for which the relationship between shear stress and shear rate is not a constant. When the shear rate is varied, the shear stress doesn't vary in the same proportion. These fluids exibit either shear thinning or shear thickening behaviour and some exhibit a yield stress. The two most commonly used equations for characterizing non-Newtonian fluids are the power law model (Eq-2) and Herschel-Bulkley model (Eq-3) for fluids.

$T = K (\gamma)n$ -------(Eq-2)

$T = T 0 + K (\gamma)n$ -------(Eq-3)

Where, T = shear stress, K = consistency constant, γ = shear rate, n = flow behaviour index,
T0 = yield stress

There are several types of non-Newtonian flow behaviour, characterized by the way a fluid viscosity changes in response to variation in shear rate (Fig-5.2). The most common non-Newtonian fluids are:

(A) Time-independent flow of non-Newtonian foods:

The fluid foods whose viscosity is not influenced by the shearing time at a constant shear rate show two distinct patterns of stress – shear rate relationship i.e shear-thinning and shear-thickening.

(i) Pseudoplastic/shear-thinning fluids: - This type of fluids will display a decreasing consistency with an increasing shear rate. Probably the most common of the non-Newtonian fluids, psedo-plastic include emulsions and dispersions of many types. This type of flow behaviour is some times called shear-thinning. The shear stress ('T' or 'ς') versus shear rate (γ) curve is convex toward the stress axis. The shear thinning behaviour of a fluid or semi-solid food is expressed by the power law model or de Waele's model:

$T = K (\gamma)+n$ ---- (Eq-4)

Where, T = shear stress, K = consistency constant (Pa s)n, γ = shear rate, n = flow behaviour index ('n' has a positive value between zero and unity)

Protein concentrates, skim milk concentrate, milk ultrafiltration retentates, concentrated fruit juices such as unpectinized apple juice (50-65 Brix), orange juice (50-65 Brix) etc., melted chocolates, thawed frozen egg, fruit and vegetable purees and gum solutions are the examples of psedo-plastic fluid food products.

(ii) Dilatant/shear-thickening flow behaviour:- This type of fluid will display an increasing viscosity with increase in shear rate. Dilatancy is frequently observed in fluids containing high level of deflocculated solids, such as candy compounds, cooked corn starch paste, certain types of honey etc. Dilatancy is also referred to as shear-thickening flow behaviour. The stress shear rate curve is concave toward the stress axis and the value of 'n' in the power law (Eq-4) is negative.

(B) Time-dependent flow of non-Newtonian foods:

Certain non-Newtonian fluids show a time-dependent stress-shear relationship which can be one of the following types:

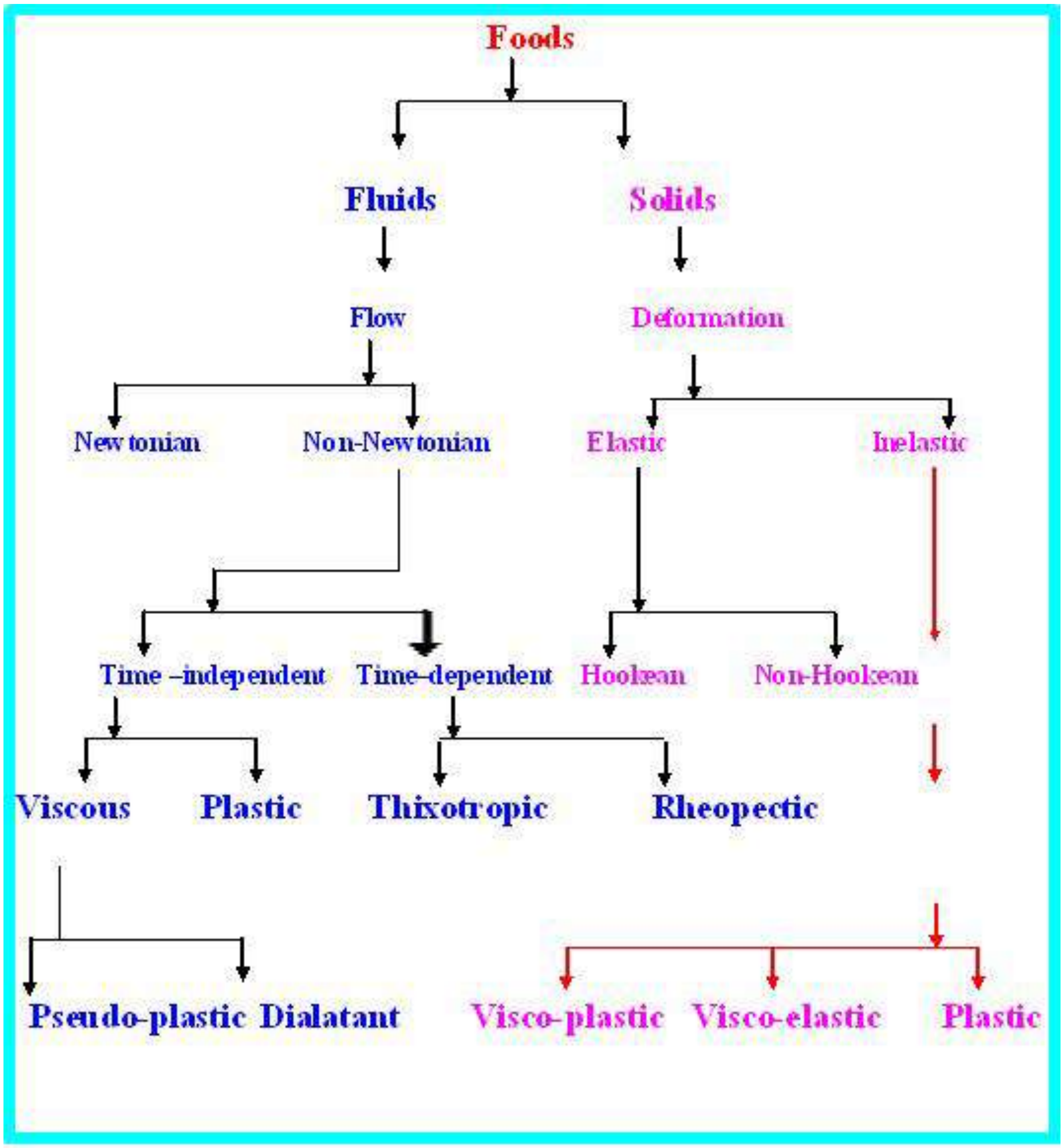

Fig 5.1 Rheological classification of foods

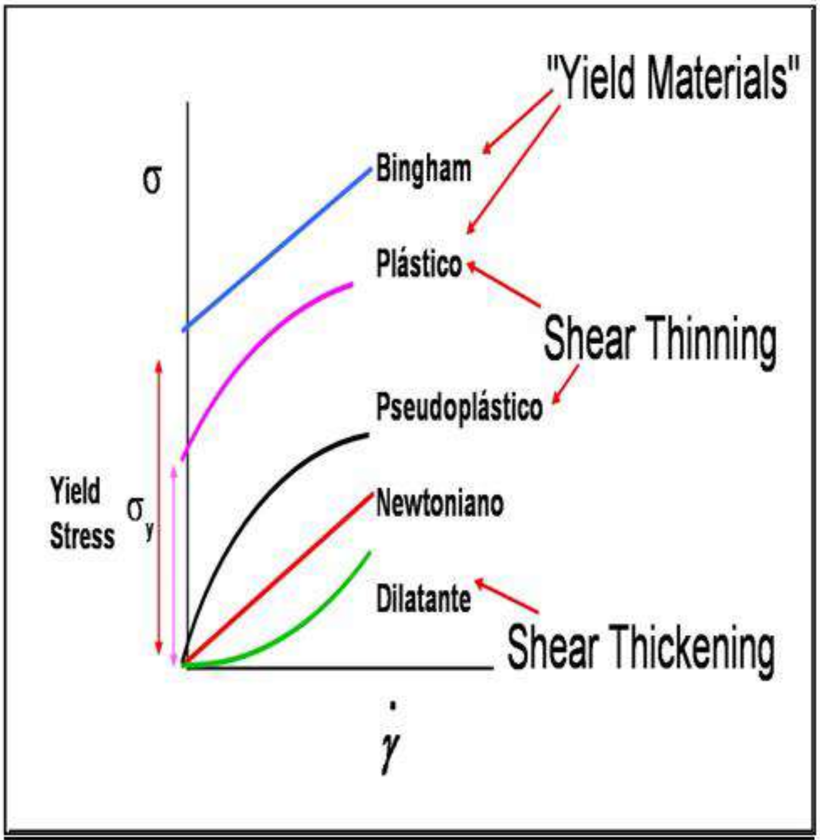

Fig-5.2: Stress-shear rate relationship in different rheological classes of fluids

(i) Thixotropy: - When at a constant shear rate, the stress decreases over a period of time due to structure breakdown until eventually it reaches a steady value, the product is said to be thixotropic. Aged condensed milk, cream and ice cream mix, egg white etc. revel thixotropy.
(ii) Rheopectic: - This essentially the opposite of thixotropic behaviour, in which the fluids viscosity increases with time as it is sheared at a constant rate. Rheopectic fluids are rarely encountered. Both thixotropic and rheopectic may occur in combination with any of the previously discussed flow behaviour, or only at certain shear rates.
(iii) Plastic: - This type of fluid will behave as a solid under static conditions. A certain amount of force must be applied to the fluid before any flow is induced, this force is called yield value. Tomato ketchup is a good example of
this type fluid, its yield value will often make it refuse to pour from the bottle until the bottle is shaken or struck, allowing the catchup to flow freely. Once the yield value is exceeded and flow begins, plastic fluids may display Newtonian, pseudoplastic, or dilatant flow characteristics.

Rheological Properties of Granular Foods and Powders

6.1. INTRODUCTION

Dry food products make up a considerable portion of the total amount of food products available. Like fluid food products they are handled in various ways in different parts of processing plant .The design of handling system for dried products requires knowledge of the flow properties of the product being handled and transported or conveyed. The manner in which granular foods or powder may flow into or out of container is of particular concern in processing plants. In addition to the density and particle size parameters, there are specific parameters which describe the flow properties of these types of food products. Two common parameters used for this purpose are the angle of response and the angle of slide. Both of these parameters lack theoretical considerations but do serve as a means of comparing different food powders. The angle of slide is a rather simply defined parameter in which the powder is placed on a horizontal plate and the angle of the plate is changed until the powder slides from the plate. The angle from the horizontal which is required for the powder to lose its position on the plate is measured and this angle will be a function of the type of surface on which the powder is placed.

Dry food products are handled in various ways in different parts of processing plants. The design of handling system for dry products requires knowledge of the properties of the product being handled.

6.2. DENSITY

Density is one of the basic properties of any material but in the case of granular food products, various types of densities have been defined:

6.2.4. Particle shape

All particles are not exactly of spherical shape, how far it is deviated from spherical shape is expressed by the term spherocity. The term spherocity ΦS which is independent of particle size is used to express shape of the particle.

$\Phi S = 6 \; Vp / Dp \; Sp$

Where Dp equivalent diameter of particle

Sp surface area of one particle

Vp volume of one particle

For a regular particle ΦS =1

For many crushed material ΦS =0.6 to 0.7

6.2.5. Particle Size and Size Distributions

A very important property of granular foods and powders is particle size and size distribution. One of the important factors to consider when discussing the mean diameter of a particle is the type of diameter being utilized. Mugele and Evans (1951) developed a generalized expression, which can be used to define all types of mean diameters.

Properties of Solid Foods

7.1. INTRODUCTION

Solid foods are generally characterized in terms of stress - strain relationship. The stress may be of tensile, compressive, tangential (shear) or torsional (acting on a transverse cross section). The classification of solid foods is even more hazy than that of fluid foods. There are two major groups : elastic and non elastic. visco - elastic foods, mostly of semi - solid and solid nature, form an important group of non - elastic foods.

7.2. ELASTIC SOLIDS

7.2. 1. Hookean or linear elasticity

Elasticity is defined as the tendency of the product to recover upon unloading the shape and dimensions it had before loading. If there is no permanent deformation after unloading, the elasticity is said to be complete elasticity.

Ideal or Hookean elasticity is characterized by a linear relationship between force (or stress) and deformation (or strain) starting at the origin (Fig. 7.1a) The body instantaneously returns to its initial form with no residual strain upon unloading.

Further, the Linear relationship is retraced when the sample is unloaded. The ratio of tensile stress to strain for these so-called Hookean bodies is termed Young's modulus (E) or elongation modulus. The ratio between shear stress to shear strain in an ideal linear elastic solid is called shear modulus (G) or rigidity.

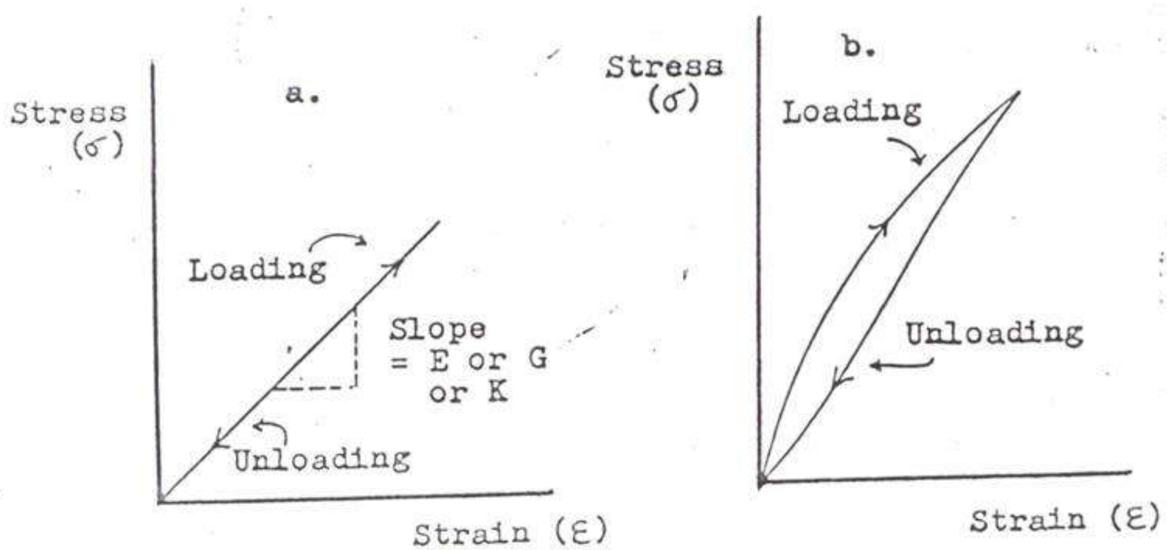

Fig-7.1: Linear (a) and Non-linear (b) elasticity: Stress-strain relationship

7.2.2. Non - Hookean or non - linear elasticity

In reality, most elastic solids exhibit a non-linear or non-Hookean elasticity, in which case the stress is not proportional to strain, and the linear dependence of stress on strain exists only at the lowest strain 'levels. In general, at higher strain levels the loading-and-unloading cycle yields two separate traces describing a hysteresis loop (Fig. 7.1b). Since the stress-strain relationship is curvilinear, the modulus of elasticity is frequently given as the tangent modulus, which is the slope of the stress-strain curve at any specified stress or strain.

7.3. NON-ELASTIC SOLIDS

A material may show elasticity, linear or non-linear, if the applied stresses and corresponding strains are small.

However, for large deformations most solids are non-elastic. Non-elastic products may exhibit failure when stress exceeds the strength of the body.

Failure may be seen as fracture or rupture.

(i) Fracture : Cracking of hard materials such as hard cheese at low temperature ultimately resulting in two or more separate pieces is termed fracture. Elastic fracture is fracture without or with a very limited amount of flow (only in the region just around the crack) of the material, as in unripe fruit flesh, tubers etc., whereas plastic fracture is fracture accompanied by flow of material as may be seen in certain soft or semi-hard cheeses.

(ii) Rupture : This term refers to tearing (in pieces) of soft materials. Rupture point is sometimes defined as a point on the stress-strain or force-deformation curve at which the axially loaded specimen ruptures. The failure in rupturing materials such as certain cheese gels, cooked egg white etc. is characterized by a multitude of failure planes.

7.4. PLASTIC SOLIDS

Certain non-elastic products may show yield value and tend to flow when the stress exceeds this point. Plasticity is found more frequently in semi-solid and soft products such as butter, spreads etc. rather than hard solids.

7.5. VISCOELASTIC FOODS

Failure resulting in rupture, fracture or plastic flow usually involves relatively large stresses and large deformation in solid foods. On the other hand, small deformation in most solids and semi-solid products may reveal what is known as viscoelasticity. Certain, shear-thinning fluids such as age thickened sweetened condensed milk also exhibits viscoelasticity.

The reaction of a viscoelastic body to stress (or strain) consists partly of a viscous component and partly an elastic one. Since stress and strain are time-dependent, the response of the material is rate dependent.

Attempts have been made to classify food products on the basis of their rheological behaviour. However, the rheological phenomena in various foods are so complex that it is not simple to categorize them into distinct groups or classes. Yet the classification of foods based on the stress-strain rate relationship for fluid and semi-solid products, and stress-strain relationship for solids would greatly facilitate comprehending the rheological behavior of various dairy and food products and relating it to their processing, handling and texture attributes.

Viscoelastic Models

8.1. INTRODUCTION

The fluids can be classified into following categories depending on the response to the applied shear force. Viscoelastic models are developed for Newtonian and non-newtonian fluids by different scientist considering different elements like dashpot and spring in series, in parallel and in combination. Widely used rheological models are

- ***Kelvin model,***
- ***Maxwell Model and***
- ***Burgers Models,*** which are described here.

Newtonian fluids are fluids which exhibit a linear increase in the shear stress with the rate of shear. These fluids exhibit a linear relationship between the shear stress and the rate of shear.
The equation for characterizing Newtonian fluid is
T = μ (-dv/dx) ----- (Eq-1)
Where, T = shear stress, μ = dynamic viscosity (η = μ/ρ) , -dv/dx = velocity gradient
A non-Newtonian fluid is broadly defined as one for which the relationship between shear stress and shear rate is not a constant. When the shear rate is varied, the shear stress doesn't vary in the same proportion. These fluids exibit either shear thinning or shear thickening behaviour and some exhibit a yield stress.
The two most commonly used equations for characterizing non-Newtonian fluids are the power law model (Eq-2)
and Herschel-Bulkley model (Eq-3) for fluids.
T = K (γ)n -------(Eq-2)
T = T 0 + K (γ)n -------(Eq-2)
Where, T =shear stress, K = consistency constant, γ = shear rate, n = flow behaviour index,
T0 = yield stress

8.2. RHEOLOGICAL MODELS

Several models have been developed to describe the viscoelastic behaviour of materials. There are two basic viscoelastic models viz Kelvin and Maxwell. Other complex viscoelastic behaviors are described by using combinations of these basic models (Fig-8.1 & Fig-8.2).

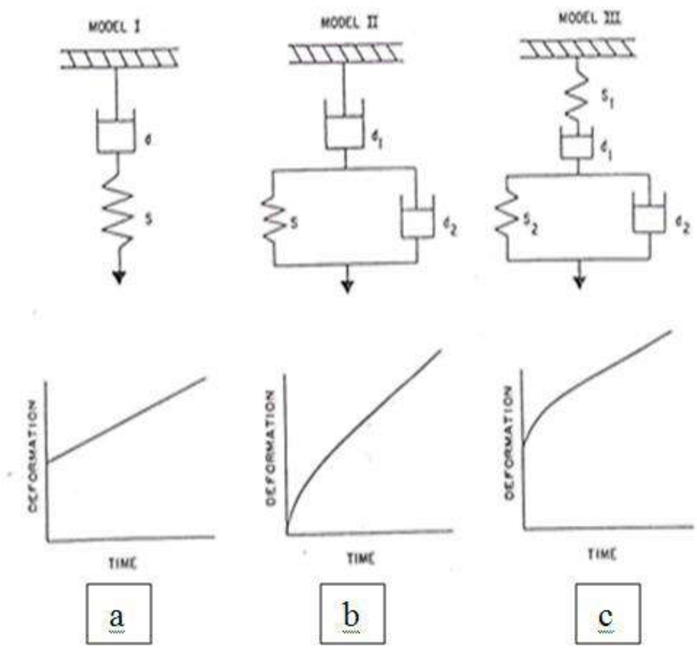

Fig-8.1: Typical creep curves for (a) Maxwell model (Model-I); (b) Kelvin Model (Model-II); (c) Burgers Model (Model-III)

(i) Kelvin model

The Kelvin model employs the spring (elastic component) and dashpot (viscous component) in parallel. In this stress is the sum of two components of which one is proportional to the strain and the other is proportional to the rate of shear. Since the elements are in parallel they are forced to move together at constant rate. When a constant load is applied to Kelvin model, initially a retarded deformation is obtained followed by a final steady state deformation. When the load is removed the Kelvin model recovers completely but not instantaneously. The model is expressed mathematically as:

$\varepsilon t = ς0 / E [1 - e (-t/ Tret)+$ …………..(Eq-5)

where εt is strain at time t, ς0 is applied stress, E is elastic modulus and Tret is retardation time.

(ii) Maxwell model

The Maxwell model employs a spring and dashpot in series. In this model the deformation is composed of two parts, one purely viscous and the other purely elastic, When a constant load is applied to Maxwell body, instantaneous elastic deformation will take place followed by continuing viscous flow, which will continue

indefinitely as it is not limited by the spring component. When load is removed, the Maxwell body recover instantly
but completely. The Maxwell body shows stress relaxation but Kelvin body does not. stress-strain-time relationship
in Maxwell model can be given as:
$\varepsilon t = \varsigma 0 / Ed [1 - e (-t/ Tret)+ + E0$…………..(Eq-6)
where, ςt is stress at time t, ςo is fixed strain, Ed is elastic decay modulus and Tred is relaxation time and E0 is equilibrium modulus.

(iii) Burgers model

This 4-element model is one of the best known rheological model which has been used to predict the creep behaviour in a number of materials. The model is composed of spring and dashpot in series with another spring and dashpot in parallel. When a burger's body is subjected to constant load, there is instantaneous deformation (E0) is followed by retarded flow. When the load is removed there is instantaneous recovery followed by incomplete and slow recovery. The stress-strain time relationship can be given as:
$\varepsilon t = \varsigma 0 / Eo + \varsigma 0 / Et(1 - e(-t/ Tret)) + \varsigma 0\ t / nv$…………..(Eq-7)
In terms of compliance function Jt which is reciprocal of Young's modulus (E) the above equation can be given as:
$Jt = J0 + Jt (1 - e(-t/ Tret)) + t / nv$ ………………………… (Eq-8)
Where, J0 is (l/E0) initial compliance, Jt is (l/Et) retarded compliance and t / nv is Newtonian compliance.

(iv) Generalized Maxwell model

A generalised Maxwell model is composed of n Maxwell elements with a spring in parallel with nth element. The elastic modulus E0 of last spring corresponds to the equilibrium modulus in the stress relaxation test. The stressstrain
time relationship is given by :
$\varepsilon t = \varsigma 0 (Ed1 + e(-t/T1) + Ed2\ e(-t/T2) +$ …………………..$+ Edn\ e(-t/Tn) + Eo)$…………..(Eq-9)
where, T1, T2……………………. Tn are relaxation times.

(v) Generalised Kelvin model

Experimental data on may viscoelastic materials including biological materials have shown more than one relaxation time or retardation time. For these materials, complete behaviour cannot be represented by a singly
Maxwell or single Kelvin model or elements model. Each or these models have only one time constant. To represent viscoelastic behaviour more realistically a chain of Kelvin models, each with its own time retardation is assumed and the model is called a generalized Kelvin model. It consists of Kelvin elements connected in series with an initial spring and final 'viscous element. The equation for generalised kelvin model is:
$\varepsilon t = \{ 1 / E0 + 1/Et1 (1 - e\ -t/T1) + 1 / Et2 (1-e\ -t/T2) +$ ------$+ 1 / E\ tn (1- e\ -t / Tn) + t / nv \}$
--------------- (Eq-10)
where, T1, T2……………….. Tn are relaxation times.

(vi) Plasto - visco - elastic or Bingham model

A more common type of body is the plasto-visco-elastic or Bingham body. When the stress is applied which is below the yield stress the Bingham body reacts as an elastic body. At stress values beyond the yield stress there are two components. One is constant and is represented by the friction element and the other is proportional to the shear rate and represents the viscous flow element. In a creep ,experiment with stress not exceeding yield value, the creep curve would be similar to the one for a elastic body. When the shear tress is greater than the yield stress, the strain increases with time similar to the behaviour of a Maxwell body. Upon removal of stress at time the strain decreases instaneously and remains constant thereafter. The decrease represents the elastic components and the plastic deformation is permanent.

8.5. VISCOELASTIC CHARACTERIZATION OF MATERIALS

There are a number of tests which may be used to study viscoelastic materials and determine the relation among stress-strain-time for a given type of deformation and a given type of loading pattern. The most important tests include stress relaxation, creep and dynamic tests.

(i) Creep measurement (Fig-8.1) In this test the stress is suddenly applied and held constant, and strain ('γ' or 'ε') is measured as a function of time. For a viscoelastic material the slope ($d\gamma/ dt = \gamma$) gives (from ς/ γ) an apparent Viscoelasticity. The deformation $\gamma 0$ is a measure of the elastic part. From the instantaneous shear modulus G0 may be calculated (ς/y0) or the instantaneous compliance J0o / ς). The whole curve gives Jt, which, in principle, can be calculated to yield Gt. The rheological model to represent the creep behaviour is the Kelvin model and 4 elements Burgers model. Creep measurement are very useful for studying stand up properties of foods. (γ

(ii) Stress relaxation (Fig-8.2)

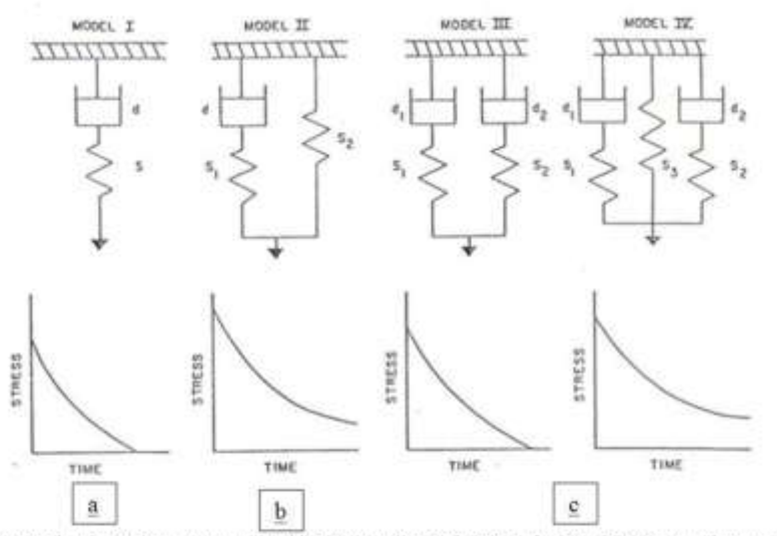

Fig. 8.2 Typical relaxation curves for (a) Maxwell Model (Model-I); (b) Three-element (Model-II); (c) Four-element Model (Model-III); Five-element (Model-IV)

In stress relaxation test the specimen is suddenly brought to a given deformation (strain), and the stress required to hold the deformation constant is measured as a function of time. The results are expressed in terms of time dependent modulus Et in tension or compression, Gt in shear or Kt in bulk compression. The rheological models representing stress relaxation are Maxwell model and generalised Maxwell model. One of the most important viscoelastic parameters which can be obtained from stress relaxation test is the relaxation time. It is the time at which the stress in the body resembling a Maxwell model decay to 1/e of initial stress. It is the measure of the rate at which a material dissipates stress after receiving a sudden force. There are a number of methods for treating experimental data on stress relaxation and finding the relaxation time.