

**CHAPTER ONE:  
INTRODUCTION**

## 1.1 REVIEW OF RESEARCH

Metal oxides such as titanium and zinc oxides are widely used in facial creams products for uv protection. Prior to making facial creams these are blended with emulsions so as to give thermodynamically stable creams with reasonably long storage stability.

In view of making creams with minimal structural defects and longer storage stability, it is important that preparation conditions be optimized. To make a product with acceptable texture and storage stability it is important that the ingredients used are formulated in proper ratios. This does not only involves optimization of oil to water mixing ratio but also involves optimization of surfactant-titanium oxide concentration ratio and water to surfactant concentration ratio.

While cream texture and its flow properties are of paramount importance in giving marketable products, their storage stability and biocompatibility are equally important. Therefore, emulsions are an example of dispersion of liquids in liquids such as oil in water with the help of surface active agent (surfactants) to prevent phase separation (thermodynamically unstable). This work focuses on the dispensability of  $TiO_2$  in microemulsion by using glycolipid as a surfactant and formulate it as a good stabilized colloidal emulsion .

The properties of these emulsion's systems are assessed through findings by researchers. It is suspected that the rheological properties of the products have a strong influence, since flow properties determine consistency and spread ability. Therefore the purpose of this study is to demonstrate whether there is any correlation between the skin feeling and rheological properties of cosmetic products.

## **1.2 OBJECTIVES OF RESEARCH**

The aims of this work are:

- 1) To study the dispensability of TiO<sub>2</sub> in microemulsion by using glycolipid as a surfactant.
- 2) To explore the rheological properties of glycolipid stabilized oil-water emulsions
- 3) To formulate a good stabilized colloidal emulsion of glucose based glycolipids.

## **1.3 ORGANIZATION OF RESEARCH**

This work explores the stability properties of some glycolipids based surfactants and accordingly its chapter 1 contains a brief discussion on conventional used surfactants in cosmetic industries and compares their properties with glycolipids. This chapter also deals with experimental techniques used in the determination of rheological parameters.

Chapter 2 describes experimental aspect of instruments and methodology utilized for this research. Chapter 3 compares the settle volume of dispersants and studies the rheological behaviors stabilized emulsion of Carrageenan, Brij 35P, Tween 20, SDS and glycolipids Chapter 4 will conclude the results obtained in this research work by summarizing all the important results in the preceding chapters.

## 1.4 THEORETICAL BACKGROUND

Emulsions are dispersing multi-phase systems of two or more insoluble liquids. It consists of at least one continuous (outer) phase (e.g water) and one isolated (dispersed or inner) phase (e.g oil.) phase. Two types of emulsions are readily distinguished depending on which kind of a liquid forms the continuous phase (Schramm, 1992):

- (a) Oil in water (o/w) for oil droplets dispersed in water.
- (b) Water in oil (w/o) for water droplets dispersed in oil.

In addition, double emulsions such as water-in-oil-water (w/o/w), in which water-in-oil emulsion droplets dispersed in continuous water phase, are also frequently found. It was used in so many ways such as cosmetic, personal care and pharmaceutical industries. Emulsion is a heterogeneous system, consisting of at least one immiscible liquid, intimately dispersed in another in the form of droplets, whose diameter, in general, exceeds  $0.1\mu\text{m}$  (Becher, 1966). Emulsion droplets are much larger, typically one micron or more, resulting in cloudy or milky dispersions. The dispersed phase in emulsion will eventually agglomerate and undergo phase separation. These phenomena are prevented by the existence of a surfactant with good emulsification properties.

In spite of the fact that Rosen (1978), surfactants are substances that possess an ability to modify the surface behavior of other substances in solution, this work is designed to formulate stabilized emulsion. Surfactants tested were Brij 35P, Tween 20, SDS and glycolipids such as  $\lambda$ -Carrageenan and DDM to stabilize paraffin oil as a stable emulsion. With growing environmental and health concerns, interest in glycolipids stems from the fact that these surfactants are biodegradable, biocompatible and non-toxic. As been noted, to

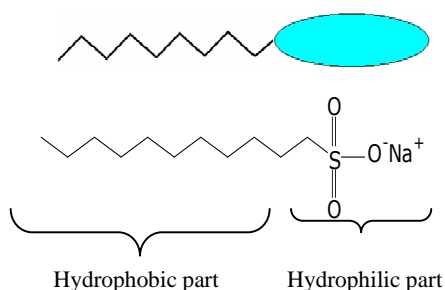
achieve stability in storage and acceptable texture with excellent criteria such as color, odor appearance, absorption and skin feeling when applying it to the skin, it will be measured by rheological parameters.

Furthermore, the study of rheology is the study of the deformation of matter resulting from the application of a force. Knowledge of the subject is essential for scientists employed in many industries, including cosmeceutical, pharmaceutical, plastic, paint, printing ink, oil (lubricants), etc (Arnold, 1964). Due to some reasons, the primary output expected from this work is to form a new formulation (emulsion) with foundation ingredient of Glycolipids with suitable rheological properties. In fact, the utility of many of the materials we make use of every day is due to their rheological behaviors and many chemists are formulating materials to have a particular range of textures, flow properties, or are endeavoring to control transport properties in a manufacturing plant based on rheology study. The aim of this study is to enable us to gain an understanding of the physical origins of viscosity, elasticity and viscous elasticity

#### **1.4.1 Classification of Surfactants**

Surfactants generally, can be classified into 4 groups (**Figure 1.1**):

- 1) Anionic - anionic surfactants ionize in solution, with long chain carrying a negative charge
- 2) Cationic - cationic surfactants ionize in solution, with the long chain bearing a positive charge
- 3) Zwitterionic - zwitterionic or amphoteric surfactants ionize in solution, with the long-chain ion carrying either a positive or negative charge
- 4) Nonionic - nonionic surfactants do not ionize in solution.



**Figure 1.1:** Schematic diagram of surface active molecule (surfactant)

	Class	Headgroups	Main applications
1.	Anionic	$-\text{CO}_2^- \text{Na}^+$	Soaps
		$-\text{SO}_3^- \text{Na}^+$	Synthetic detergents
		$-\text{O}-\text{SO}_3^- \text{Na}^+$	Personal care products, detergents
		$-\text{O}-\text{PO}_3^- \text{Na}^+$	Corrosion inhibitors, emulsifiers
		$-(\text{OCH}_2\text{CH}_2)_n-\text{O}-\text{SO}_3^- \text{Na}^+$	Liquid detergents, toiletries, emulsifiers
2.	Cationic	$-\text{N}(\text{CH}_3)_3^+ \text{Cl}^-$	Bitumen emulsions
			Bactericides, antistatic agents
		$>\text{N}(\text{CH}_3)_2^+ \text{Cl}^-$	Fabric and hair conditioners
3.	Zwitterionic	$-\text{N}(\text{CH}_3)_2-\text{CH}_2-\text{CO}_2^-$	Shampoos
		$-\text{N}(\text{CH}_3)_2-\text{CH}_2-\text{SO}_3^-$	Cosmetics
4.	Non-ionic	$-(\text{OCH}_2\text{CH}_2)_n\text{OH}$	Detergents, emulsifiers
5.	Semi-polar	$-(\text{CH}_3)_2\text{N} \rightarrow \text{O}$	Foam enhancers

**Table 1.1:** Some classes of surfactant and their applications

### **1.4.2 BIOSURFACTANTS**

Biosurfactants of microbial origin have become important products of biotechnology for potential industrial application. As high value microbial products, they are specific in action, nontoxic and easily produced. Preliminary toxicity tests carried out on non-purified biosurfactants were found to be non-toxic at concentration of less than 0.3% (w/v). They are produced generally by certain microorganisms grown on hydrocarbons, although it is also possible to produce them for other substrates such as carbohydrates. These microbial cultures are able to produce high yields of surface active substances that emulsify or wet the hydrocarbon phase thus making it available for cellular absorption. Microbial surfactants offer two important advantages relative to synthetic ones. Firstly, the structural diversity of biosurfactants offer a wide range of surface active compounds which may be better suited for specific applications. Secondly, as environmental considerations are becoming increasingly important for the selection of industrial chemicals, biosurfactants which are biodegradable appear promising for application in bioremediation and the dispersion of oil spills.

### **1.4.3 Classification of Biosurfactants**

Microbial surfactants include a variety of chemical compounds and are predominantly lipids. Most biosurfactants consist of distinct hydrophilic and lipophilic moieties. Based on the characteristics of the hydrophilic moiety, biosurfactants are grouped as follow:

- 1) Glycolipids

- 2) Lipopeptides
- 3) Lipopolysaccharides
- 4) Phospholipid

#### **1.4.4 Glycolipid**

Glycolipid based surfactants are classified under the nonionic surfactant group since the surface-active portion in them do not bear any charge (Chelebick, 1998). The basic structure of Glycolipids consists of a carbohydrate molecule source like glucose, sucrose, and mannose esterifies with long chain aliphatic acids such as palmitic acid or long chain alcohols.

In this work we showed a strong interest in glycolipid group surfactants due to their special properties. These include its non-toxic nature, low hydrophile-lipophile balance (HLB) value and biocompatibility. Low HLB value means it possesses excellent emulsifying properties that can help produce stable emulsions and creams (Vasudevan, 2002) such as DDM and meanwhile,  $\lambda$ -Carrageenan are non digestible polysaccharides, extensively used in cosmetic formulations where they function as thickeners, emulsifiers, stabilizers, etc. (Dickinson et al., 1999).

#### **1.4.5 Thickening Agent**

Thickening agent refers to an ingredient or agent that can be added to other emulsion ingredients in order to modify the viscosity to create a stiffer or a more dense cream mixture. In addition, some thickeners assist to disperse solids within a mixture, thus

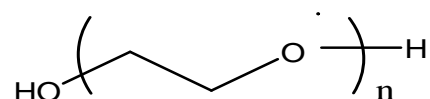


increasing the viscosity and making the substance less fluid. In personal care or pharmaceutical industries, thickening agents such as Carrageenan and Polyethylene Glycol are used as thickeners, stabilizers or binders.

#### 1.4.6 Polyethylene Glycol (PEG)

Polyethylene glycol (PEG) is a condensation polymer of ethylene oxide and water with the general formula  $H(OCH_2CH_2)_nOH$ , where  $n$  is the average number of repeating oxyethylene groups typically from 4 to about 180. PEG is water soluble and soluble in many organic solvents. They were used to make emulsifying agents and detergents, and as plasticizer, humectants, and water-soluble textile lubricants (**Figure 1.3**).

Polyethylene glycol is non-toxic, odorless, neutral, lubricating, non-volatile and non-irritating and is used in a variety of pharmaceuticals and in medications as a solvent, dispensing agent, ointment and suppository bases.

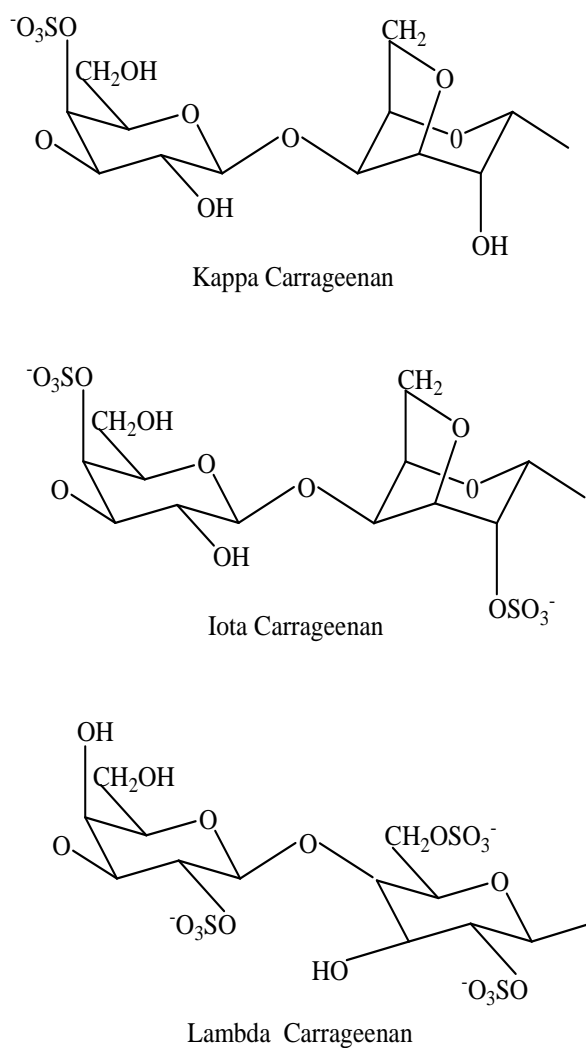


**Figure 1.3:** Molecular structure of Polyethylene glycol.

#### 1.4.7 Carrageenan

The different types of carrageenan differ only in the position and number of ester sulfate groups, which determine the physical properties (viscosity and gelation characteristics) of

the carrageenan (**Figure 1.4**). The visco-elasticity of the sol and gel phases can be varied to suit almost any application. There are three types of carrageenan, kappa, iota and lambda.



**Figure 1.4:** Molecular structure of Kappa, Iota and Lambda Carrageenans.

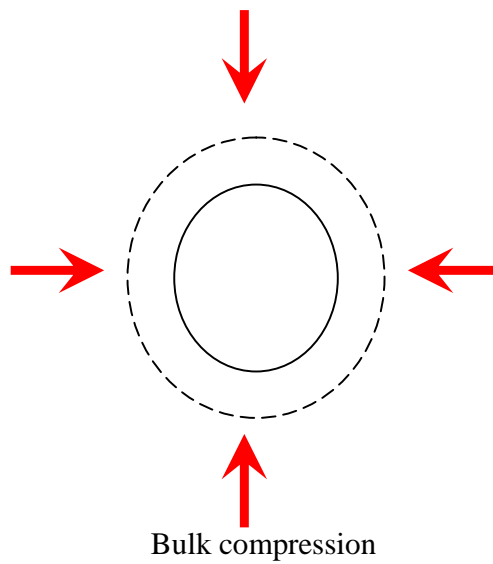
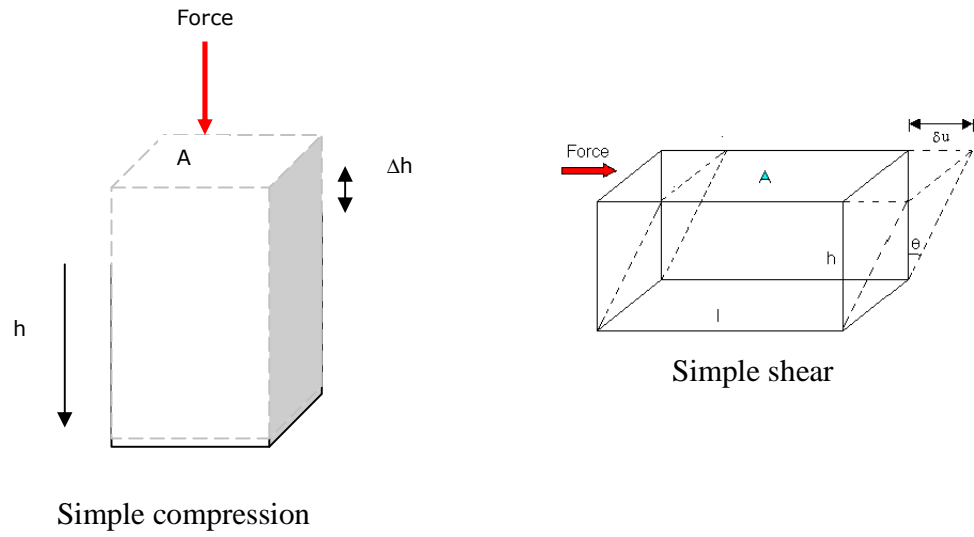
## 1.5 RHEOLOGICAL BEHAVIOR OF EMULSION

As mentioned previously, the rheological behavior of emulsions has been of great interest not only for fundamental scientific understanding but also for practical industrial applications (Barnes, 1994; Tadros, 1994). However, emulsions exhibit contrasting rheological behavior to that of suspensions of hard spheres, due to the droplet deformation, the surface mobility and the internal fluid circulation. At low volume fractions, the internal fluid circulation in droplets plays an important role in determining emulsion viscosity. For example, Taylor (1932) derived an equation to predict the relative viscosity of emulsions using hydrodynamic theory. Unfortunately, applicability of the Taylor's equation is limited, because the internal fluid circulation in droplets can be easily interfered by surfactants that are normally used to stabilize emulsions (Nawab et al., 1958).

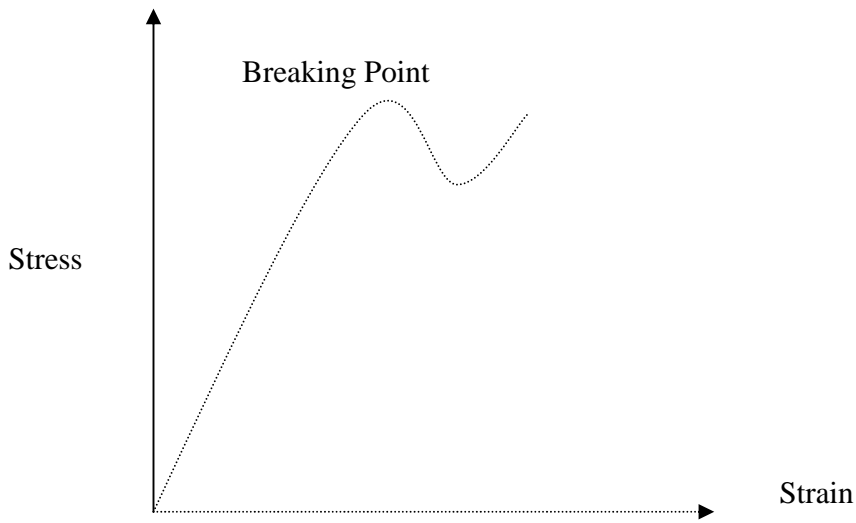
Consideration as proposed by Professor Bingham of Lafayette College, rheology is the study of the deformation of matter resulting from the application of a force. Many of the giants of classical physics have contributed to rheology, commemorated by *Hookean* solid, *Newtonian* liquids, the *Navier-Stokes* equation and *Einstein's* equation. Since the rheological response of bulk matter to applied mechanical forces is rooted in the interactions of its constituent molecules, the science of rheology makes a useful tool in this study. The same consideration, of course, applies to the rheological behaviour of colloidal dispersion especially in cosmetic (emulsion). Commonly, these rheological or flow studies were contributed by two major measurements with steady state rotational shear (Viscometry) and small amplitude oscillation (Oscillatory). (Barnes et al., 1993; Walter, 1975).

## **1.6 RHEOLOGY PROPERTIES**

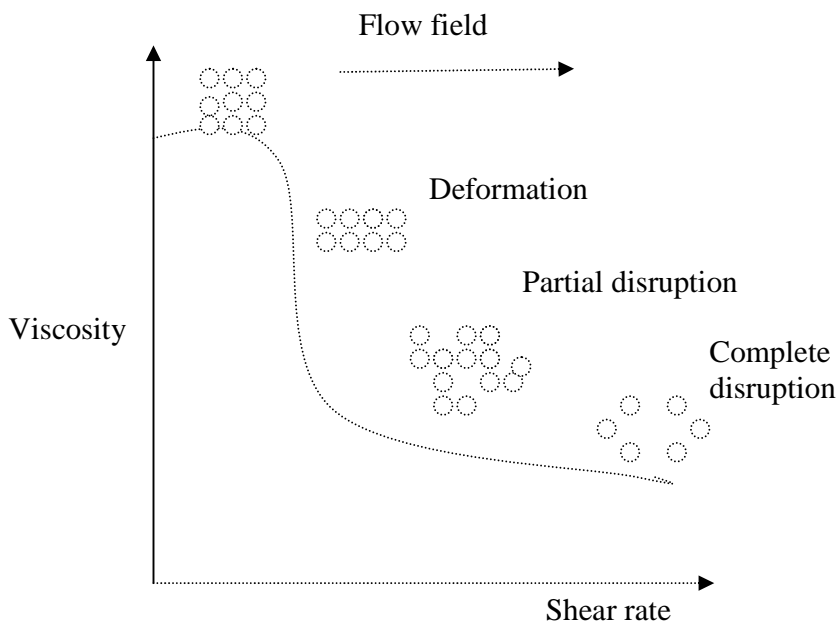
The rheological properties of a liquid are dominant features that can be quantified to characterize its behavior, and the response of a liquid to a forced shearing flow is the basis for determining the specific rheological properties of a given liquid. General qualitative terms used to describe these properties are viscoelastic, Newtonian, non-Newtonian, thixotropic and dilatant. Quantitative parameters used are viscosity, elasticity, shear rate, shear strain, and shear stress. The broadest view of liquid rheology is obtained by using oscillatory flow at a selected frequency because both viscous and elastic properties are revealed. Steady flow reveals only viscous properties. Values of shear stress, shear rate, and shear strain are primary parameters for quantitative specification of both the flow condition and the liquid response. It is from these quantities that the components of the viscoelastic modulus, the viscosity and the elasticity (or alternatively the loss and storage moduli) are obtained. These numbers form the basis for quantitative specification of the liquid's properties for quality control or other applications.



**Figure 1.5:** An elastic solid can be deformed in a number of different way



**Figure 1.6:** At small deformation, there is a linear relationship between the applied stress and the resultant strain for an ideal elastic solid. At higher deformations, the stress is no longer linearly related to strain and the material will eventually break.



**Figure 1.7:** An emulsion that contains flocculated droplets exhibits shear thinning behavior because the flocs are deformed and disrupted in the shear field.

## 1.7 RHEOLOGICAL PROPERTIES OF MATERIAL

### 1.7.1 Solids

In our everyday lives, we come across to use daily needed which exhibit quite different rheological characteristics. Some may be soft, others hard; some may be brittle, and others rubbery; some may break easily, others may not. Despite this range of different behaviors, it is possible to characterize the rheological properties of many solid emulsions in terms of a few simple concepts.

### 1.7.2 Ideal Elastic Solids

An ideal elastic solid is often referred to as a *Hookean* solid, after Robert Hooke, the scientist who first described this type of behavior (Whorlow 1992, Macosko 1994, Rao et al., 1995). Hooke observed experimentally that there is a linear relationship between the deformation of a solid material and magnitude of the force applied to it, provided the deformation is not too large (**Figure 1.5**). He also observed that when the force was removed from the material, it returned back to its original length. Hooke found that the force per unit area (or stress) was proportional to the relative deformation (or strain). Hooke's law can therefore be summarized by the following statement:

$$\text{Stress} = G \times \text{strain} \quad (1.1)$$

where  $G$  is defined as shear modulus or more reliable as rigidity modulus.

A stress can be applied to a material in a number of different ways, including simple shear, simple compression, and bulk compression (**Figure 1.6**). Equation 1.1 is applicable to each of these situations, but the values of the stress, strain, and shear modulus used depend on the nature of deformation (**Figure 1.7**).

The elastic behavior of a solid is related to the intermolecular forces which hold the molecules together. When stress is applied to a material, the bonds between the molecules are compressed or expanded, and therefore they store energy. When the stress is removed, the bond gives up this energy and the material returns to its original shape. The elastic modulus of an ideal elastic solid is therefore related to the strength of the interactions between molecules within it. This Hookean behavior is analogous to a mechanical spring that stretches when a weight is suspended from it.

Consider the case of the tube of material as described before but assuming that the material behaves as an ideal fluid. When a constant shear stress is applied, the material will be deformed as before but in this case the deformation will continually increase at a constant rate. The rate of change of strain is referred to as shear strain rate often abbreviated to shear rate and is found by the rate of strain as a function of time or  $\frac{\text{Strain}}{\text{time}}$  (Goodwin et al., 1993).

$$\gamma = \frac{\delta u \times l}{h \times S} \quad (1.2)$$



The shear rate obtained from an applied shear stress will be dependent upon the material's resistance to flow, which is viscosity. Since the flow resistance is equal to force through the displacement and its follow that (Goodwin et al., 1993):

$$\text{Viscosity } (\eta) = \frac{\text{Shear stress, } \sigma}{\text{Shear rate, } \dot{\gamma}} \quad (1.3)$$

The units of viscosity are  $\text{Nm}^{-2}\text{s}$  and are known as Pascal second (Pas). If a material has a viscosity that is independent of shear stress, then it is referred to as an ideal or Newtonian fluid. The mechanical analogue of a Newtonian fluid is a viscous dashpot that moves at a constant rate when a load is applied.

### 1.7.3 Ideal liquids

The ideal liquid is often referred to as Newtonian liquid, after Isaac Newton, the scientist who first described this behavior (Whorlow 1992, Macosko 1994, Rao 1995) Newton behaviors in experiments conducted at constant temperature and pressure have the following characteristics (Barnes et al., 1993; Harris, 1977):

- (1) The only stress generated in simple shear flow is the shear stress  $\delta$ , which means the two normal stress differences being zero. Normal stresses are the different type of stress components which applied perpendicularly to the cube material while shear stress component applied tangentially to the cube material.
- (2) The shear viscosity does not vary with shear rate.
- (3) The viscosity is constant with respect to the time of shearing and the stress in the liquid falls to zero immediately the shearing is stopped. In any

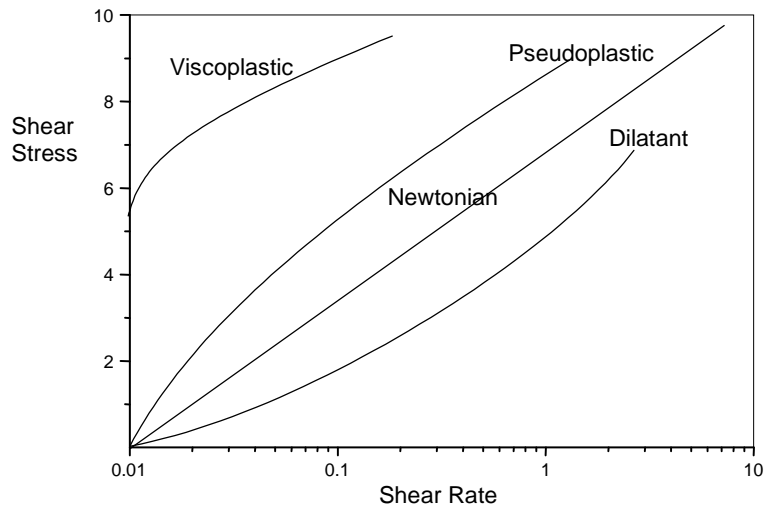
subsequent shearing, however long the period of resting between measurements, the viscosity is as previously measured.

- (4) The viscosities in different types of deformation are always in simple proportion to one another, the viscosity in a uniaxial extensional flow is always three times the value measured in simple flow. (Any liquid showing divergence from the above behaviors is considered as a non-Newtonian fluid.)

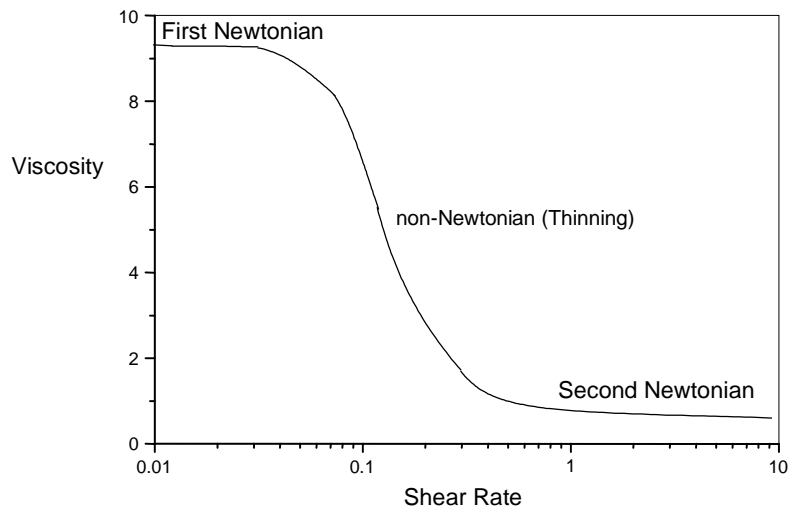
#### **1.7.4 Rheological Classification of Non-Newtonian Behaviors (Time Independent and Time Dependent Fluid)**

Majority of cases in nature where time is not a considerable role of parameter, the viscosity of fluids was found to decrease with increase in shear rate, giving rise to what generally called ‘shear thinning’ behaviors although the term temporary viscosity loss and ‘pseudoplasticity’ have also been employed (Arnold, 1964). Nevertheless, there are cases (albeit few in number) where the viscosity increases with shear rate. Such behavior is generally called ‘shear thickening’ although the term ‘dilatancy’ has also been used. All the general type of behaviors for non-Newtonian fluids are illustrated in **Figure 1.8**. In a typical viscosity-shear rate curve (**Figure 1.9**), in the limit of very low shear rate (or stresses) the viscosity is constant, whilst in the limit of high shear rate (or stresses) the viscosity is again constant, but at lower level. These two extremes are known as lower and upper Newtonian regions, respectively, the *lower* and *upper* referring to the shear rate and not the viscosity. The higher constant value is called ‘zero-shear viscosity,  $\eta_o$ ’, noting that

the liquid does not show a ‘yield value’ or ‘yield stress,  $\delta_y$ ’ and does not obey Bingham plastic behaviors. Yield stress is a critical and minimum value of shear stress to effect deformation (Ronald, 1976).



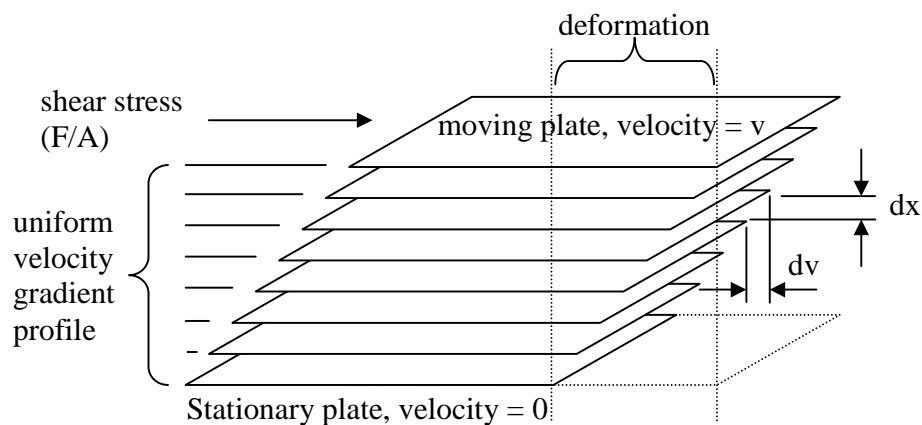
**Figure 1.8:** Flow curve of Newtonian and non-Newtonian behaviors



**Figure 1.9:** Typical behaviors of non-Newtonian fluid system with thinning properties.

### 1.7.5 Viscosity

Fluid-like behavior is associated with flow, that is, matter being deformed continually with time. Fundamental rheological variables can be defined by reference to an imaginary purely fluid sample confined between two parallel plates (**Figure 1.10**).



**Figure 1.10:** Laminar flow of a Newtonian liquid in simple shear.

The plates are separated by a distance  $dx$  that is small compared to the linear dimensions of the plates. The bottom plate is held stationary, while parallel to the top plate a certain force per unit area (or shear stress,  $\delta_y$ ) is applied so that it moves. The fluid in contact with the upper plate moves at an equal speed, with velocity  $v$ . The fluid in contact with the bottom plate remains stationary. Hence there is a difference in the fluid's velocity throughout the bulk: the sample experiences a velocity gradient  $\frac{dv}{dx}$ , which is the shear rate,  $\dot{\gamma}$ . If the force ceases to be applied, the upper plate comes to a rest. Isaac Newton

discovered that ‘the resistance which arises from the lack of slipperiness originating in a fluid – other things being equal – is proportional to the velocity by which the parts of the fluid are being separated from each other. The proportionality constant is the shear viscosity of the liquid,  $\eta$ :

$$\sigma = \eta \dot{\gamma} \quad (1.4)$$

where  $\dot{\gamma} = \frac{dv}{dx}$  and  $\sigma = \text{shear stress}$  (1.5)

Thus, the shear viscosity  $\eta$  is the tendency of the fluid to resist flow and is defined by:

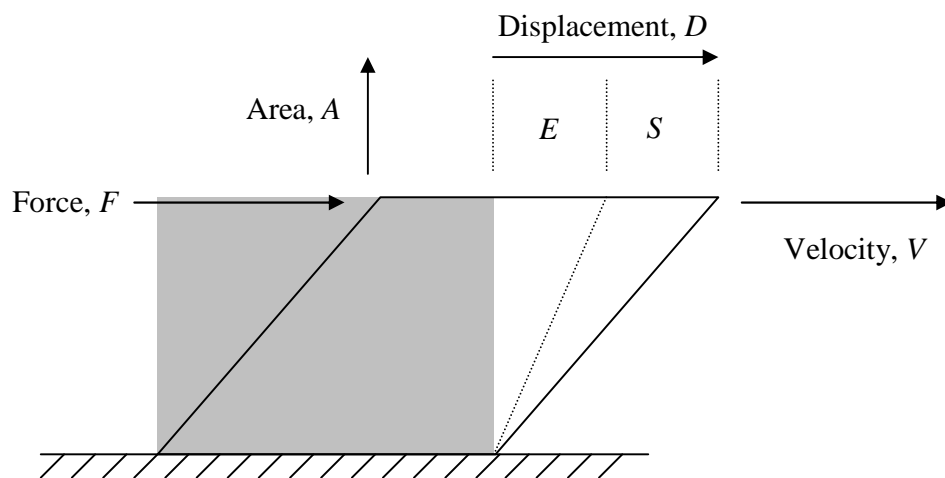
$$\eta = \frac{\text{shear stress}}{\text{shear rate}} \left( Pa s \right) \quad (1.6)$$

If the viscosity of the fluid is independent of shear rate, then the sample is Newtonian. However, many fluids are non-Newtonian, their viscosities decreasing with increasing shear rate. Such shear-thinning behavior is commonly observed for dispersions, where the suspended particles endow the sample with a certain structure. The structure is gradually destroyed with increasing shear forces; hence the sample viscosity is lowered.

### 1.7.6 Viscoelasticity

Many hydrocolloids are capable of forming gels of various strength dependent on their structure and concentration plus environmental factors such as ionic strength, pH and temperature. The combined viscosity and gel behavior (viscoelasticity) can be examined by determining the effect an oscillating force has on the movement of the material.

With viscoelastic hydrocolloids, some of the deformation caused by shear stress is elastic ( $E$ ) and will return to zero when the force is removed. The remaining deformation or slippage ( $S$ ) will not return to zero when the force is removed (**Figure 1.11**).



**Figure 1.11:** Laminar flow of a Newtonian liquid in viscoelastic shear.

The elastic deformation is accompanied by storage of elastic energy within the structure of the material, while the slippage is associated with continuous input of viscous energy. When the force is removed, the deformed material undergoes a partial recovery of shape as the elastic energy is recovered, while the shape change due to slippage is

permanent. Under a constant force the elastic displacement remains constant whereas the sliding displacement continues, and so is increasing.

If the force varies sinusoidally with time, then the viscous (sliding) energy is always positive and lost as heat whereas the changes in the elastic energy may be positive or negative and is recouped.

Generally, fluids with suspended particles have a certain structure, which is sensitive to shear. Hence, steady-shear viscosimetry is not ideally suited if one wants to probe the rheological characteristics of an unperturbed dispersion. However, in oscillatory rheometry, the specimen is subjected to a very small oscillatory stress, such that its structure remains intact. An additional advantage of the method is that both the viscous and the elastic response characteristics of the sample can be obtained, expressed as the viscous modulus ( $G''$ ) and elastic modulus ( $G'$ ) respectively.

Most emulsions used in pharmaceutical and cosmeceutical products show a combination of shear thinning property and pseudo-plastic behavior characterized by yield stress ( $\sigma_y$ ). Emulsions showing higher degree of shear thinning at low shear rate domain spread easily, whereas emulsions showing higher values of  $\sigma_y$  offer a larger degree of resistance to an external force before they start flowing. These imply that the higher the  $\sigma_y$  the greater the degree of emulsion structuring and the greater the degree of its stability.

Overall, all creams, semisolids and emulsions used in pharmaceutical and cosmetic products exhibit viscoelastic properties usually described by a combination of degree shear thinning, value of yield stress and frequency dependence profiles of dynamic moduli.

For example, in oscillatory shear mode, domination of elastic modulus ( $G'$ ) over viscous modulus ( $G''$ ) at a high frequency ( $\omega$ ) domain indicates good emulsion stability, whereas domination of  $G''$  over  $G'$  at a low frequency domain indicates that emulsions are easily spread over skin. As far as viscoelastic model is concerned, fluids showing Maxwell model type flow behavior usually display a semicircular shape of the Cole-Cole plot, whilst their  $G'$  responses scale with  $\omega^2$  and  $G''$  responses scale with  $\omega$ . Ideal viscoelastic material usually shows a phase angle ( $\delta$ ) of around  $45^\circ$  at a wide range of frequency. The

$\delta$  is described as a ratio of loss modulus to storage modulus and it is given by  $\tan^{-1}\left[\frac{G''}{G'}\right]$ ,

where  $\delta$  can range from  $0^\circ$  for ideal elastic material to  $90^\circ$  for ideal viscous material. Material showing a  $\delta$  of  $< 45^\circ$  are usually more elastic in nature, whilst those showing  $\delta$  of  $> 45^\circ$  are more viscous in nature. Profiles of  $\delta - \omega$  thus indirectly tell us about the degree of viscoelasticity of the emulsion. Higher value of  $\delta$  indicates that emulsions are more liquid like in nature, whereas lower values of  $\delta$  indicate that emulsions are more solid like in nature.