CHAPTER 4

RHEOLOGICAL STUDY OF MOISTURISER

4.1 Introduction

Cosmetic products must have certain flow properties to be accepted and liked by consumer. They should be stable during their shelf life and must be easy to dispense. Cosmetic scientists are interested in the rheology of the cosmetic product since it also affects mixing, packaging and its ultimate use characteristics (Ward *et. al.*, 1974). The performance of the cosmetic products before, during and after its application is of major importance so that cosmetic scientist could make an early predictions as to whether the product is stable, good and acceptable for consumer use. Herh *et. al.* (1998) has reported that rheological measurements are performed in order to understand the fundamental nature of a system, for quality control of raw materials, final products and manufacturing processes and to study the effect of different parameters such as formulation, storage time and temperature on the quality and acceptance of a final product.

Ward *et. al.* (1974) has indicated the word "rheology" was first recognised in the work of Bingham and Crawford in 1929. Rheology describes the study of how materials deform and flow under the influence of external forces (Nae, 1993) or stresses (Schram, 2000). As stated by Scram (2000), ideal solids deform elastically where the energy required for the deformation is fully recovered when the stresses are removed. On the other hand, ideal fluids such as liquids and gases deform irreversibly, they flow. The energy required for the deformation is dissipated within the fluid in the form of heat and cannot be recovered simply by removing the stresses. Real materials are neither ideal solids nor ideal fluids, hence they can deform irreversibly under the influence of forces of sufficient magnitude.

A viscosity curve (viscosity versus shear rate) across a wide range of shear rates can provide important information about storage stability, optimal conditions for mixing, pumping, transferring and for end-user applications. Besides this, it can also provides information regarding the ways in which the structure changes to comply with the applied shear in different conditions such as upon storage, during processing and product's application (Herh *et. al.*, 1998). If the shear rate changes during application, the internal structure of the sample will change and the change in stress or product's viscosity can be seen from this curve.

4.1.1 Newtonian and non-Newtonian Flow

The materials deformation and flow can be classified into two types that are Newtonian and non-Newtonian, Figure 4.1. Newtonian is an orderly flow pattern in which the shear rate is directly proportional to shear stress. Under Newtonian behaviour, the viscosity of the substances will not change under shear rate and shear stress. Example of Newtonian flow is water, glycerol, silicone fluid and some low molecular weight mineral oils. non-Newtonian fluid is a flow which shear rate is not proportional to shear stress of the respective fluid. The fluids can be either shear-thinning or shear-thickening. This group of fluids are called shear dependent and can be classified as follows:

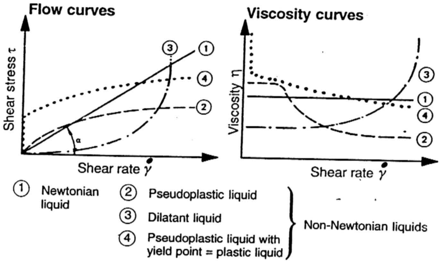


Figure 4.1: Various types of liquids common flow behaviour

(a) Plastic

For this type of flow, a certain force or shear stress (yield value) must be exceeded before the flow starts.

(b) Pseudoplastic

This is a characteristic for most natural and synthetic gums where the viscosity will decrease under shear rate and shear stress.

(c) Thixotropic

Thixotropy describes a behaviour of substances to change from high viscosity (gel state) to a much lower viscosity (***sol state***) as the result of exerted high shear. The viscosity of substances with this property decrease when sheared due to structure break-down in the substance. This is due to the orientation of the structure's molecules or particles that will change to align with the flow direction. However, the substances will regain their viscosities and original orientations after shearing has stopped. An important criteria of thixotropy is the reversible process of re-thickening of the substance when left at rest, thus is time-dependent. As reported by Ward *et. al.* (1974), this phenomenon is observed to preferentially occur in a system with elongated flat or long particles. Initially the system behaves as Newtonian liquid but in course of time, it thickens. Here the particles adhere to each other but the adhesion is so weak that it could be completely destroyed by shaking. However, the particles will reconstitute, forming their original state on standing, retaining entangled intermicellular.

(d) Dilatant

It is a characteristic of products containing high levels of deflocculated solids such as slurries and mud. The product's viscosity increase as the shear rate is increased. This is the reverse of thixotropy. With increasing shear rate, the inter-particles friction increases, resulting in an overall increased resistance to flow. Example of this shear-thickening behaviour is quicksand.

(e) Rheopectic

The viscosity of the substances under this behaviour will increase under shear (structure build-up). The substances will eventually regain their viscosity after the shearing has stopped.

Many cosmetic emulsions products exhibit shear-thinning properties. The reason for this behaviour is generally attributed to the realignment of the internal structure caused by shearing action, making the fluid less resistant to flow. The types of flow that is normally encountered for cosmetic products are pseudoplastic and thixotrophic.

4.1.2 Viscosity

Viscosity is a measure of fluid's resistance to flow. A force is needed to create flow of a fluid and depending on its internal friction (viscosity), the fluid may move rapidly, slowly or remain unmoved. In rheology, the term shear rate is used to describe the measure of this movement. Shear rate is also referred to as "velocity gradient" because it measures the fluid's velocity changes with respect to distance. Issac Newton defined viscosity as the ratio of shear stress to shear rate (Lin, 2000). In this study, the viscosity measurement is conducted to gain information on the overall thickness of the products' formulated.

4.1.3 Hysteresis

The area between the ascending and descending shear stress flow curves is called hysteresis area. This area is proportional to the energy required to break down the thixotropic or intermicellular structure in the product (Schramm, 2000, Lin, 2000, Nae, 1993). This means the more stable the product, the higher the hysteresis area will be acquired.

4.1.4 Yield Stress Phenomenon

Yield stress or yield point is a measure of the amount of force required to make a resting fluid begin to flow. Thus, it describes a limit stress exists below which a sample behaves as a solid. Above the yield stress, the sample starts to flow. The yield stress value of a product will show the stand-up properties of the respective product because it give the information on the strength of the product's structure at rest conditions, thus may be used as one of the criteria to indicate the product's stability. Yield stress measurement is crucial for cosmetic products in determining not only their shelf life but also the ease of application for the end user. Lin (2000) has reported that most shear-thinning fluids have some degree of yield stress value. He also stated that many cosmetic creams have high yield values and these yield values increases with the product's viscosity, thus yield value can be correlated to the stability of a product.

Increase temperature and addition of surfactants can often remarkably reduce the product's viscosity, therefore will also reduce yield value of the product.

The cause of shear-dependent property is often a changing of internal structure of the fluid subjected to shear stress and consequently, it may cause the fluid to take time to restore its original structure (Lin, 2000). This means the viscosity of the material before shear stress is applied may be different from that of the same material taken after shear stress is removed. Prencipe *et. al.* (1995) who has reported that the higher the yield stress value, the product will exhibit more structure due to more molecular interactions and networking formed in the product. According to Holland (1991), creams require a yield stress so that they do not flow at low shear conditions. As a result, they would remain where they are applied and not flow off. However, the viscosity of the cream should reduce immensely upon the application of shear so that they are not difficult to rub and spread. Ward *et. al.* (1974) has also discussed the work carried out by Martin *et. al.* in 1960 which pointed out that the product should have high viscosity at negligible shear rate for good "stand-up" appearance in the pot, also inferring good chances of product's shelf life. The yield value associated with most thixotropic products make them appear thick when poured at low shear rate and the shear-thinning property will reduce the product's viscosity upon rubbing at high shear rate, for easier spreading on the skin. A low product's viscosity at high shear rates allows free flowing of the product during its manufacturing.

The global popularity of cosmeceuticals has encouraged the incorporation of many active ingredients of functional materials into cosmetic preparations. Since the rate of absorption of these active ingredients by the skin can impact on their effectiveness, hence controlling this parameter in formulating efficacy-oriented products is essential.

From a psychological point of view, consumers prefer a thixotropic type of product. Creams are usually rubbed on and a shear-thinning characteristic would be desirable for rapid absorption, but it should not be too rapid because complete diffusion requires time (Lin, 2000). Controlling flow characteristics is crucial in formulating and manufacturing of cosmetic products because these properties are often closely related to product quality, stability and performance. Since rheology strongly influences the physical stability of the product, changes in rheological properties during the product's shelf life can cause serious viscosity change or phase separation, leading to marketing failure. Generally, non-Newtonian products (emulsions and suspensions) cause more stability problems than do homogenous Newtonian solutions. This is because they are non-equilibrium systems and their physical properties, including rheological characteristics easily change with time, simply caused by the systems's natural tendency to reach an equilibrium.

4.1.5 Objective of the Study

The objective of the research is

(1) to determine types of moisturiser product's rheological behaviour and study their correlation to the stability profile obtained

(2) to find out the moisturiser product's viscosity regression profile when they are stored at RT and at 50°C stability testing condition

4.2 Material and Methods

The rheological profile and viscosity property of moisturiser products developed were determined using the air bearing rheometer, HAAKE Rheostress®, Model R75. The measuring cup used is Z20 (D48mm) type and the spindle/rotor is a coaxial cylinder geometry Z20 DIN 53019/ISO 3219. The samples' temperature was kept constant with a small allowable temperature deviation of 0.5°C using the HAAKE F3-C circulator. A CR flow curve programme was used where the shear rate was assigned and the shear stress was measured, producing a flow curve diagram. Nevertheless, the viscosity curve flow seems to be more meaningful as it defines how the non-Newtonian liquids shear-thin with increasing shear rates (Schramm, 2000). However, viscosity cannot be measured directly but can be calculated from the relationship between shear stress and shear rate by using the following equation:

$$\text{Viscosity, } \eta = \text{shear stress } (\tau) \,/\, \text{shear rate } (\gamma)$$

Once the product's viscosity was calculated, a best fit curve model was then selected to determine the best viscosity curve profile for each moisturiser product's samples studied. The types of moisturiser product's flow behaviour was identified by performing a test whereby the product was sheared from a low shear rate value of 0.1288 s^{-1} to the highest value of 60s^{-1} (which will produce the ascending flow curve) and then from the highest shear rate value of 60 s^{-1} to the lowest shear rate value of 0.1288 s^{-1} (the descending flow curve). The temperature was set to 25°C and the deviation was fixed to 0.5°C. The total time taken to produce this flow curve profile is 6 minutes with the ascending and descending curves were each performed for 3 minutes. A thixotropic analysis was carried out to determine the hysteresis value of the product.

Determination of moisturiser product's viscosity was carried out using a steady state CR flow curve programme. The viscosity was measured at 5 shear rates' points that is at 0.1288 s^{-1} (the lowest allowable value), 0.2 s^{-1}, 0.5 s^{-1}, 1.0 s^{-1} and 1.2 s^{-1}. The temperature used to perform this programme is fixed at 25°C for the products stored at RT (Week 0) and at 50°C for accelerated product stability testing conditions. The allowable temperature deviation was also fixed at 0.5°C and the maximum waiting time is set at 20 seconds before another reading was taken. When measuring the viscosity of the products either stored at RT or at 50°C, the products samples were poured into the measuring cup and let to stabilise for 3 minutes at that respective temperature before the experiment was performed. For a Newtonian product, viscosity measurement using a single shear rate point may be sufficient to define its flow property. But for a non-Newtonian product, viscosity may be shear dependent as well as time-dependent, thus a viscosity value obtained at an arbitrary shear rate may be meaningless unless the instrument used and the condition of measurement are also clearly specified (Lin, 2000). In this study, once the viscosity of the moisturiser product at each shear rate points set was obtained, a viscosity curve regression analysis was performed to find the best fit viscosity curve model for the samples studied. This is done by selecting the best-fit curve analysis from the programme. The viscosity curve regression profile obtained will allow us to determine any intermediate shear stress or viscosity values needed which can be calculated from the equation of the curve acquired.

4.3 Result and Discussions

4.3.1 Moisturiser Product's Rheological Profile

All the moisturiser products formulated showed a similar flow curve profile where they follow Ostwald-de-Waele regression pattern when sheared at high shear rate. Figure 4.2 is an example of a flow curve profile for moisturiser product containing 13 wt/wt% of *Baccaurea motleyana hook f.* fruit's extract. The different ascending and descending flow curve path showed that the moisturiser product is thixotropic in nature. Many products or substances such as dispersions and emulsions that look homogenous are actually composed of molecules or particles of irregular shapes and/or droplets of one liquid dispersed into another liquids. At rest, these molecules or particles can build up an intermolecular or inter-particle network of binding forces such as polar forces and van der Waals forces. These forces restrict positional change of volume elements and give the product a solid character with an infinitely high viscosity. The primary particles or molecules in the product agglomerates and form a networking structurē. These molecules or particles will maintain their irregular internal order and are characterised by a sizeable internal resistance against flow, that is their high viscosity.

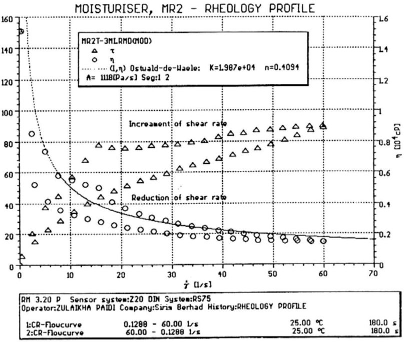


Figure: 4.2 Flow curve profile of moisturiser product at high shear rate

At very low shear rate, the Brownian motion of molecules keeps all molecules or particles at random causing the pseudoplastic and thixotropic liquids to behave similarly like Newtonian fluids. At this state, the viscosity of these liquids are independent of shear rate. If the force acting from outside is smaller than those forming the molecular or particle networking structure, will deform the shape of the product elastically. Only when the outside forces are strong enough to overcome the network forces, surpass the threshold or critical shear stress called the "yield point or yield stress", cause the network to collapse. This is achieved when the shear rate is increased to such an extent that the shear is able to induce molecular or particle orientation by far exceeds the randomising effect of the Brownian motion of the product. The molecules or particles can now change position irreversibly. The product starts to flow and the viscosity drops drastically.

For many products such as dispersions and emulsions, they show an additional time-related particle or molecule interaction due to the thixotropic nature that will lead to bonds creating a three dimensional network structure which is often called a gel (Schramm, 2000). Schramm (2000) has also reported that in comparison to forces within particles or molecules, these bonds are often hydrogen or ionic bonds and are relatively weak. They rupture easily when the product is subjected to shear over an extended period of time, Figure 4.3.

With increasing shear rates, more force is added to the product which can be seen in the increase of the shear stress magnitude, Figure 4.2. As the result, this could change the shape and form of the molecules in the product. The sphere shape molecules or particles maybe deformed to a smaller in diameter but longer like rugby balls or a chain type of molecules could be stretched and disentangled and orient themselves parallel to the driving force of the flow. This action will continue until it reached to a certain point where further shearing the product will breakdown the network structure of the molecules or particles in the product and change the molecular orientation and alignments cause them to flow easily, following the direction of forces imposed to the product. At this stage, the product can flow easily and the energy needed to cause the flow is very much reduced. This can be seen in the reduction of shear stress magnitude for the ascending flow curve in Figure 4.2.

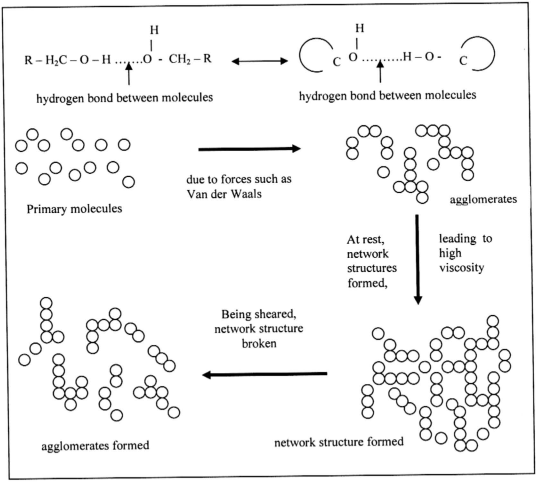


Figure 4.3: Example of possible molecules interaction in thixotropic dispersions

When the network structure is disrupted, the viscosity also drops. With the new orientation and alignments of the molecular structures formed, a new phenomenon takes place. Little force is needed to continue the flow of the product. This is seen with small increase in the shear stress magnitude at higher shear rates of the ascending flow curve, Figure 4.2. The viscosity of the product continue to drop until it reach the asymptotically a finite constant level (the lowest possible level) where even at higher shear rates cannot cause further shear thinning to the product. At this state, the optimum of perfect orientation has been reached (Schramm, 2000). From the ascending flow curve, the viscosity decreases with increasing shear rates as the result of combined breakdown of thixotropic structure and change in molecular orientation.

In second part of the experiment, showed by the descending flow curve in Figure 4.2, the shear rate is continuously reduced but the viscosity increases much less than it dropped initially and the shear stress values obtained are also much less than the value acquired from the ascending flow curve when these properties are compared at similar shear rate point. The second part of the experiment deals with the new molecular alignments and orientation of the product which is possibly composed of smaller network molecular structure chains and/or molecular agglomerations as the result from structure breakdown in the first part of the experiment. In the first part of the experiment, a gel turns rapidly to a sol when being sheared; end-up with reduction in the product's viscosity. When the shear rate is decreased, as in the second part of the experiment, less force is required to make the product flow. As the result, the shear stress magnitude is reduced. At this stage, the sol converts back to a gel. However, it will take time to restructure the inter- and intra-molecular interactions of the product and the rate of this transformation depends a lot on the nature of the thixotropic product and its temperature (Bruin, 1994).

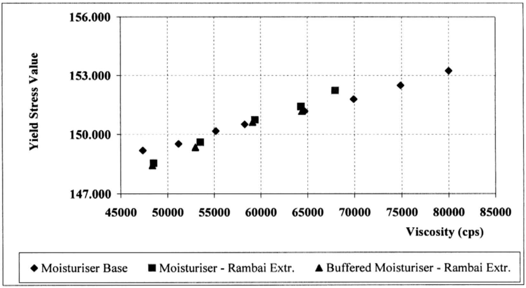
As reported by Schramm (2000), it may take seconds or minutes to break down a thixotropic structure but in many cases it requires minutes, hours or even days to fully recover the emulsion system to its origin gel status. For most product, the shear thinning effect is reversible, often with some time lag, that is the products regain their origin high viscosity when the shearing is slowed or even terminated. The chain-type molecules return to their natural state of non-orientation, deformed droplets return to sphere shape, and the aggregates reform are due to Brownian motion (Schramm, 2000).

Ward *et. al* (1974) has also stated that higher electrolytic and hydrogen ion concentration (low pH) will increase the time of solidification.

4.3.2 Correlation of Yield Stress and Hysteresis Value With Moisturiser Product's Stability

As earlier discussed, the intermolecular and/or interfacial bonds within the dispersions or emulsions results in a temporary networks structure. These structures which hold the samples together make the product stable and resist destruction by shearing forces below a critical stress level. This critical stress level is termed as yield stress or yield point. Therefore, the higher the product's yield stress value, the more stable is the product. The moisturiser product require a yield stress such that flow will be hindered under low shear conditions, that is before and after product's application. In this study, all moisturiser products, either the base or the products containing *Baccaurea motleyana hook f.* fruit's extract (with or without citrate buffer), showed a similar thixotropic profile. An analysis carried out on the yield stress value and hysteresis area for all these products gave a similar yield stress and hysteresis value trend, Figure 4.4 and Figure 4.5, which showed an increase in both product's properties as the product's viscosity increased.

The increase trend observed in the moisturiser product's yield stress value and the hysteresis area are related to the structure of the product formulation. As previously discussed, the molecules at rest will maintain their irregular internal order and can build up an intermolecular network of binding forces and form a networking structure which give the products a solid character with an infinitely high viscosity. As more networking molecular structures in the product were formed, the higher is the viscosity of the product. As the result, the product becomes more stable and difficult to flow. The yield stress value of the product measured would also increased. Consequently more energy is needed to breakdown these networking structures to flow the product. This energy is described by the hysteresis area formed when the products are sheared at low



Note: Rambai Extr. means Baccaurea motleyana hook f. fruit's extract

Figure 4.4: Yield stress value profile of moisturiser products

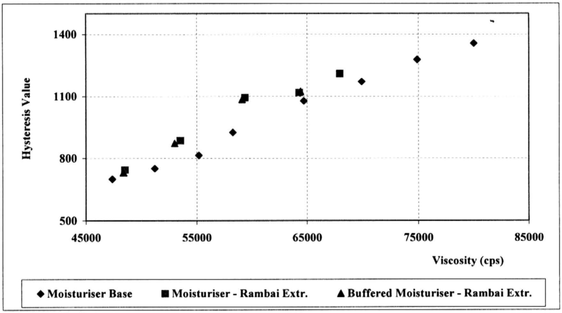


Figure 4.5: Hysteresis profile of moisturiser product

to higher shear rates and then back again to the lower shear rates. The higher the product's viscosity, the more stable is the product and the higher the hysteresis area obtained, Figure 4.5.

From this experiment, we could also predict the ease of dispensing the product from its container and also the ease of spreading the product on the skin due to the reduction of the viscosity value at high shear rate. Rubbing or spreading the product on the skin is similar to shearing the product at high shear rates. Since the viscosity of the moisturiser product decreased tremendously at high shear rates, it is assumed that the product would be easily and evenly applied on the skin.

4.3.3 Moisturiser Product's Viscosity Regression Profile at RT and 50°C Stability Testing Conditions

The viscosity of the moisturiser products were studied at RT (Week 0) and at 50°C stability testing condition. Example of the viscosity profile acquired for moisturiser product containing 13 wt/wt% of *Baccaurea motleyana hook f.* fruit's extract stored at RT (Week 0) and 50°C (Week 5) stability testing condition were shown in Figure 4.6 and Figure 4.7 respectively.

In this study, the moisturiser product's viscosity profile followed Bingham regression curve model at RT (Week 0) condition. The moisturiser product followed Ostwald-de-Waele regression curve model at 50°C stability testing condition and at high shearing condition. At these conditions, the products' viscosity drops drastically. When these products were measured at higher shear rate, the products' viscosity further drops immensely and this can be seen in the Ostwald-de-Waele regression curve model which showed a more sharp reduction bend, Figure 4.7 as compared to Bingham curve model profile, Figure 4.6 which is more dampen at this similar shear rate. This is the reason

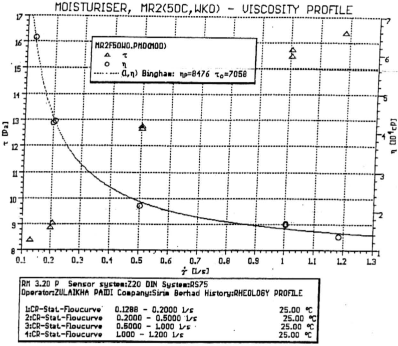


Figure 4.6: Viscosity profile of moisturiser containing 13 wt/wt% of B*accaurea motleyana hook f.* fruit's extract at RT condition

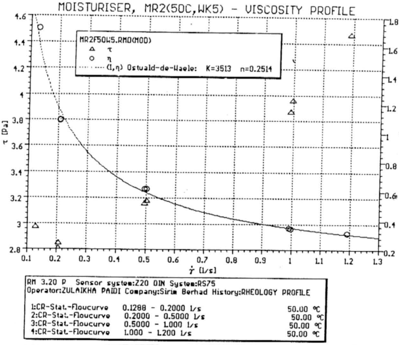


Figure 4.7: Viscosity profile of moisturiser containing 13 wt/wt% of B*accaurea motleyana hook f.* fruit's extract at 50°C stability testing condition (Week 5)

for the moisturiser products viscosity at 50°C stability testing condition measured showed an Ostwald-de-Waele regression curve model and a Bingham regression curve model profile was observed for those products with higher viscosity.

The product's viscosity was measured at five different shear rate points and the results obtained represent only these shear rates points. By constructing a viscosity regression curve on the viscosity results acquired, the product's viscosity at any shear rates point can be determined by calculating the product's viscosity value using the respective viscosity curve equation obtained. In this study for example, the Bingham viscosity curve equation can be used for calculating the viscosity of the product kept at RT and Ostwald-de-Waele viscosity curve equation can be used for products which are stored at 50°C. However, it should be noted that the regression curve obtained is the result of the best fitting procedure chosen in this study. This means that there will be some viscosity points that do not fall exactly on the curve plotted. Hence, it is expected to get a slight difference in the product's viscosity values when they were calculated using the respective Bingham or Ostwald-de-Waele regression equation, from the actual viscosity value obtained when measured at the selected shear rates points (that is at $0.1288s^{-1}$, $0.2s^{-1}$, $0.5s^{-1}$, $1.0s^{-1}$ and $1.2s^{-1}$).

4.4 Conclusion

A higher yield and hysteresis value were obtained from the plot of shear rate vs. shear stress. This showed that a strong network had developed, suggesting that the right proportions of emulsifiers, stearic acid and NaOH had been used in the system. The strong networking produced prolongs stability for all the formulated products.

Two models were used to describe the system behaviour under different storage conditions. The Bingham regression was fitted to the higher viscosity samples stored at RT and the Ostwald-de-Waele curve to the lower viscosity samples kept at 50°C.