

Chapter 4

Organo-LDH/Oil suspensions

The study considers fatty acid-intercalated Mg_2Al -LDH as a rheological additive in Jojoba oil. The 20 wt.% LDH in the Jojoba oil formulation was found to be stable (does not bleed out). In this investigation 30 wt.% LDH-stearate was selected. The viscosity of the neat Jojoba oil is Newtonian, whereas the LDH/oil formulation shows shear thinning, which is a typical non-Newtonian behaviour. The viscosity was observed to increase rapidly with an increase in LDH content. The viscosity, at a constant shear rate, shows complex temperature behaviour for the long-chain fatty acids C_{16} – C_{22} . Although LDH-palmitate and LDH-behenate also showed complex viscosity behaviour, particular attention was paid to LDH-stearate. The viscosity increase is assumed to be caused by a reversible loss of excess fatty acid and/or the insertion of Jojoba oil constituents.

The preliminary investigation of the suitability of LDH-stearate as a rheology modifier for Jojoba oil revealed that:

- The viscosity of the 30% LDH-stearate formulation showed complex temperature behaviour at a constant shear of 30 s^{-1} .
- FT-IR analysis showed changes in the configuration of the surfactant chains of the 30% LDH-stearate formulation, which changes as temperature increases.
- XRD analysis showed that the LDH-stearate in the formulation is no longer intercalated.

4 ORGANO-LDH/OIL SUSPENSIONS

4.1 INTRODUCTION

Organoclay suspensions are of importance in that rheological properties are achieved economically (i.e. at low volume fraction); organoclays exhibit good thermal stability (may be used where polymer thickening agents would fail); and the gels formed are resistant to gel-breaking effects from other chemicals. In addition, the dispersion of organoclay is seen as essential in property enhancement for clay-based polymer composites (King *et al.*, 2007). The dispersion of organoclays, particularly in their delaminated form, is of importance in self-assembling monolayers (SAM), Langmuir Blodgett film preparation, as well as emulsion stabilisation (Adachi-Pagano *et al.*, 2000).

This section discusses the potential use of stearate-intercalated LDS as a rheological modifier in Jojoba oil. It is a liquid wax ester mixture with an average molecular weight of 606 g/mol (MSDS). The ester mixture is composed mostly of eicosenyl eicosenoate, docosenyl docosenoate, eicosenyl docosenoate and docosenyl eicosenoate, as well as wax esters from C₃₆–C₄₆ (Miwa, 1971; Spencer *et al.*, 1976). Its chemical composition is closest to that of human sebum and it can therefore control the natural balance of the skin, while maintaining the flow of sebum. Jojoba oil possesses non-allergenic and non-comedogenic (non-clogging) properties (Sandha & Swami, 2009).

4.2 RHEOLOGY

Rheology was defined as the study of deformation and flow by Professor Bingham. This definition was accepted by the American Society of Rheology in 1929. In 1687 Isaac Newton made the hypothesis, ‘The resistance which arises from lack of slipperiness of the parts of the liquid, other things being equal, is proportional to the velocity with which the parts of the liquid are separated from one another’ (Barnes *et al.*, 1989). Viscosity can therefore be described as the resistance of a substance to flow. It is best understood by considering the flow between parallel plates (see Figure 4.1). The viscosity law states that the force per unit surface area (shear stress) is proportional to the velocity gradient (shear rate), i.e. for laminar flow in a Newtonian fluid.

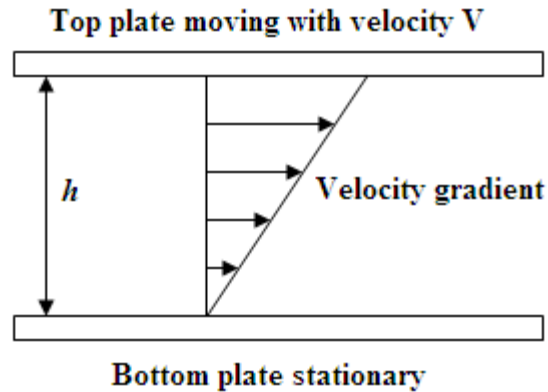


Figure 4.1. The parallel plate depiction of steady state viscous shear flow (Focke, 2012)

Dynamic viscosity or shear viscosity (η) is expressed as a ratio of shear stress (τ) to the corresponding shear rate ($\dot{\gamma}$):

$$\eta = \tau / \dot{\gamma} \quad [8]$$

Shear stress is given by the expression:

$$\tau = F/A \quad [9]$$

where

F = shear force (N)

A = shear area (m²)

The shear rate $\dot{\gamma}$ is given by the equation:

$$\dot{\gamma} = v/h \quad [10]$$

where

v = velocity (m/s)

h = distance between the plates

The flow behaviour of fluids can be described as either Newtonian or non-Newtonian. A Newtonian fluid exhibits a directly proportional relationship between the applied shear stress and the rate of shear. It has no solid-like properties and has a characteristic viscosity. Examples of Newtonian fluids include mineral oil, water, sugar solution, etc. Non-Newtonian fluids have a non-linear relationship between the applied shear stress and the rate of shear, as shown in Figure 4.2. Typical non-Newtonian fluids include pastes, emulsions and cosmetic

formulations. In this particular study we refer to clay particles dispersed in Jojoba oil; this system is more likely to exhibit complex viscosity behaviour. Under non-Newtonian flow behaviour there are further classifications (see Table 4.1 for definitions and examples).

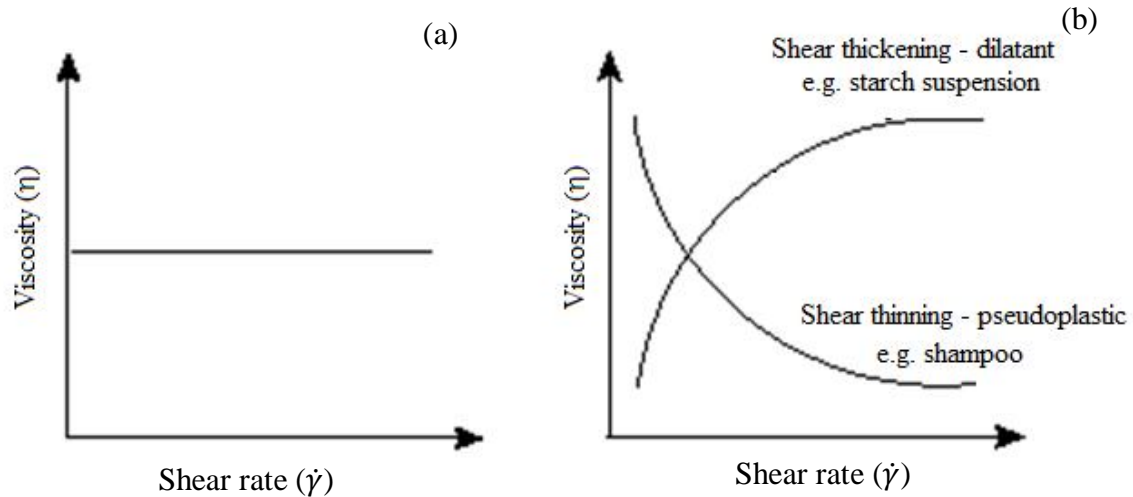


Figure 4.2. Viscosity curve of (a) Newtonian and (b) non-Newtonian fluids

Viscosity is affected by temperature, pressures and additives. It is also affected by the size and shape of the molecules/additives. In addition, intermolecular forces play a role in changes in viscosity, i.e. if the forces of attraction are high, then the viscosity of the liquid will be high.

Table 4.1. Different types of non-Newtonian fluids (Adapted from Shenoy, 1999)

Fluid type	Definition	Typical examples
Pseudoplastic	Exhibit decrease in viscosity with increasing shear rate and hence are often referred to as shear-thinning fluids.	Filled polymer systems Shampoo Lotion
Dilatant	Materials that depict an increase in viscosity with increasing shear rate and hence are often referred to as shear thickening fluids.	Wet sand Starch suspension Gum solutions
Bingham plastics	Fluids that do not flow unless the stress applied exceeds a certain minimum value, referred to as yield stress, and then show a linear shear stress vs shear rate relationship.	Toothpaste Tomato ketchup
Pseudoplastic with a yield stress	Fluids that exhibit a non-linear shear stress vs shear rate relationship in addition to the presence of yield stress.	Heavy crude oils with high wax content Filled polymer systems
Thixotropic	These fluids depict a reversible decrease in shear stress with time at a constant rate of shear and fixed temperature. However, the shear stress approaches a limiting value.	Mayonnaise Brush paint Synovial fluid
Rheopectic	Fluids that show a reversible increase in shear stress with time at a constant rate of shear and fixed temperature. At a given shear rate, the shear stress increases to approach an asymptotic maximum value.	Some clay suspensions, e.g. laponite
Viscoelastic	These fluids have an added feature of elasticity apart from viscosity. They exhibit properties that lie in between those of viscous liquids and elastic solids.	Filled polymer systems Polymer melts Polymer solutions

4.3 THICKENING MECHANISM

Thickening agents may act as gelling agents by dissolving in the liquid phase as a colloid that forms a weakly cohesive internal structure. Pastes are complex fluids with the properties of both solids and liquids. An underlying feature of these materials is the presence of an internal structure that gives a space-filling network capable of supporting its own weight under gravity (see Figure 4.3). They consist of ordered nanostructures and microstructures. Stokes and Frith (2008) describe such materials as “soft matter”, which they further categorise as either “soft-glass” or gel. The elasticity of soft glass arises from caging effects, whereas gels

arise from a percolated network structure that typically occurs due to attractive interactions between at least one of its components (Stokes & Frith, 2008).

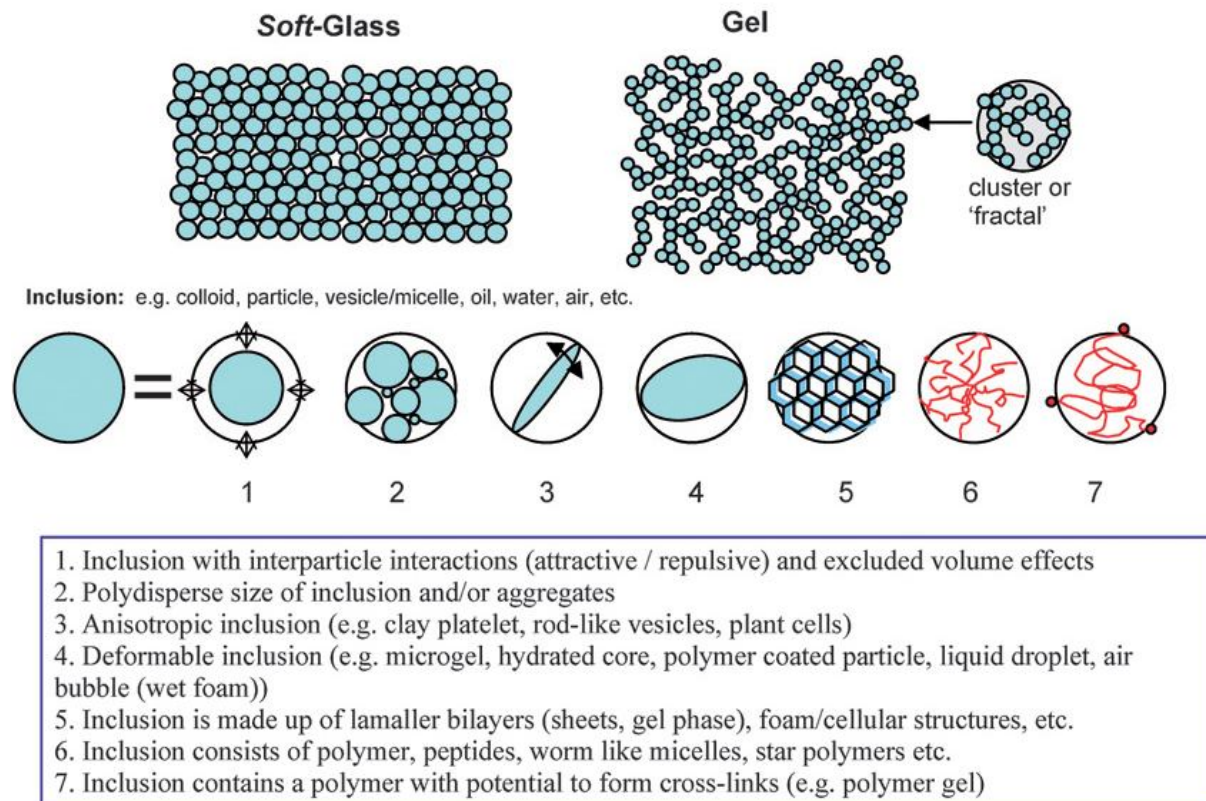


Figure 4.3. Soft microstructure, characterising the system as a “soft-glass” or “gel” (Stokes & Frith, 2008)

4.4 COLLOIDAL DISPERSIONS

IUPAC defines a *colloidal dispersion* as a system in which particles of colloidal size (at least in one direction a dimension roughly between 1 nm and 1 μm) of any nature (e.g. solid, liquid or gas) are dispersed in a *continuous phase* of a different composition (or state). On the other hand, a *suspension* describes solid particles that are dispersed in a liquid. Forano *et al.* (2006) interpreted the colloidal solutions of LDHs in two ways: firstly as a suspension of LDH particles, and secondly as a dispersion of exfoliated single layers of LDH (i.e. delaminated LDH). The delamination of surfactant intercalated LDH was pioneered by Adachi-Pagano and co-workers (2000). The hydrophobisation of clay minerals is a prerequisite for the

preparation of stable dispersion of clays in organic solvents (Lagaly & Malberg, 1990).

Dispersibility is governed by:

- Degree of hydrophobisation
- Polarity and chemical nature of the solvent molecules
- Extent of intercrystalline swelling
- Water content (Yun & Pinnavaia 1995; Adachi-Pagano *et al.*, 2000; Leroux *et al.*, 2001).

4.4.1 Clay dispersion in aqueous media

These types of dispersion are not as common as those in non-aqueous media. The delamination of LDHs in water was pioneered by Hibino and co-worker (Hibino & Jones, 2001; Hibino, 2004; Hibino & Kobayashi, 2005). Hibino (2010) prepared an aqueous colloidal dispersion of delaminated LDH-lactate in a hot aqueous solution of agarose. The mixtures gelled when cooled to room temperature. A uniform dispersion was obtained for the modified LDH; in contrast, the LDH-CO₃ particles agglomerated (Hibino, 2010). Albiston (1996) considered the rheology and microstructure of LDHs in aqueous suspension. Thickening and gelling was controlled by addition of electrolytes; the latter was found to be driven by the interaction of predominately rod-shaped aggregates formed from face-to-face association of the primary LDH particles. Iyi and co-workers (2011) studied the delamination of LDHs intercalated with short chain organic sulphonates. The LDH-isethionate exhibited water-swelling behaviour and formed viscous gels on contact with water (Iyi *et al.*, 2011). In another study, they delaminated LDHs intercalated with short chain carboxylates in water, which yielded a colloidal suspension via a gel state (Iyi & Sasaki, 2008).

4.4.2 Clay dispersion in non-aqueous media

The dispersion of LDH is widely reported in alcohols (Adachi-Pagano *et al.*, 2000; Leroux *et al.*, 2001; Venugopal *et al.*, 2006). Alcohols are composed of non-polar and polar segments that can interact with the alkyl chains and hydroxyl groups of the metal hydroxides respectively, leading to good solvation/delamination (Jones, 1983; Venugopal *et al.*, 2006). The study by Venugopal and co-workers (2006) revealed that the degree of dispersion differs among alcohols. An increase in the chain length of the alcohol led to an increased degree of

dispersion. A typical delamination entails refluxing the organo-LDH in the alcohol at 120 °C (Adachi-Pagano *et al.*, 2000). Peptisation has also been achieved by amino acid intercalation and subsequent treatment with formamide (Hibino & Jones, 2001, 2004). Although delamination of modified LDH was stated to occur readily in organic solvents, poor dispersion was observed in non-polar organic solvents such as hexane (Venugopal *et al.*, 2006). Moreover, dispersions of modified LDHs in more polar solvents are kinetically and thermodynamically unfavourable.

An increase in the dipole moment of the solvent molecules decreases chain solvation, which consequently depresses the rate of solvent incorporation within the interlayer (Jobbágy & Regazzoni, 2004). A higher extent of delamination and stability of colloids was obtained in LDHs containing long surfactant anions and a low $M^{II}:M^{III}$ ratio (Venugopal *et al.*, 2006). Jobbágy and Regazzoni (2004) reported delamination and restacking of LDH-DS in chloroform (CCl_4) and toluene. They rationalised delamination in terms of the miscibility of the organo-LDH and the selected solvent. In their study, dispersion was viewed as a two-component solution. Each dodecyl sulphate-LDH platelet was regarded as a solute molecule, hence the solubility in a given solvent was determined by interplay of the main attractions, i.e. chain-chain, solvent-chain and solvent-solvent. They also attributed it to an entropic contribution due to the loss of the interdigitated dodecyl chain structure, caused by the incorporation of the solvent in the hydrophobic gallery space. These researchers further explained delamination by means of Flory-Huggins theory in which the entropic contribution is modified. This correction was made to account for changes in the interdigitation of aliphatic chains. Hence, above a critical temperature (T_c), the transition from a swollen LDH-DS to delaminated form must be continuous and take place once a critical concentration is surpassed. Below T_c , delamination is only possible at higher dilutions (Jobbágy & Regazzoni, 2004).

Dèkány *et al.* (1997) reported that hydrophobisation of LDHs led to an increase in the adsorption capacity towards organic liquids. Interlamellar swelling of both the LDH-DS and DBS was observed in *n*-heptane. On the other hand, preferential adsorption of propanol by the dodecyl benzene sulphonate derivative was observed, whereas the dodecylsulphate derivatives adsorbed propanol and toluene in almost equal amounts (Dèkány *et al.*, 1997).

Martin *et al.* (1991) explored the potential use of intercalated-LDHs as argillaceous minerals in various oils for gel formulations. The organically modified LDHs were found to demonstrate good swelling properties. The study reported negative aspects of the use of montmorillonite in gel formulations. These included the fact that during gel formulation a high percentage of activators, such as alcohols, acetone and quaternary ammonium salts, could possibly cause skin irritations and allergic reactions. The impurities in the montmorillonite clay and organic additives give it an unpleasant colour and odour. However, LDHs are white in colour and would be advantageous to use as a substitute for montmorillonite.

4.4.3 Clay dispersion in emulsions

Solid particles of colloidal size are employed as stabilisers for Pickering emulsions. These emulsions are encountered in cosmetics, food, pharmaceuticals, oil recovery and waste treatment (Yang *et al.*, 2006). A combination of LDHs and smectite clays was used in the stabilisation of paraffin oil-in-water emulsions, by forming envelopes around the oil droplet (Abend *et al.*, 1998; Lagaly *et al.*, 1999). LDHs have also been employed in the stabilisation of Pickering emulsions (Yang *et al.*, 2006; Yang *et al.*, 2007; Wang *et al.*, 2010). The use of such particulate emulsifiers has the following advantages (Abend *et al.*, 1998):

- The amount of emulsifier may be reduced and/or organic emulsifying agents can be completely replaced.
- The Pickering emulsions obtained therefrom are difficult to break by changing the chemical parameters such as pH, salt concentration, temperature and composition of the oil phase.
- Changes in the solid content or type of solid result in changes in viscosity and type of flow. Hence the emulsifier is easily adjusted to the required practical applications.
- The type of emulsion – oil-in-water (O/W) or water-in-oil (W/O) – changes at different compositions of the solid stabiliser.

Yilmaz *et al.* (1999) studied kaolinite dispersions in water and water-alcohol mixtures. They attributed the increase in viscosity to ‘face-to-edge’ interaction between clay particles at the lower alcohol concentration on the other hand the viscosity decreases again because, the kind of interaction between the particles changes ‘edge-to-edge’ interaction at higher alcohol

concentration. This non-ideal plastic behavior is characteristic of flocculated/aggregated colloidal dispersion, in which every collision between particles results in the formation of a temporary or permanent association.

Yan and co-workers (1991a, 1991b) studied the rheology of oil-in-water emulsions with added solids. The addition of solids appeared to increase viscosity and shear-thinning tendencies (non-Newtonian behaviour). Viscosity was also found to be influenced by other aspects, such as:

- Solids with irregular shapes or surface irregularities gave a much higher viscosity than spherical solids (glass beads), i.e. at the same solids volume fraction.
- Smaller solids gave higher viscosity than larger solids. However, as size ratio of the solids to the oil droplets increases, the size effect decreases.

It is clear that the delamination of organoclays plays a vital role in the formation of stable gels, in either aqueous or non-aqueous media. Limited literature is available on the use of LDHs as rheological modifiers in oils. A preliminary study showed that the viscosity at constant shear of the Jojoba oil /LDH-stearate formulation presented complex temperature behaviour. However, it is important to note that this observation is consistent with a certain morphology and size. This investigation reports anomalous viscosity-temperature behaviour of Jojoba oil LDH-stearate suspensions.

4.5 EXPERIMENTAL

4.5.1 Materials

The materials used in the modification of LDHs are stated in Section 2.5.1. Jojoba oil (100% pure cold pressed) was obtained from Cr  d   Natural Oils.

4.5.2 Preparation of fatty acid-intercalated hydrotalcite

Fatty acid-intercalated LDHs were prepared using the same procedure described in Section 2.5.2 and Appendix B.

4.5.3 Preparation of 30 wt.% LDH-fatty acid/Jojoba oil formulation

Preliminary studies showed that the formulation should contain at least 20 wt.% LDH-stearate, otherwise the oil bleeds out. For this investigation 30 wt.% LDH-stearate was selected. Other formulations using LDH-laurate, -myristate, -palmitate, -oleate and -behenate were also attempted. Three grams of LDH-derivative and 7 g of Jojoba oil were mixed using a pestle and mortar at room temperature. The formulation was then heated up to 80 °C in an oven with occasional stirring to ensure good mixing. The product was allowed to cool down to room temperature overnight. Additional samples were prepared at room temperature, with no heating employed. The samples showed no marked difference as both exhibited complex rheological behaviour.

The 30 wt.% Mg-stearate and 30 wt.% Al-stearate formulations were prepared according to the above procedure, but replacing the LDH-derivatives with Mg-stearate and Al-stearate respectively. In addition, formulations containing stearic acid and Jojoba oil were prepared, having percentage weight ratios of Jojoba oil to fatty acid of 95:5, 90:10, 80:20 and 70:30 respectively.

4.5.4 Characterisation

Phase identification was carried out by XRD analysis on a PANalytical X'pert Pro powder diffractometer with variable divergence and receiving slits and an X'celerator detector using Fe-filtered Co K-alpha radiation (0.17901 nm). X'Pert High Score Plus software was used for phase identification. Temperature-resolved XRD traces were obtained using an Anton Paar HTK 16 heating chamber with a Pt-heating strip. Scans were measured between $2\theta = 1^\circ$ to 40° in a temperature range of 25 to 45 °C at intervals of 5 °C, with a waiting time of 1 min and a measurement time of 6 min per scan. Si (Aldrich 99% pure) was added to the samples so that the data could be corrected for sample displacement using X'Pert High Score Plus software. In the case of the Jojoba/LDH-stearate formulation, the formulation was pocketed in a plastic film and analysed from 25–50 °C.

Differential Scanning Calorimetry (DSC) data were collected on a Mettler Toledo DSC 1 instrument. Samples of 5–10 mg were placed in a 40 μ l alumina pan and heated from -40 °C

to 150 °C and then cooled back to -40 °C at a scan rate of 10 °C/min and an N₂ flow rate of 50 ml/min. A pin hole was made in the lid.

Polarised optical microscopy (POM) was used to study the crystallisation behaviour of the formulations using a Carl Zeiss POM. The samples were sandwiched between two glass slides and heated on a Linkam THMS hot stage (Linkam Scientific Instruments Ltd) from room temperature (\approx 25 °C) to 90 °C at a rate of 10 °C/min, and held at this temperature for 2 min before being cooled back to room temperature.

Standard FTIR was carried out on a Perkin Elmer 100 Spectrophotometer with a MIRacle ATR attachment with diamond Zn/Se plate; spectra were recorded between 4000 and 650 cm⁻¹ at a resolution of 2 cm⁻¹ and the data collected after 32 scans. The temperature scan FTIR spectra were traced between 4000 and 400 cm⁻¹ on a Perkin Elmer Spectrum RX I FTIR. The sample was heated from 25 to 130 °C at a ramp rate of 5 °C/min. Data were obtained from an average of 32 scans, recorded at a resolution of 2 cm⁻¹, background-corrected, using the KBr windows which sandwiched the sample.

Viscosity measurements were carried out on an Anton Paar MCR 301 Rheometer with a Peltier heating system using a 50 mm parallel-plate measuring system. The effect of temperature on the viscosity was measured by placing the sample in the centre of the stationary plate, and the shear rate of the rotating plate was kept constant at 5 s⁻¹. Different shear rates were explored, i.e. 10 and 50 s⁻¹, but no substantial difference was noted. The formulation was heated from 10 to 90 °C and cooled back down to 10 °C. The temperature ramp was 10 °C/min.

The effect of shear rate on the viscosity of the sample was investigated, during which the temperature of the system was maintained at 30 °C. The shear rate of the rotating plate was increased from 1 to 100 s⁻¹.

4.6 RESULTS AND DISCUSSION

4.6.1 Organo-layered double hydroxides (organo-LDHs)

The properties of the organo-LDHs are briefly revisited here as the study showed that intercalation results in different products.

The main difference in the LDH-stearates used is in the platelet size and shape (see Figure 4.4). LDH-stearate (E) had very large rhombohedral-shaped (euhedral) platelets ranging from 10 to 50 μm , and showed very little particle-particle interaction. On the other hand, LDH-stearate (S) had a combination of anhedral- and subhedral-shaped platelets with a size less than 5 μm . Heavy agglomeration was also observed. Euhedral crystals have flat, easily recognisable faces with sharp angles. The well-defined edges are oriented in a specific way relative to the underlying atomic arrangement of the crystal. Crystal faces are defined by indicating their intercepts on the crystallographic axes; this is usually denoted by their Miller indices.

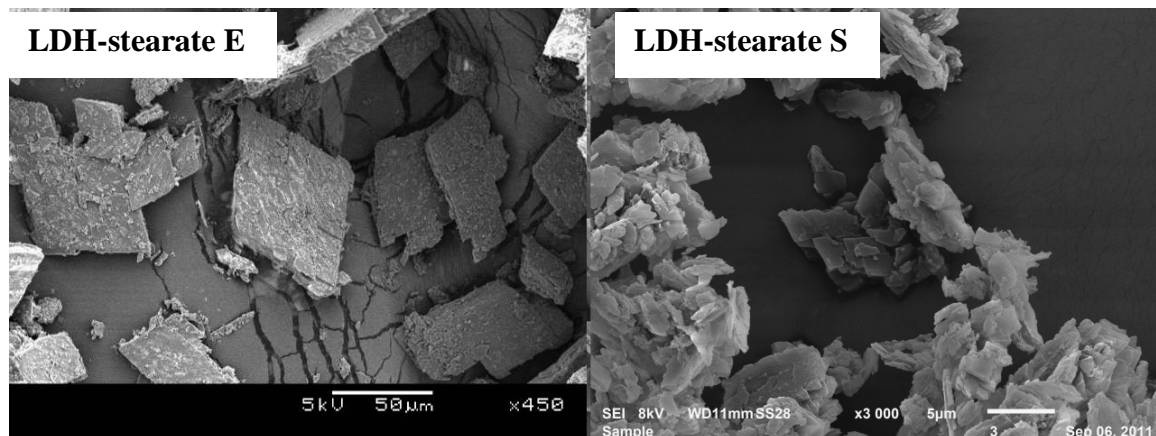


Figure 4.4. SEM micrographs of the LDH-stearates E and S used in the Jojoba oil formulation

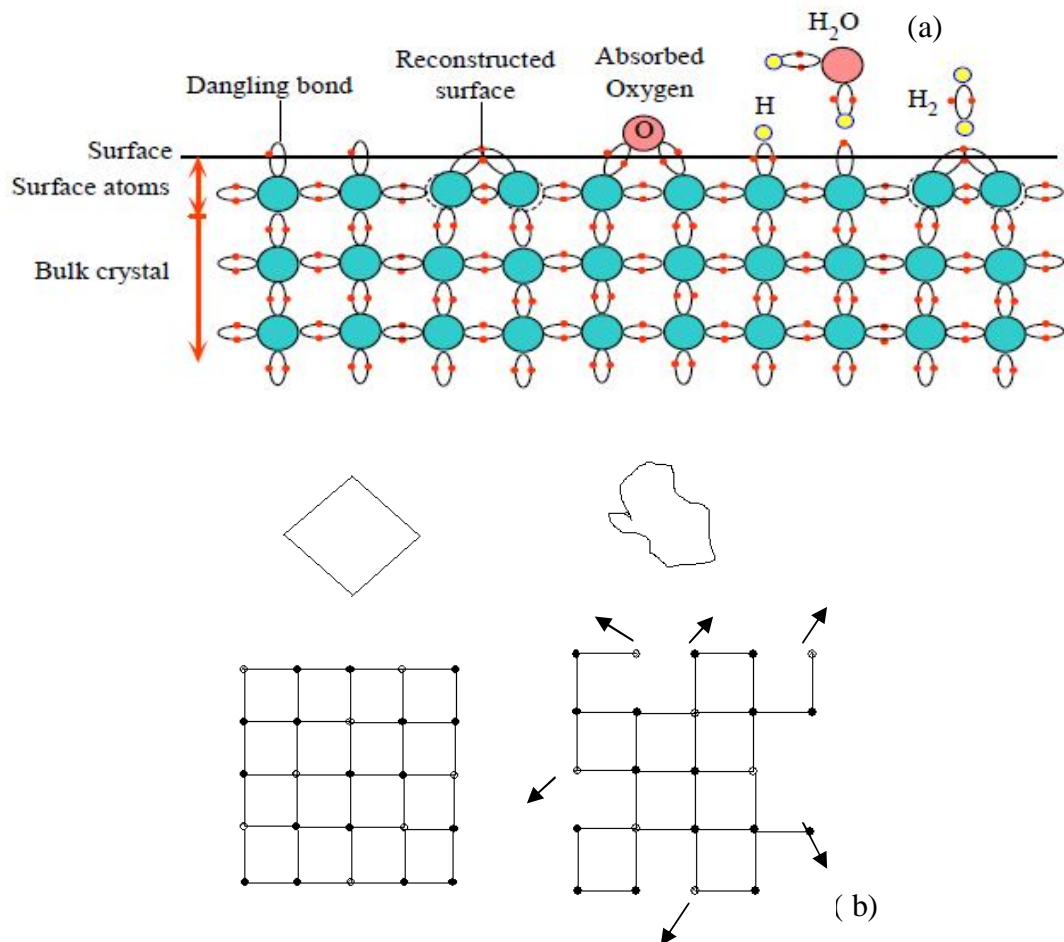


Figure 4.5. (a) Schematic illustration illustration of silicon dangling bond (Kasap 2001) and (b) euhedral and subhedral crystals arrows indicating dangling bonds

A hypothetical 2-D crystal (Figure 4.5a) has on its surface atoms that cannot fulfil their bonding requirements and therefore have broken or dangling bonds (Kasap 2001). These surface atoms can either bond with each other in the case of surface reconstruction or have physisorbed and chemisorbed atoms (Kasap 2001). The rough edges have a lot of ‘dangling’ bonds (Figure 4.5b), to which new atoms/molecules can easily bond to, as the crystal grows. The smooth planes have fewer dangling bonds, and new atoms cannot easily attach, so these planes grow outwards more slowly. This is corroborated by the findings of Schofield and Samson (1954). In their studies they found that the edges of kaolinite crystals with imperfections are a result of bond breakages and these sites carry positive charges. These broken bonds can therefore act as sites for further chemical reaction.

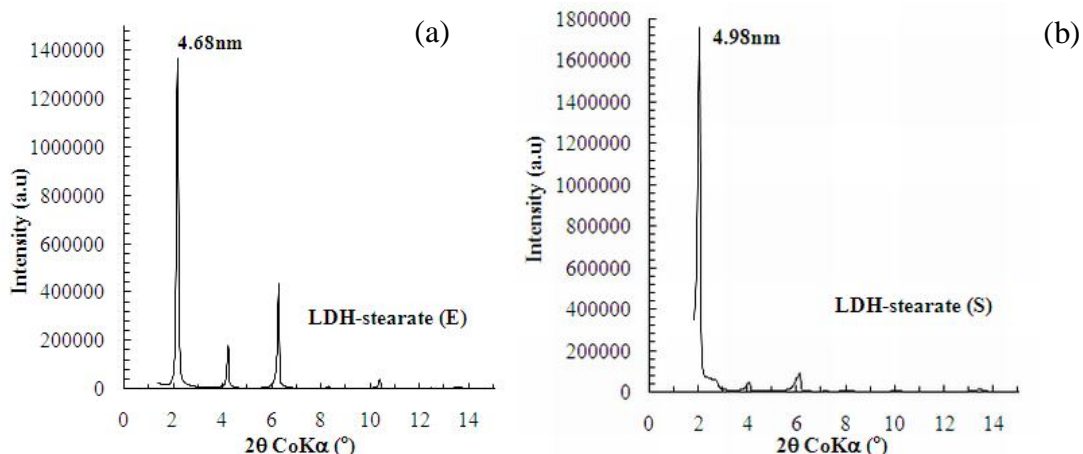


Figure 4.6. XRD diffractograms of: (a) LDH-St (E) and (b) LDH-St (S)

Figure 4.6 shows the diffractograms of each of the respective species of platelets. It is evident that the LDH-stearate (E) had a well-developed crystal form and good ordering, due to the symmetry of the reflections observed. On the other hand, the LDH-stearate (S) exhibited a strong primary basal reflection, although the other peaks are not symmetrical, this is an indication of crystal irregularities. These observations support the observed morphology of platelets.

The properties of the LDH used in the formulation with Jojoba oil are summarised in Table 4.2.

Table 4.2. Summary of XRD and TGA results for the LDH-CO₃, LDH-stearates (E and S), magnesium stearate and aluminium stearate samples

Sample	d-spacing (nm)	TG residue (wt.%)	Intercalation (multiples of AEC)
LDH-CO ₃	0.76	59.7	-
LDH-CO ₃ + Tween 60	0.76	58.4	-
LDH-stearate E	4.68	10.36	3.22
LDH-stearate S	4.88	9.73	3.48
Mg-St/Al-St	5.08	8.23	5.16
Magnesium stearate	4.94	7.30	(5.70)
Aluminium stearate	4.01	8.57	(5.11)

Figure 4.7. shows the FTIR spectrum of the LDH-stearate. The observed bands are consistent with those found in previous investigations (Nhlapo *et al.*, 2008; Focke *et al.*, 2010). Each respective assignment is found in the caption to the figure. Being a bilayer intercalated LDH-stearate, both derivatives (S) & (E) have very similar spectra.

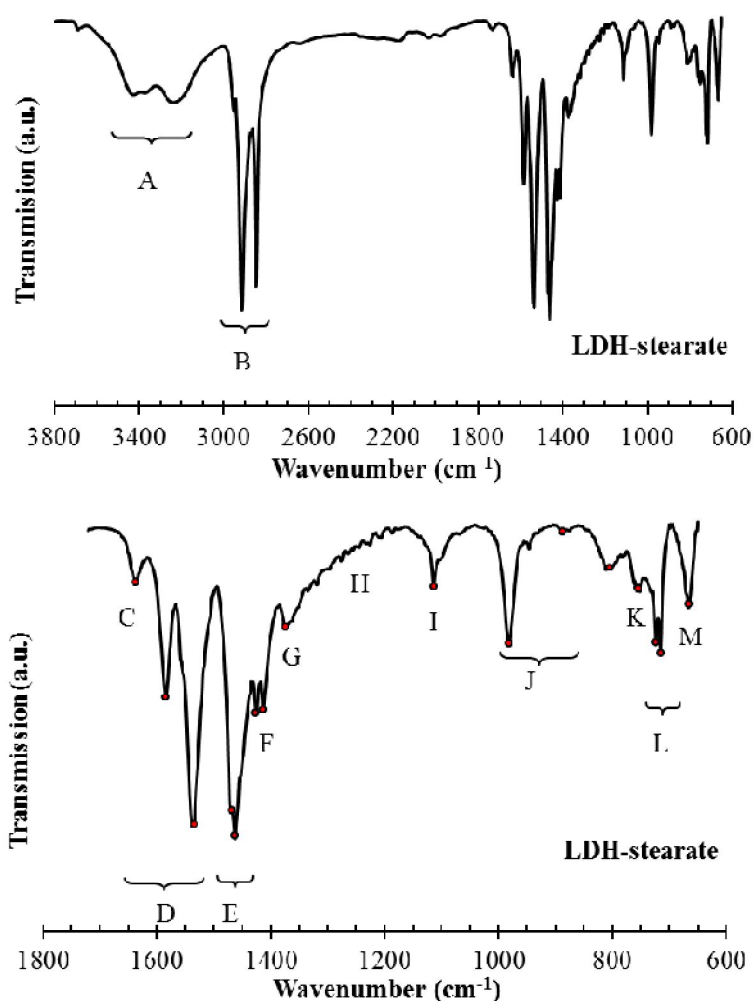


Figure 4.7. FTIR spectrum of the LDH-St

Legend: (A) broad O-H stretch, 3460 cm^{-1} ; (B) C-H stretch, $2954, 2917, 2870\text{ cm}^{-1}$; (C) H_2O bending modes, 1637 cm^{-1} ; (D) asymmetric carboxylic C=O stretch, $1588, 1554$ and 1540 cm^{-1} ; (E) C-H bend (scissoring), $1472, 1466\text{ cm}^{-1}$; (F) C-O-H bend (involving O-H interaction), 1415 cm^{-1} ; (G) CO_3^{2-} ν_3 antisymmetric vibration, $1367, 1363\text{ cm}^{-1}$; (H) $-\text{CH}_2-$ wagging bands; (I) ν_1 CO_3^{2-} , 1114 cm^{-1} ; (J) M-OH deformation modes, $984, 877\text{ cm}^{-1}$; (K) M-OH translation mode, 757 cm^{-1} ; (L) $-\text{CH}_2-$ in-phase rocking vibrations, $724, 716\text{ cm}^{-1}$; (M) ν_4 (in-plane bending) vibrations of CO_3^{2-} , 668 cm^{-1}

In all other characterisation techniques the two LDH-stearates showed similarities. However, the dispersion of LDHs resulted in different viscosity and flow behaviours as a function of temperature. The LDH-stearate (S) in Jojoba oil had a substantially higher viscosity and a

complex flow behaviour as temperature was increased. On the other hand, LDH-stearate (E) had a much lower viscosity and showed a slight bump in the very same area (see Figure 4.8). This anomaly is thought to be attributable to the shape and size of the LDH particles. The LDH-stearate (S) has a considerably smaller particle size, which leads to a greater area of contact and, in turn, a greater particle interaction. In addition, the unassociated atoms/ions shown in Figure 4.5 could potentially be ‘active sites’ for further chemical reactions. When a crystal grows, new atoms attach easily to the rougher and less stable parts of the surface, but less easily to the flat, stable surfaces. Therefore, the flat surfaces tend to grow larger and smoother, until the whole crystal surface consists of all plane surfaces.

It was therefore of interest to explore this anomaly, clearly seen with the LDH-stearate. However, from this point onwards the LDH-stearate referred to is the form that has subhedral platelets, unless stated otherwise.

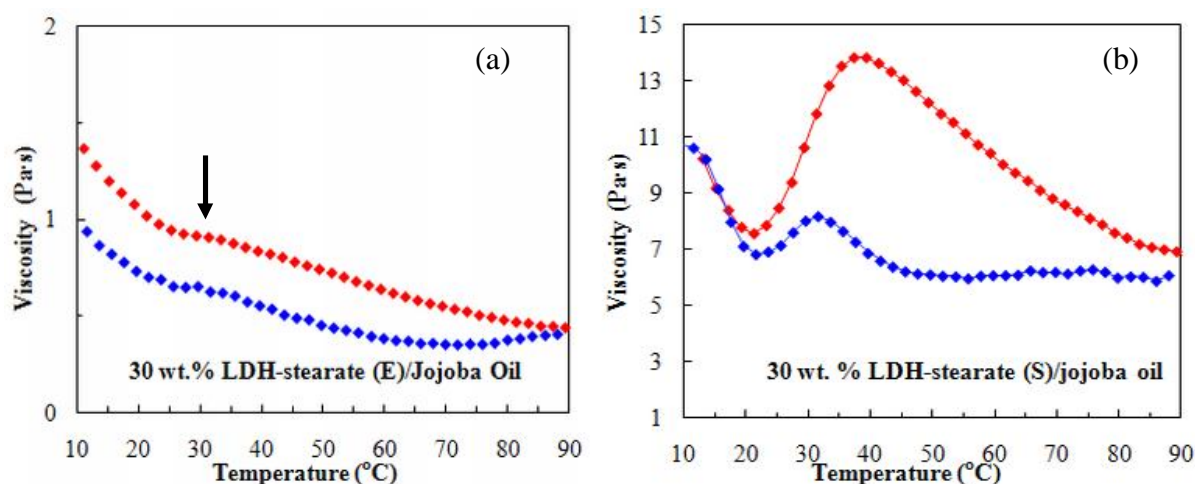


Figure 4.8. Viscosity curves as a function of temperature of: (a) 30 wt.% LDH-St (E) and (b) 30 wt.% LDH-St (S) (The heating run is shown in red and the cooling run in blue)

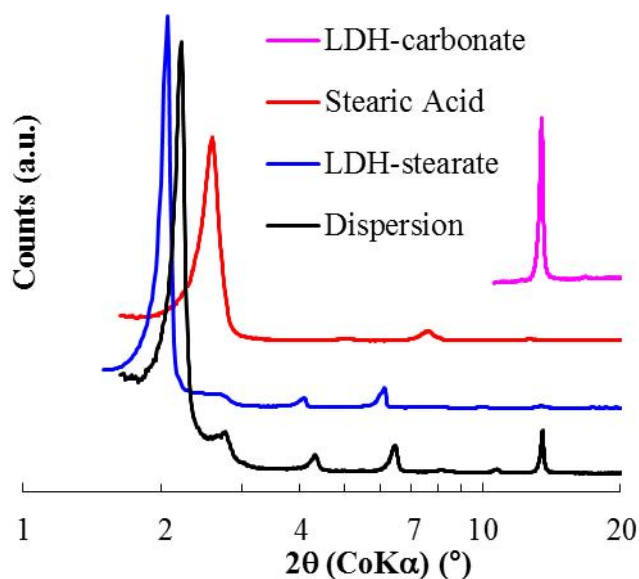


Figure 4.9. Arbitrarily scaled X-ray diffractograms for stearic acid, LDH-CO₃, LDH-stearate (S) and a 30 wt.% dispersion of LDH-stearate (S) in Jojoba oil prepared at a temperature of 80 °C

Figure 4.9 shows the X-ray diffractograms for stearic acid (99%), LDH-CO₃ and LDH-St prepared with Tween 60 as surfactant at an intercalation temperature of 80 °C. It also shows a diffractogram for the gelled Jojoba oil dispersion containing 30 wt.% LDH-St. The reflection at 0.76 nm ($2\theta = 13.49^\circ$) for LDH-CO₃ is present in the LDH-St and its Jojoba oil dispersion, confirming that the former is present as an impurity. The reflections at 4.98 nm ($2\theta = 2.06^\circ$), 2.51 nm ($2\theta = 4.08^\circ$) and 1.68 nm ($2\theta = 6.12^\circ$) are consistent with bilayer intercalated LDH-St. The d-spacing of the LDH-stearate decreased slightly to 4.65 nm in the 30 wt.% in the Jojoba oil dispersion.

4.6.2 Jojoba oil/LDH-derivative formulation

4.6.2.1 Viscosity of stearic acid suspensions

Figure 4.10 shows the effect of temperature on the apparent viscosity of selected stearic acid suspensions in Jojoba oil. The DSC traces are shown in Figures 4.11 and 4.12 show optical micrographs of the 20 wt.% stearic acid suspension, which is roughly the same amount contained in the LDH-stearate/Jojoba oil formulation. The observations with regard to Figures 4.10 to 4.12 can be summarised as follows. Figure 4.10 shows that the low-

temperature viscosity of the suspensions increases dramatically with stearic acid content (also shown in Appendix D). However, when the samples are heated, a rapid drop is observed to values comparable to or lower than the viscosity observed for the Jojoba oil at higher temperatures.

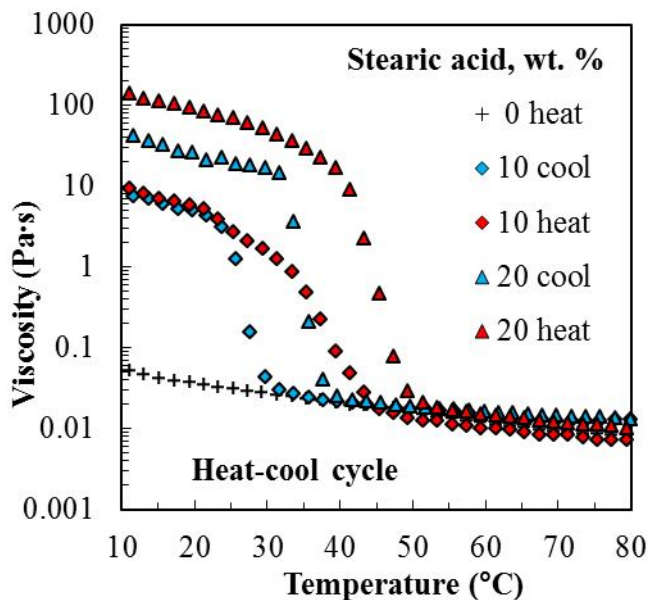


Figure 4.10. Viscosity-temperature curves of Jojoba oil/stearic acid suspensions heated at 5 °C/min from 10 to 90°C and cooled at the same rate back to 10 °C (The heating runs are shown in red and the cooling run in blue)

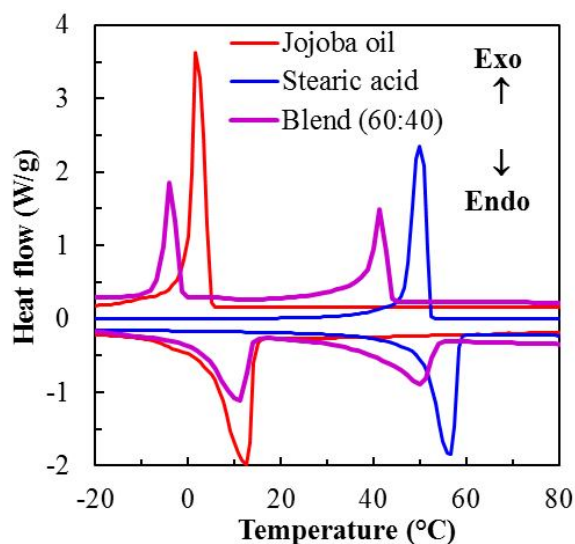
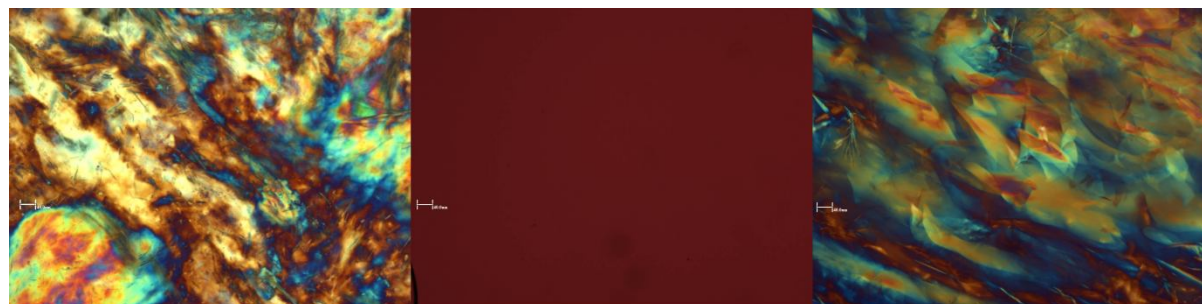


Figure 4.11. DSC traces for neat Jojoba oil and stearic acid as well as a 60:40 blend of the oil with the acid; samples were heated at 5 °C/min from -40 to 200 °C and cooled at the same rate back to -40 °C

Figures 4.11 and 4.12 confirm that this step change in the viscosity can be associated with the melting of the stearic acid. Figure 4.11 also shows that Jojoba oil and stearic acid are fully molten above 15 and 60 °C respectively. In the presence of Jojoba oil, the stearic acid melts at a lower temperature, but the converse does not hold.



A. Heating: 50°C

B. Heating: 60°C

C. Cooling: 49°C

Figure 4.12. Hot-stage optical microscopy of Jojoba oil suspension containing 20 wt.% stearic acid (magnification bar: 40µm)

The heats of melting and of crystallisation, for the suspended stearic acid, are nearly in proportion to the amount of acid present. This implies that the stearic acid is partially soluble in Jojoba oil at low temperatures. This is corroborated by the fact that even a 10 wt.% suspension increases the viscosity of the oil by two orders of magnitude. This observation can be explained by the formation of a space-filling network of fat crystal (Thareja *et al.*, 2010) (see also Figure 4.11). The network crystal interaction provides firmness or gel-like character. Note also that the crystallisation of both the stearic acid and the Jojoba oil is more sluggish in the blend. This implies that the presence of stearic acid in the Jojoba oil matrix retards the crystallisation of Jojoba oil chains.

From the above data it is clear that colligative properties exist between stearic acid and Jojoba oil. Figure 4.13 illustrates a phase diagram of a generalised temperature versus composition for the Jojoba oil-stearic acid formulations. The left side of the curve intersects the ordinate at the melting point of pure Jojoba oil; on the right it intersects the ordinate at the melting point of pure stearic acid. The minimum is the eutectic and a horizontal line is drawn along the eutectic temperature. The left side can be considered as the ‘freezing-point-depression’ curve for stearic acid dissolved in Jojoba oil, and the curve to the right Jojoba oil dissolved in stearic acid. This is typical of binary systems in which the liquids are completely

miscible and the solids completely insoluble in each other (clearly demonstrated in Figures 4.11 and 4.12).

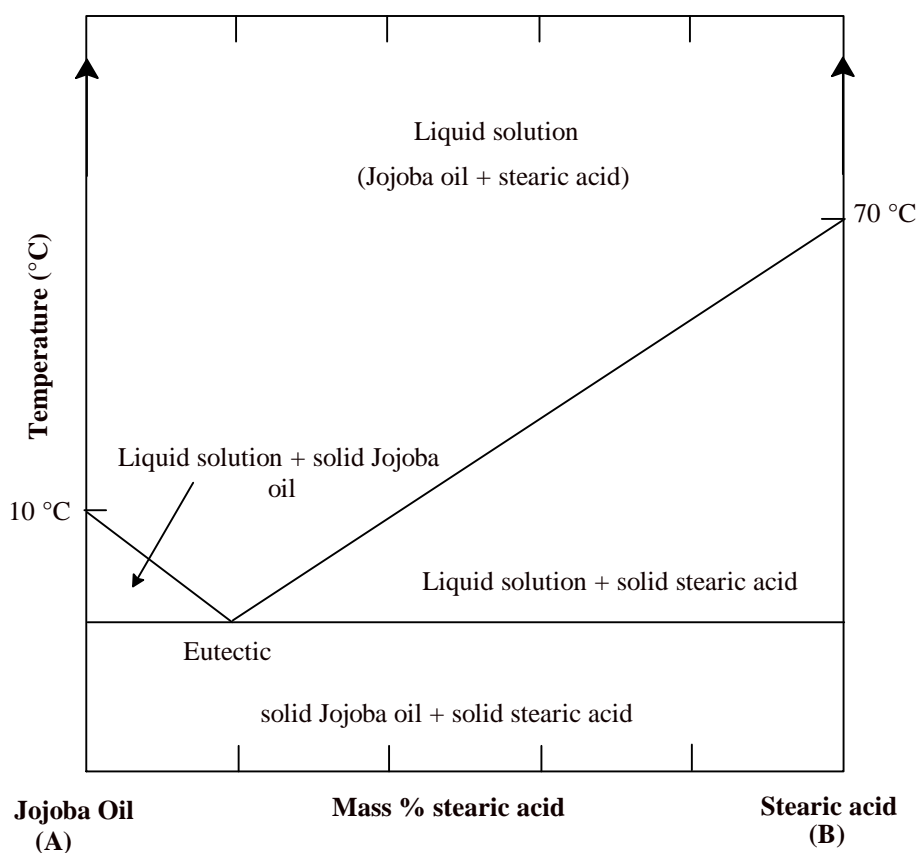


Figure 4.13. General illustration of a Jojoba oil-stearic acid phase diagram

4.6.2.2 Effect of concentration on viscosity of the Jojoba oil formulation

Figure 4.14 shows the relationship that exists between viscosity and increase in the LDH-stearate content in the Jojoba oil matrix. All samples continue to exhibit shear-thinning behaviour, which is an indication of the internal structure within the matrix. As the shear rate increases, the LDH particles will tend to align themselves to the direction of flow. Viscosity continues to increase with the increase in the amount of LDH-stearate used in the formulation. This is due to 'jamming up' of the suspension giving rise to a continuous three-dimensional contact through out the system, thus making flow restricted (Barnes *et al.*, 1986). Since the material under consideration also contained derivatives of magnesium and aluminium stearates, it was decided to study the effect that adding them would have on the viscosity of the Jojoba oil suspensions. Figure 4.15 shows the effect of Al-stearate, Mg-

stearate and LDH-stearate on the viscosity of Jojoba oil as the shear rate changes. The viscosity of Mg-stearate is much higher than that of both Al-stearate and LDH-stearate. Interestingly, the LDH-stearate depicts a viscosity that is in between that of Al-stearate and Mg-stearate.

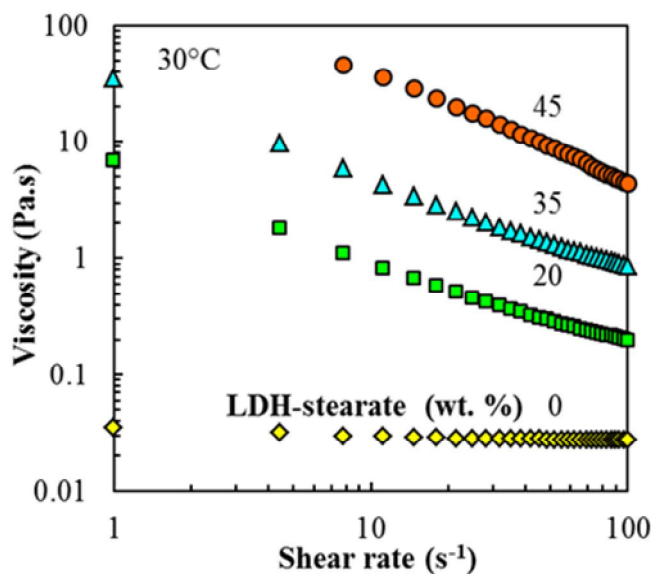


Figure 4.14. The effect of shear rate and LDH-St content on the viscosity of Jojoba oil suspensions (the temperature was kept constant at 30 °C)

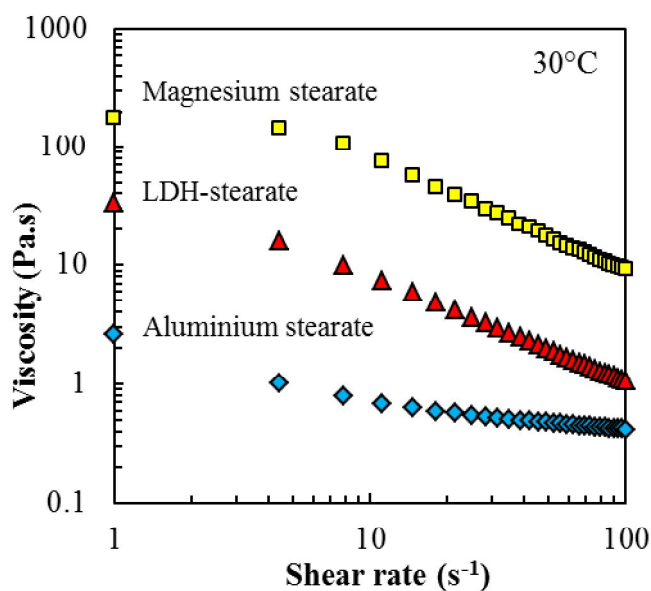


Figure 4.15. Comparison of the Jojoba oil thickening efficiency of 30 wt.% Mg-stearate, Al-stearate and LDH-St (the temperature was 30 °C)

It is usual to add small organic/polar molecules that act as activators in organoclay suspensions. The effect of addition of 5 wt.% of alcohol on the LDH-St/Jojoba oil formulation is shown in Figure 4.16. The apparent viscosity of the dispersion seemed to decrease with increase in chain length. This is an indication that the presence of alcohol helps in the dispersion of the organo-LDH in the Jojoba oil matrix. The LDH-St is partially covered with the stearate chains, meaning that there are areas with exposed OH groups that are able to interact with the alcohol hydroxyl groups. This enhances the wettability and dispersion of the LDH-St particles in the Jojoba oil. As the chain length increases, there is better compatibility of the alcohol hydrophobic tail with the matrix (which is typically composed of liquid wax esters of C₁₆–C₂₂). Better dispersion or solvation of fatty acid chains by the alcohol leads to lower apparent viscosity.

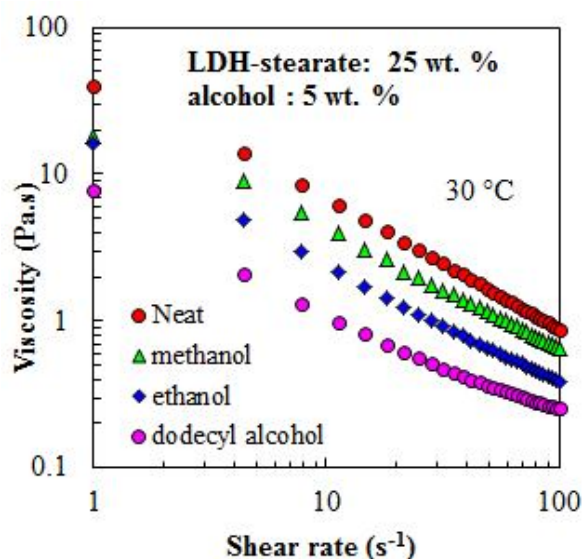


Figure 4.16. Effect of the presence of small amounts of alcohols (5 wt.%) to 25 wt.% LDH-St suspension in Jojoba oil on the suspension viscosity

4.6.2.3 Effect of temperature on viscosity of the Jojoba oil formulation

Generally, viscosity tends to decrease with increasing temperature. Surprisingly, when a 30 wt.% suspension of LDH-St in Jojoba oil was heated, it showed an increase in viscosity in a certain temperature region (Figure 4.17). When heated, the viscosity initially decreases with temperature, but then increases in the temperature range of 25 to 35°C before decreasing again. This is an indication of changes in flow behaviour, as well as of probable

microstructures forming during the rheological study at the given temperature ranges. An increase in temperature results in an increase in the molecular or particle movement.

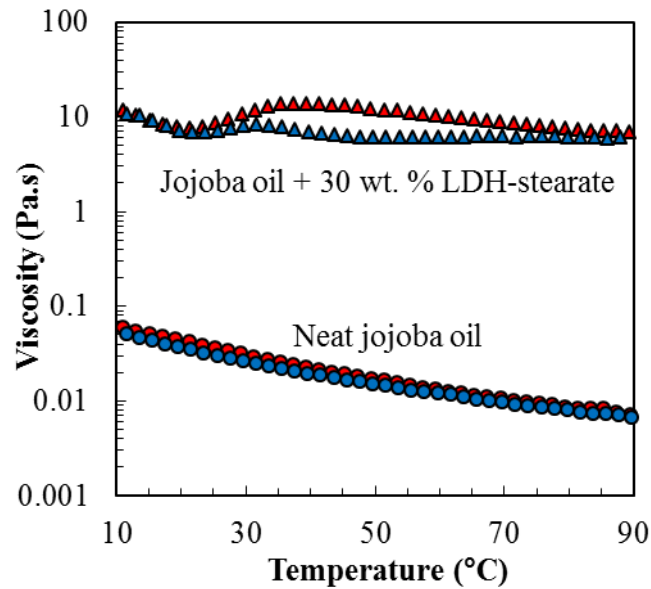


Figure 4.17. The effect of temperature on the viscosity of Jojoba oil and a 30 wt.% LDH-St suspensions subjected to a heating-cooling cycle (The shear rate was 30 s^{-1} ; the temperature was scanned at 5 °C/min from 10 to 90 °C and back. The heating run is shown in red and the cooling run in blue)

As demonstrated in previous sections, free stearic acid molecules are exuded into the Jojoba oil matrix as the temperature increases. Depending on the concentration of stearic acid in the Jojoba matrix, the acid begins to melt at as low as 20 °C (see Appendix D). This means that the matrix is composed three components, i.e. LDH-St particles, Jojoba oil chains and the expelled stearic acid. As molecular/particle mobility increases as a function of temperature, so do the chances of particle-particle, particle-molecule and molecule-molecule interactions taking place. Figure 4.18 shows the viscosity-temperature curve of 30 wt.% of the LDH-St/Jojoba formulation. The heating run that is divided into three sections according to the different flow behaviour. The stages have been assigned the following events:

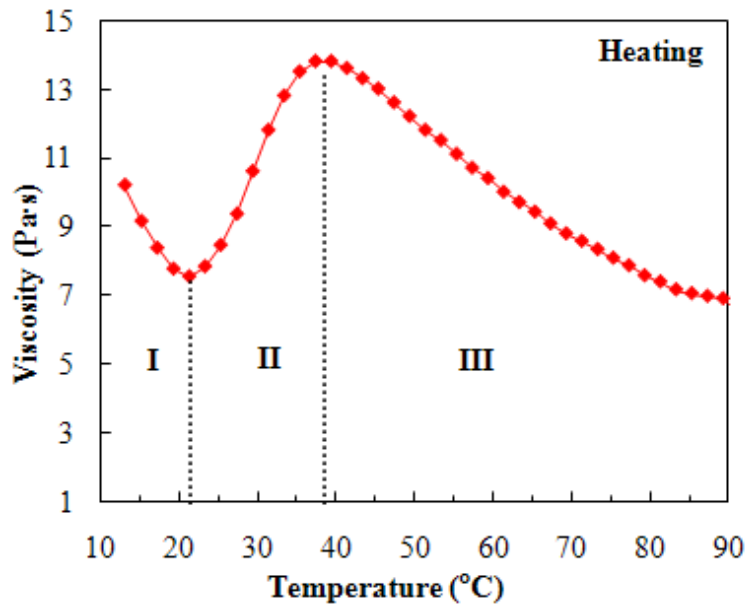


Figure 4.18. Viscosity-temperature heating run subdivided into three stages

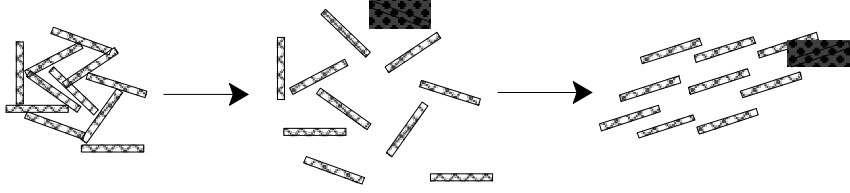
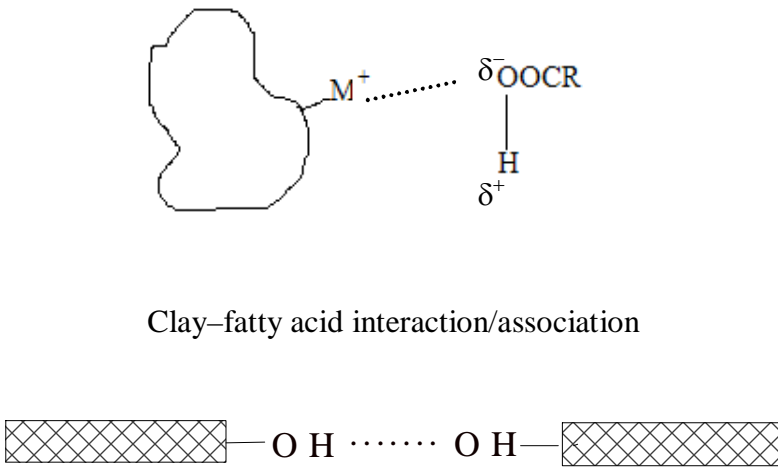
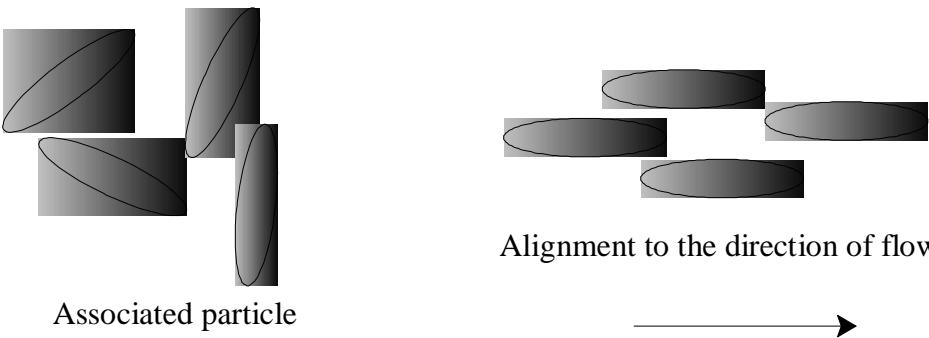
I – This stage is not unusual; the inverse relationship of decrease in viscosity as a function of temperature increases is strongly exhibited. As temperature increases, the Jojoba oil becomes less viscous and flows readily. Particles introduced into a liquid at rest usually assume a state of thermodynamic equilibrium forming aggregated microstructures (Barnes *et al.*, 1989). The microstructures breakdown from edge-to-face (house of cards) aggregation due to shear and align themselves to the direction of flow as shown in the Figure 4.18 and Table 4.3.

II – This stage exhibits an increase in viscosity as temperature increases. This begins at about 20 °C; at this temperature bilayer intercalated LDH begins to exude excess stearic acid into the Jojoba oil matrix. Addition of stearic acid into the Jojoba oil matrix would naturally increase the viscosity. The presence of ‘dangling bonds’ on the subhedral LDH-St particles previously mentioned can result in an inductive effect on the neighbouring acid group, as shown in Table 4.3. These associations could substantially increase the size of the LDH-St particle. This in turn will cause viscosity drag, resulting in a higher resistance to flow. On the other hand, the external hydroxyl groups of the LDH-St can also form hydrogen bonds. However, because of the presence of shear, the neighbouring platelets are envisaged to have edge-to-edge interaction, as shown in Table 4.3. These flocculated platelets also contribute to resistance to flow. Flocculated structures give rise to greater resistance to flow by enclosing and immobilising some of the continuous phase (Jojoba oil) hence increasing the apparent phase volume.

III – As temperature increases, the continuous phase (Jojoba oil) flows readily and the newly associated particles move as one mass and align to the direction of shear. Hence a steady

decrease in viscosity as a function of temperature is observed. Another plausible explanation is shearing of flocculated suspensions could possibly deform or even break them down at elevated temperatures.

Table 4.3. Illustration of the different stages associated with the heating run in the viscosity-temperature curve

Stage	Illustration
I	 <p>House of cards structure Deaggregation Orientation</p>
II	 <p>Clay-fatty acid interaction/association</p> <p>Clay-clay platelet interaction/association</p>
III	 <p>Associated particle</p> <p>Alignment to the direction of flow</p>

When cooled, the apparent viscosity decreases slightly (Stage I) (see Figure 4.19), and then starts to increase at 54 °C. This marks the beginning of Stage II when the free stearic acid in the matrix begins to crystallise out. The viscosity continues to increase as the stearic acid crystallises, forming a fatty acid crystal network. In stage III the viscosity decreases; this could be explained by the fact that the fatty acid crystal network has been broken down due to continued shear action. Thareja *et al.* (2011) also cite the breakdown of some of the fatty acid crystal network due to applied strain. Stage IV shows another increase in the viscosity. The temperature in this region is low, the mobility of the matrix is greatly reduced and resistance to flow increases. The excess stearic acid molecules that continue to crystallise out and form networks also add to the viscosity increase in this stage.

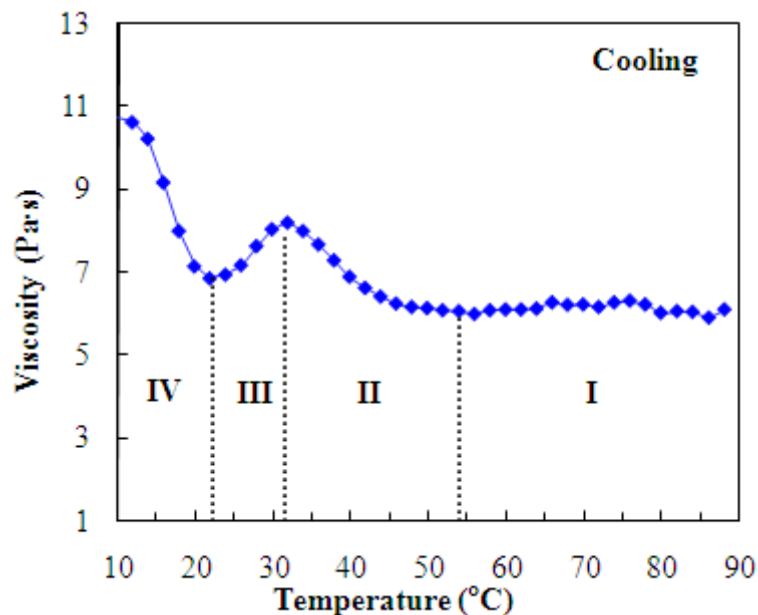


Figure 4.19. Viscosity-temperature cooling run subdivided into four stages

Figure 4.20 shows the viscosity-temperature behaviour of Mg-stearate, Al-stearate and LDH-stearate. The complex behaviour observed in the LDH-stearate is absent in both Al-stearate and Mg-stearate.

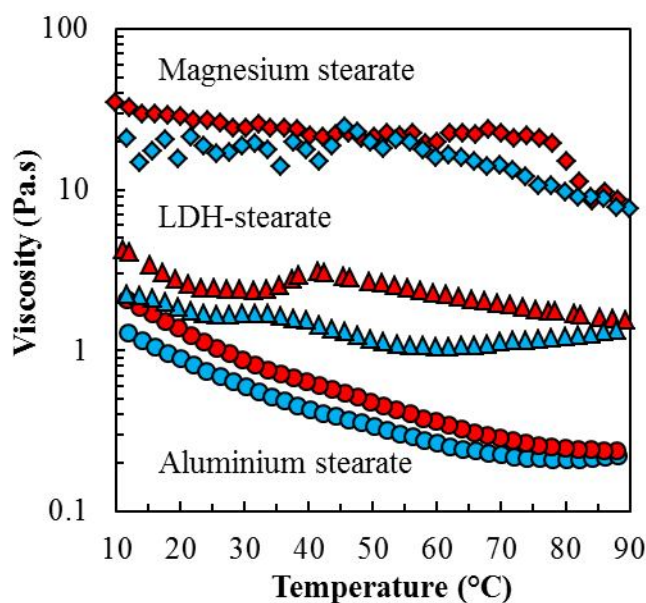


Figure 4.20. Comparison of the Jojoba oil thickening efficiency of Mg-St, Al-St and LDH-St, all at a loading of 30 wt.%. (The shear rate was 5 s^{-1} ; temperature was scanned at $5 \text{ }^\circ\text{C}/\text{min}$ from 10 to $90 \text{ }^\circ\text{C}$ and back. The heating runs are shown in red and the cooling runs in blue coloured symbols)

4.6.2.4 State of LDH-St in Jojoba oil matrix

Figure 4.21 shows the diffractograms of stearic acid, LDH-St and the LDH-St/Jojoba oil formulation. The d-spacing of the LDH-St used is 4.98 nm. Next to the primary basal reflection is a shoulder which could be an indication of unreacted stearic acid. The typical characteristics of stearate-intercalated LDH have been previously discussed in other sections. After the heating and cooling run on the rheometer of the 30 wt.% formulation, XRD analysis was carried out on the sample and showed a slight decrease in the d-spacing (4.86 nm). This reduction could be a result of the exudation of the excess stearic acid. The peaks appear broader, especially the primary peak, which indicates the presence of numerous phases, as well as poor ordering. Such observations point to the possibility of delamination occurring to a certain extent.

The temperature scan XRD showed very little change within the anomalous region of 30–45 $^\circ\text{C}$ (see Appendix D). The d-spacing remained effectively the same. However, the element of shear was absent in the test and hence the results cannot be accurately correlated.

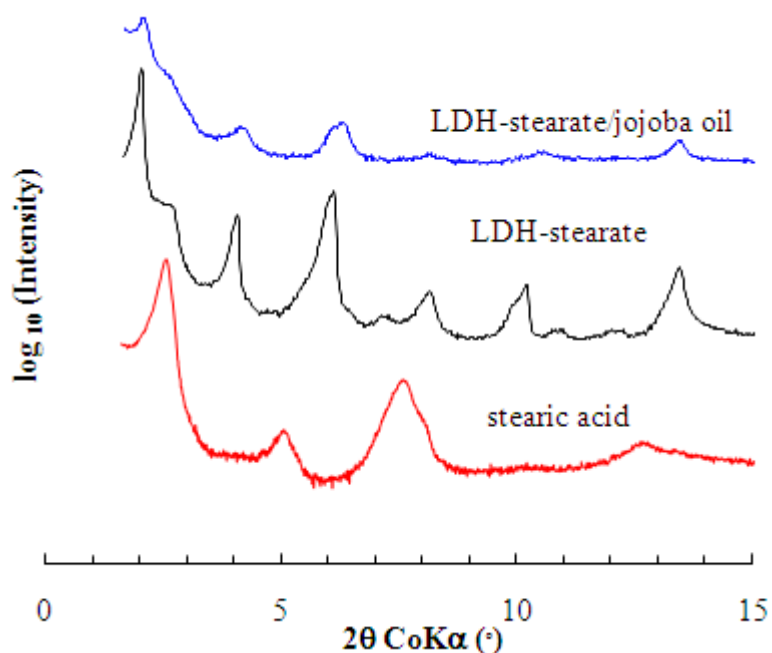


Figure 4.21. X-ray diffractograms of stearic acid, LDH-St and the LDH-St/Jojoba oil formulation

Figure 4.22 shows the FTIR spectra of the LDH-St/Jojoba oil formulation as temperature is increased. The spectra remained very similar to those of the bilayer intercalated LDH-St, which has previously been characterised to contain both un-ionised and ionised fatty acid species. A major change in the spectra was observed at 80 °C where the 1541 cm^{-1} peak, shoulder at 1643 cm^{-1} , disappears. Borja & Dutta (1992) assigned these peaks to unassociated carboxylic acid.

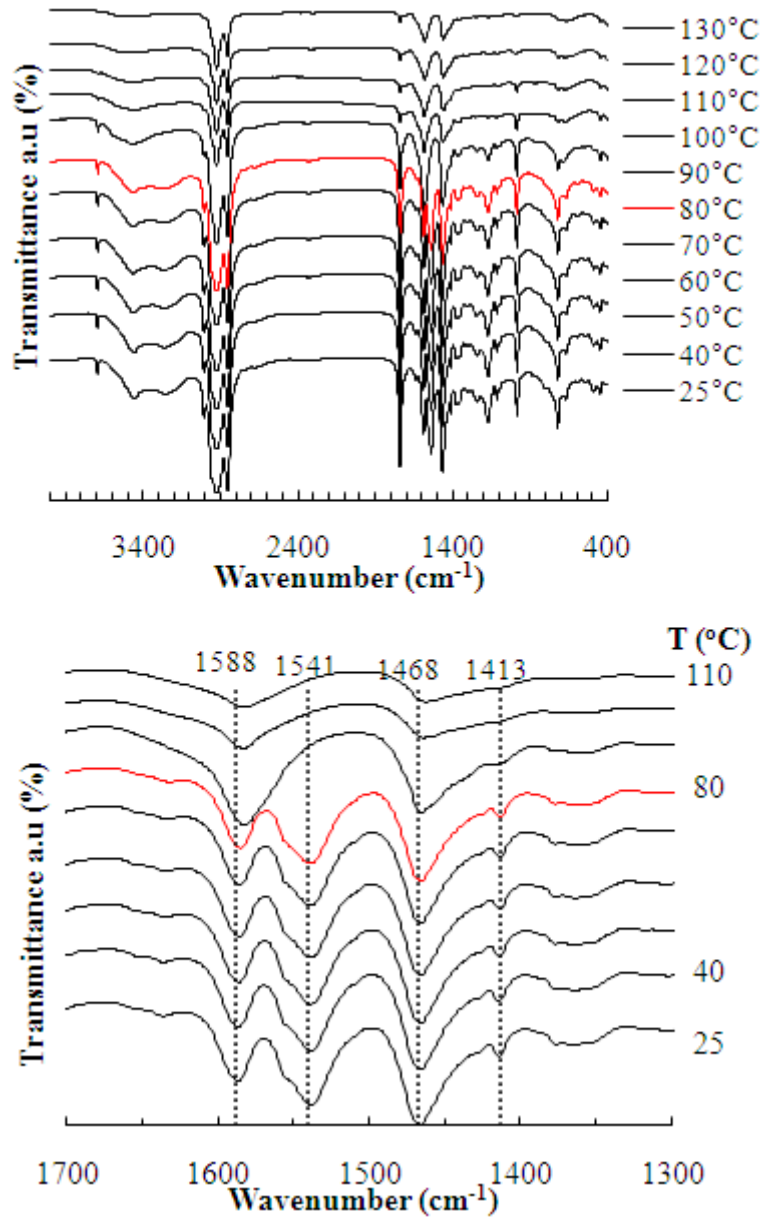


Figure 4.22. FTIR spectra of 30 wt.% LDH-St/Jojoba oil formulation obtained as temperature is increased

4.7 CONCLUSION

The viscosity of the 30 wt.% LDH-St formulation shows complex temperature behaviour at a constant shear of 30 s^{-1} . It was initially thought that the increase and decrease in the apparent viscosity on heating and cooling respectively, in the low-temperature range 20 to 35 °C, is caused by reversible delamination and reassembly to a partially intercalated form. However, experiments such as temperature-scanned IR, DSC and XRD conducted on the LDH-St Jojoba oil formulation did not correlate well with the proposed hypothesis. The XRD analysis of the gel exposed to a cycle of heating and cooling shows a reduction in the d-spacing which could be explained by the exudation of the excess stearic acid. On the other hand, the reduction in the d-spacing could also be explained by delamination. This is further supported by the lack of ordering shown by peak broadening and symmetry changes. However, there is no concrete evidence of restacking. A more plausible explanation is the formation of a fat crystal network formed from the anchoring of exuded stearic acid molecules to the subhedral LDH particles. The observed anomalous response appears to be strongly related to the crystal structure of the platelets used. Association between platelets and platelet-free fatty acid molecules results in flocculated structures and substantially larger particles respectively. These are envisaged to cause ‘viscosity drag’, hence increasing the apparent viscosity of the matrix.

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Chapter 5

Conclusion and Recommendations

The chapter presents the general conclusions and makes recommendations regarding the findings of the research. The more specific conclusions are found at the end of each chapter.

5. CONCLUSION AND RECOMMENDATIONS

The work described in the thesis is a further contribution to the Hydrotalcite Project at the Institute of Applied Materials, University of Pretoria. The one-pot fatty acid intercalation technique was developed by Landman *et al.*, 2005.¹ Different types of starting material were used, i.e. LDH-CO₃ and LDO. Nhlapo *et al.* (2008)² undertook a follow-up study using sodium dodecyl sulphate as a surfactant, and it was found that excess stearates were intercalated as their sodium salt. In this current study Tween 60 was employed, yielding sodium-free fatty acid-intercalated LDH. The carbonate form of layered double hydroxide (LDH-CO₃) was successfully intercalated with fatty acids (C₁₄–C₂₂) in a direct one-pot synthesis. The method yielded a product with minimal carbonate contamination. The highlights of this work with regard to the intercalation chemistry are:

- The different sizes and shapes of platelets formed during the modification process indicate that the intercalation entails dissolution and recrystallisation of the LDH-lattice.
- Intercalation can yield a mixed product, either aluminium-rich and/or magnesium-rich platelets or LDH platelets with the correct magnesium and aluminium ratio. Researchers have hardly probed the composition of the individual platelets, but from this study it would appear to be a worthwhile practice.
- High levels of intercalation are envisaged to be driven by the insertion of both ionised and un-ionised fatty acids.
- Changes occur in the interlayer structure as temperature is increased and the excess fatty acids are eventually exuded at elevated temperatures.

Polymer composites containing 5 and 10 wt.% LDH-St or LDH-CO₃ were prepared via melt-compounding. No marked difference in characteristics was observed and hence the 10 wt.% formulation formed the basis of the current study. The polymer matrices employed were EVA, LLDPE and EVAL. The LDH fillers appear to act as nucleating agents for EVA and LLDPE as the DSC crystallisation temperatures increased. However, in the EVAL

¹ Landman, E. P. (2005) Stearate intercalated layered double hydroxides: Methods and application. PhD thesis, Pretoria: University of Pretoria.

² Nhlapo, N., Motumi, T., Landman, E., Verryn, S. M. C. & Focke, W. W. (2008). Hydrotalcite: Surfactant-assisted fatty acid intercalation of layered double hydroxides. *J. Mater. Sci.*, 43(3): 1033–1043.

composites nucleation appeared to be retarded. A marked improvement in the Charpy notched impact strength was noted for the EVAL/LDH-St composite. The difference in the performance of the EVAL/LDH composites, compared with the less-polar polymers, is tentatively attributed to strong hydrogen bonding interaction between the -OH groups on the polymer backbone and those on the clay sheets. The melt-compounding process involved the removal of excess interlayer stearate anions, resulting in a monolayer arrangement. The exuded stearate ions were found to have lubricating and plasticising effects on the matrices. Although various improvements were obtained, it would be more beneficial to make composites from low-melting polymer matrices. In this instance the true nature of the organo-LDH is conserved.

In order to make a more detailed interpretation of the changes in mechanical properties presented earlier, an in-depth study of other factors, such as processing, thermomechanical history and structure development, is essential. Changes in molecular weight, orientation of polymer chains and filler, as well as crystallinity, all play a major role in the properties observed.

Although LDH-based composites appear to be attractive, their utilisation is hampered by their small aspect ratio (an aspect ratio of less than 80). Within a specific area ($A_{sp} < 100 \text{ m}^2/\text{g}$), the platelets are thin (about 0.5 to 0.8 nm) and fragile (as seen by the platelet size reduction after melt processing). These properties can be manipulated in the use of LDHs as rheological modifiers in cosmetic or personal care product formulation. This section of the Hydrotalcite Project demonstrated the effectiveness of LDH-St as a rheological modifier by increasing the viscosity of the Jojoba oil. When viscosities of organo-LDH/Jojoba oil formulations were studied as a function of temperature, gelling was observed. This has been attributed to the formation of a fatty acid crystal network from the exuded excess acid. However, the gels were observed to form preferentially from subhedral-shaped LDH particles. Further study is essential to ascertain the effect of platelet shape on the anomalous viscosity observation. Particles with a uniform size distribution should be employed in the study. Modified LDHs could also be used for emulsion stabilisation.