



RHEOLOGICAL CHARACTERISTICS OF PETROLEUM JELLY FORMULATIONS CONTAINING ORGANICALLY MODIFIED LAYERED DOUBLE HYDROXIDES

DAMODAR MOSANGI^{1,2,3}, SREEJARANI KESAVAN PILLAI^{1*},
LUMBIDZANI MOYO¹ AND SUPRAKAS SINHA RAY^{1,2}

¹DST/CSIR National Centre for Nanostructured Materials, Council for Scientific and Industrial Research, 0001, Pretoria, South Africa.

²Department of Applied Chemistry, University of Johannesburg, Droonfontein 2028, Johannesburg, South Africa.

³AMKA Products Pty Limited, Innovation Building, 14 Ellman Street, Sunderland Ridge, Centurion 0157, Pretoria, South Africa.

AUTHORS' CONTRIBUTIONS

This work was carried out in collaboration between all authors. Author DM designed the study, performed the experimental work and wrote the protocols. Authors SKP and LM managed the analyses, managed literature and wrote the first draft of the manuscript. Suprakas Sinha Ray reviewed and corrected the manuscript. All authors read and approved the final manuscript.

ARTICLE INFORMATION

Editor(s):

(1) Nagatoshi Nishiwaki, Kochi University of Technology, Japan.

(2) Ling Bing Kong, Nanyang Technological University, Singapore.

Reviewers:

(1) Ayi A. Ayi, Federal University, Nigeria.

(2) Joel Obed Herrera Robles, Autonomous University of Ciudad Juarez, Mexico.

(3) Margarita Teutli León, Benemerita Universidad Autónoma de Puebla (BUAP), Mexico.

Received: 04 June 2018

Accepted: 20 August 2018

Published: 08 September 2018

Original Research Article

ABSTRACT

The effectiveness of stearic acid modified layered double hydroxides (OLDH) as viscosity modifier and stabilizer in petroleum jelly (PJ) formulations has been studied and its rheological properties evaluated. Mg-Al-LDH was organically modified using stearic acid which is anionic surfactant widely used in topical formulations. Successful incorporation of stearate anion into LDH interlayers was confirmed by XRD, FTIR, SEM, and TGA results. PJ formulations were prepared using different OLDH contents (0.5, 1, 1.5 and 2 wt. %) using a high shear mixer. The incorporation of OLDH significantly increased the viscosity of the PJ formulations which is explained by strong interaction between OLDH particles and hydrocarbon chains of PJ. The percolation threshold was observed to be at 1.5 wt.% of OLDH loading suggesting the presence of a well-developed interface between the filler and the polymer matrix. The non-Newtonian shear thinning indicated the formation of gel-like structure. Dynamic state rheological data of PJ formulations showed a dominance of elastic property imparted by solid phase in OLDH based system. OLDH, therefore, showed great promise as an efficient structural ingredient in cosmetic formulations offering viscosity enhancement as well as shear thinning behaviour which could result in formulation stability, better skin feel and spreadability.

*Corresponding author: Email: SKPillai@csir.co.za;

Keywords: Layered double hydroxide; organically modified layered double hydroxides; characterization; petroleum jelly; rheological properties.

1. INTRODUCTION

Petrolatum (petroleum jelly (PJ) or Vaseline) is one of the ancient skin treatment products and are widely used in cosmetics and pharmaceuticals industries [1]. In pharmaceutical industry, PJ is used as a base material in a variety of topical ointment formulations to minimize various skin diseases. Its occlusive, as well as healing characteristics render this substance particularly efficient against dry and damaged skin [2, 3]. Because of its lipophilic character, physical and chemical inertness, PJ is also used as an essential ingredient in many formulations of cosmetic products providing different types of skin care and protection by minimising friction or moisture loss or by functioning as a grooming aid [4].

PJ is chemically similar to mineral oil. While mineral oil contains mainly liquid hydrocarbons, PJ is a mixture of solid and liquid hydrocarbons (normal, iso and ring paraffins) in the form of 3D gel structure and hence is in a solid state at room temperature [5]. PJ is thus considered as a soft microcrystalline wax with high oil content [6]. Although PJ is petroleum (fossil fuel) based product, components derived from synthetic sources can be added to overcome its drawbacks such as greasiness and resistance to washing in cold soap and detergent solutions [7,8]. However, in such formulations, obtaining the desired stability, viscosity and 3D-network structure formation remain a challenge. Disruption of 3D-network structure causes liquid components to separate from the heavier components leading to an unstable formulation. In such cases, ingredients that can act as binders are required to obtain a stable formulation [8,9].

The incorporation of synthetic additives can greatly alter the rheological properties of PJ itself which is very crucial in deciding the quality and function of final products in cosmetics where PJ is used as a main or supportive ingredient. The problems such as liquid separation, lack of structure and required viscosity could be related to the poor dispersion of the internal phase as well as the degree of shear sensitivity of PJ formulation [9]. There have been many studies to investigate the rheological properties of PJ during past decades [3, 10-12]. However, only a little attention has been given to PJ compositions containing additives that could have great impact on its performance characteristics. The use of synthetic wax components such as Fischer-Tropsch wax in petrolatum formulation that can alter the rheological properties and hence the skin sensation has been reported recently [13]. US patent 3852475 [7]

describes topical compositions containing solid starch and hydrophobic starch. The invention claims that the inclusion of hydrophobic starch reduces the greasy appearance and its resistance to washing although the rheological property of the formulation was not investigated.

Layered double hydroxides (LDHs) are synthetic anionic clay minerals represented by the molecular formula $M_{(1-x)}M_{3x}(OH)_2^{x+} \cdot (A^-)_x \cdot nH_2O$ where M_2 , M_3 and A^- represent divalent, trivalent cations and anions respectively [14]. They have well-ordered brucite like layer structure in which the cations are octahedrally coordinated by six oxygen atoms as hydroxides. The substitution of the M^{2+} with M^{3+} ions imparts a net positive charge to the sheets which are compensated by exchangeable interlayer anions and water [15]. The intrinsic hydrophilic surface property of LDHs can be modified through surface modification or intercalation with anionic surfactants [16-19]. Organo-LDHs are oil compatible hydrophobic organic compounds and hence could be used as phase stabilizers and rheology modifiers in oil rich formulations. Focke et al. [20] showed strong shear thinning behaviour and anomalous temperature dependence of jojoba oil containing stearic acid intercalated Mg-Al-LDHs. Naime Filho et al., [21] incorporated glycine or alanine modified LDHs into a silicone matrix containing Dimethicone, PEG-8 phosphate (PE-100) and obtained a drastic change in the rheological behaviour, due to an extensively developed gel-like structure for the nanocomposite derivatives. While shear-thinning nature was evident, the critical concentration was observed to be 5% suggesting the presence of a largely developed interface between the filler and the polymer. The increase in viscosity was explained by the rather strong attrition phenomenon between amino acid anions and the silicone chains.

Inspired by these early investigations, the objective of this work is to study the effectiveness of stearic acid modified layered double hydroxides (OLDH) as a binder/stabilizer in PJ formulation and to evaluate shear flow properties of corresponding formulations. The interest is to develop an improved PJ composition in terms of flow properties, stability as well as colour and feel of the product on the skin.

The use of organic modified layered double hydroxides (OLDH) in PJ products is largely unknown. OLDH is expected to provide multifunctional benefits such as thickening, a 3D-network structure, prevention of phase separation, colour and consistency through interaction of organic

surface layer with oil phase of the formulation. The fact that no reference to OLDH in petroleum jelly formulations could be found in literature indicates that the process and the product are unique.

2. EXPERIMENTAL

2.1 Materials

Hydrotalcite (Pural MG 70) of chemical formula $Mg_{2x}Al_2(OH)_{4x+4}CO_3 \cdot nH_2O$ was supplied by Sasol Germany (referred to as LDH), which was synthesized by hydrolysis of hetero-metallic alcoholates. Stearic acid was supplied by Bio-zone chemicals, Kempton Park, South Africa. Distilled water was used in all experiments. Other chemicals used were sodium dodecyl benzene sulphonate (Fluka 98%), ammonium hydroxide (25%, Sigma Aldrich) mineral oil and microwax (Akulu, South Africa), paraffin wax (Sasol, South Africa), Amka wax (Amka, South Africa).

2.2 Methods

2.2.1 Synthesis of organically modified LDH (OLDH)

The surfactant assisted intercalation method [19] was used for the organic modification of LDH. In a typical procedure, 50 g LDH, 33.3 g stearic and 40 g of sodium dodecyl benzene sulphonate were suspended in 1.5 L de-ionized water. The mixture was heated to 80°C for 8 h and allowed to cool overnight. The pH of the mixture was kept above 10 using ammonium hydroxide. Two additional portions of stearic acid (33.3g) were added in second and third cycle. The mixture is further allowed to stir for 8 h at 80 °C and then cooled slowly to ambient temperature. The sample was recovered by centrifugation and washed several times with water, ethanol and acetone to remove excess stearic acid.

2.2.2 Preparation of PJ formulation containing OLDH

To a weighed mineral oil in a beaker specific concentration of OLDH was added and mixed with high shear mixer (silverson, USA) at 2000 rpm for 2-3 minutes. This was followed by the addition of micro wax, paraffin wax and finally Amka wax. All the ingredients were mixed with spatula for 1-2 minutes and heated to 75-80°C, while continuously stirring to help the waxes dissolve faster. The mixture was left to cool down about 40°C. After packing, the sample was sent for stability and rheology testing. Table 1 shows the constituents of the formulations used in the current study. A series of formulations were prepared by varying the amount of OLDH.

Table 1. Composition of PJ formulations

Entry	Ingredients	Percentage (%)
1	Mineral oil	Q.S.
2	Microwax	10-27
3	OLDH	0.1-2.0
4	Paraffin wax	10-25
5	Amka wax	1

2.2.3 Characterization of OLDH

X-ray diffraction (XRD) studies were conducted using an X'Pert PRO X-ray diffractometer (PANalytical, Netherlands) operating with Cu K- α radiation (wavelength of 0.15406 nm) at 45 kV and 40 mA. The exposure time and scan speed for the XRD measurements were 19.7 min and 0.036987 °/s, respectively. The presence of stearate moieties on LDHs was confirmed by Fourier transform infra-red spectroscopy (Perkin-Elmer Spectrum 100 spectrometer, USA) with the MIRacle ATR attachment and a Zn/Se plate. A small amount of sample was pressed onto the Zn/Se plate and spectra over the range of 550 to 4000 cm^{-1} were collected. Morphological characteristics of neat LDH and OLDH were obtained using scanning electron microscopy (JEOL, JSM 7500F, Japan) at 3-kV acceleration voltage. Thermogravimetric analysis of neat LDH and OLDH was performed using thermogravimetric analyzer (TGA, TA instruments, model Q500, USA). The temperature was ramped at 10°C min^{-1} in air, from 25°C to 900°C. The stearic acid loading capacity of LDH was determined from the residue weight percentage analysis.

2.2.4 Rheological measurements

The steady and dynamic state rheology properties of PJ formulations containing different concentrations of OLDH and neat PJ were measured on an Anton Paar MCR501 rheometer using parallel plate geometry (PP50) with the gap set at 1.15 mm. The sample was placed at the centre of the stationary plate. In steady state measurements, the shear rate was increased from 0.01 to 100 s^{-1} and the flow curves were obtained under isothermal condition (26°C). In dynamic mode, amplitude sweep was performed to determine the linear viscoelastic region as well as the flow point (yield) of the samples. The angular frequency was set at 6.28 rad/s and the strain varied from 0.01-200%. The frequency-sweep tests were carried out by varying the angular frequency between 0.1 and 100 $rad s^{-1}$ at a fixed strain of 0.002%. The samples were kept at rest for 2 min before shearing and all experiments were carried out in triplicates.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of OLDH

Fig. 1 shows the X-ray diffractograms for neat LDH and OLDH. LDH shows sharp reflections at $2\theta = 11.65^\circ$, 23.28° and 35.05° , due to (003), (006) and (009) diffraction planes respectively. The (003) reflection at $2\theta = 11.65^\circ$ corresponds to the basal spacing close to 0.78 nm that is typical of highly crystallized LDH structure [22]. The basal spacing is composed of an Al-bearing brucite-like octahedral layer whose thickness and interlayer spacing is influenced by the size and alignment of the interlayer anion [23]. Assuming the brucite-like layer thickness of approximately 0.48 nm as reported by Miyata et al. [24], the interlayer spacing can be calculated as 0.3 nm which is in good agreement with the spacing of the CO_3^{2-} intercalated Mg-Al-LDH.

However, a shift of LDH peaks to lower 2θ was observed in the case of OLDH which is indicative of intercalation of stearate anions in to LDH inter layers. The sharp and symmetric peaks indicate highly ordered structure in OLDH. The modification of LDH with stearate ions increased the clay interlayer distance from 0.78 nm to 5.23 nm, suggesting intercalation and self-assembly of stearate anions within the interlayer space [25]. The reflections at 5.23 nm ($2\theta = 1.7^\circ$), 2.61 nm ($2\theta = 3.4^\circ$) and 1.74 nm

($2\theta = 5.06^\circ$) are in agreement with bilayer arrangement of carboxylic acids as per the previous reports. According to Xu and Braterman [26], the slant (contact/tilt) angle of the intercalated fatty acid anion can be calculated using the equation, $d = 1.48 + 0.26(n-2) \sin\phi$ where d is the d-spacing n is the carbon number in the stearate chain, ϕ is the slant angle of stearate anions. As per this equation, the tilt angle of stearate anion in this case is calculated to be 62° , which is in close agreement with the reported value of 61° by Itoh et al. [25]. The existence of characteristic peaks of pristine LDH in OLDH shows that the intercalation of stearate ions was not complete and it rather shows co-existence of unmodified LDH minor phase with different interlayer spacing. This observation is agreement with Eshwaran et al. [27] who proposed the presence of pristine and intercalated phases of Zn-Al LDH-stearate nanohybrid.

To substantiate XRD results, FTIR analysis of LDH and OLDH was done and the spectra are compared in Fig. 2. The neat LDH showed a broad band in the range of $3400\text{--}3500\text{ cm}^{-1}$ which is attributable to --OH stretching vibrations of the intercalated water molecules and octahedral layer of LDH [28,29]. The band in the range $1650\text{--}1600\text{ cm}^{-1}$ is assigned to the bending vibration from the interlayer water. The presence of carbonate anion is confirmed by the characteristic peaks observed at $850\text{--}880\text{ cm}^{-1}$, $1350\text{--}1380\text{ cm}^{-1}$, and $670\text{--}690\text{ cm}^{-1}$ [18]. The bands

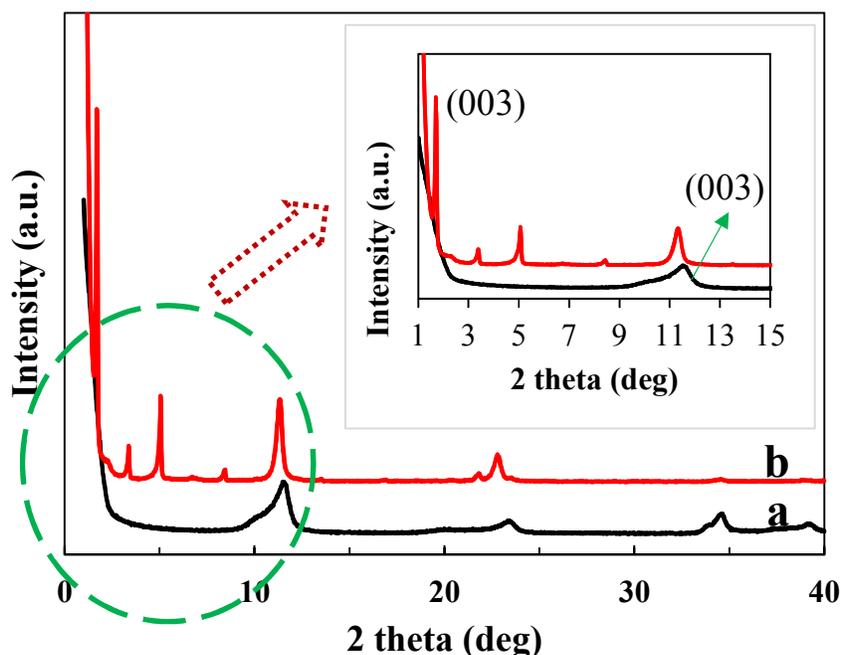


Fig. 1. XRD spectrum of (a) Neat LDH (b) OLDH

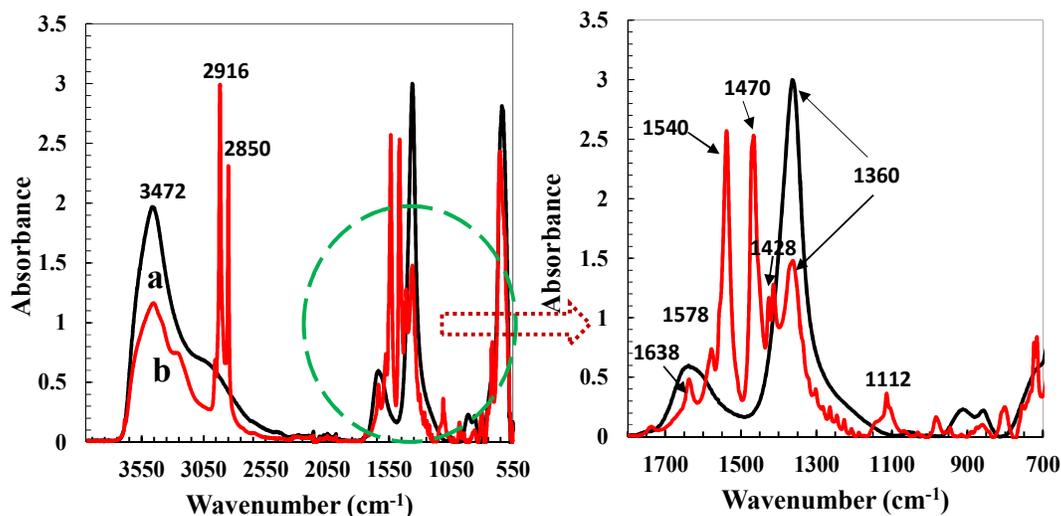


Fig. 2. FTIR spectrum of (a) Neat LDH (b) OLDH

recorded at low-frequency region of 400–700 cm^{-1} correspond to the vibration of M-O bond in the brucite like lattice that is typical of this kind of layered solids [30,31]. For OLDH, additional bands at 2918 cm^{-1} and 2850 cm^{-1} appeared which are attributed to asymmetric and symmetric stretching vibrations of $-\text{CH}_2-$ group of the alkyl chain of stearate anion respectively [32]. The presence of bands at 1638, 1578, and 1540 cm^{-1} is related to asymmetric while the bands at 1470, 1428 cm^{-1} are associated to symmetric stretching vibrations of carboxylate (COO^-) anion which confirms the intercalation of the stearate anions into the interlayer region of LDH [33]. The intensity of the peak at 1360 cm^{-1} gives an indication of the degree of exchange of the carbonate anion by stearate anions, of which in this case significantly reduced showing replacement of carbonate anion with stearate ions in the interlayer region [34]. However, the presence of low-intensity carbonate peak in OLDH indicates that with stearic acid modification, complete removal of carbonate anion from the interlayer space was not achieved. According to Anbarasan et al. [35], this might be due to the high charge density of LDH layers and rapid uptake of CO_2 by water molecule from atmosphere leading to re-substitution reactions. This result is in agreement with the XRD spectrum of OLDH where the existence of neat LDH as minor phase impurity was evident.

Fig. 3 shows the SEM images of the neat LDH and LDH-St hybrid. The neat LDH (Fig. 3(a)) had hexagonal plate-like morphology. Generally, the neat LDH exhibits hexagonal platelet morphology at the micro scale resulting in the preferential growth of *ab* faces (i.e., perpendicular to the stacking direction

[36]. Whereas, the steric acid intercalated LDH hybrid materials shows larger platelet and retained the hexagonal structure with coarse or irregular surface morphology. This may indicate that the intercalation process involves dissolution and recrystallization of the neat LDH to LDH-organo materials [18,37]. Furthermore, the change in crystal size morphology shows that the intercalation process was followed by recrystallization process.

TGA and DTG curves of neat LDH and OLDH are shown in Fig. 4. A continuous mass loss in four stages is observed in the thermograms till 500°C after which a plateau is reached. The thermal decomposition of unmodified LDH showed four decomposition steps related to loss of physically adsorbed and interlayer water molecules (50-150°C), dehydroxylation (190°C), a combination of dehydroxylation-decarbonation reaction (306°C) and oxidative degradation of anions attached to LDH within interlayer (394°C), respectively [38]. OLDH showed additional decomposition peaks which may be attributed to the decomposition of intercalated stearate ions. The residual weight percentage comparison of LDH and OLDH suggest that the total organic component in OLDH is approximately 30%.

3.2 Rheological Properties of PJ Containing OLDH and Its Relevance to Real Life Application

Fig. 5 presents the steady state shear viscosities of standard PJ and PJ formulations containing varying concentrations of OLDH. In steady state rheology measurement, the sample is exposed to increasing rotational shear stepwise and the viscosity of the

sample is measured as a function of shear rate. The viscosity curves thus obtained represent the flow behaviour of the sample over a wide range of shear rate simulating the behaviour of the fluid under different conditions (e.g. low shear rate simulate the sample at rest, while high shear rates simulate the sample during application [39]. From Fig. 5, it is clear that the initial viscosity of PJ formulations containing OLDH is always higher than that of the standard PJ indicating that the OLDHs function as a thickening agent. The absolute value of initial viscosity observed for standard PJ and PJ formulation containing 0.5, 1, 1.5 and 2 % OLDH are 221, 1610, 12900, 7200 and 5000 Pa.s respectively which indicates highest thickening effect in system containing 1.5 % OLDH. Increasing concentrations of OLDH up to 1.5 wt. % created 3D network structure thus resulting in higher viscosities. Based on the report by Xu et al. [40] and Sochi et al. [41] higher viscosity of OLDH systems can be attributed to some strong interaction between

particles and the polymer chains in the wax where OLDH forms a 3D network structure that acts as a barrier to the polymer flow. This network formation may hinder the relaxation of the hydrocarbon polymer matrix when subjected to increasing shear. Decrease in viscosity for formulation containing 2 wt.% ODH indicates possible aggregation of OLDH particles at higher concentrations.

From Fig. 5 it is also clear that all the systems including standard PJ show non-Newtonian behaviour and the shear viscosity gradually decreases with increase in shear rate demonstrating shear thinning which is the common flow behaviour of most of the cosmetic formulations. According to Park et al. [3], the shear thinning behaviour at high shear rate guarantees a high degree of mixability and spreadability during their processing and actual usage (as well as in other pharmaceutical and cosmetic products). The shear rate dependency of these

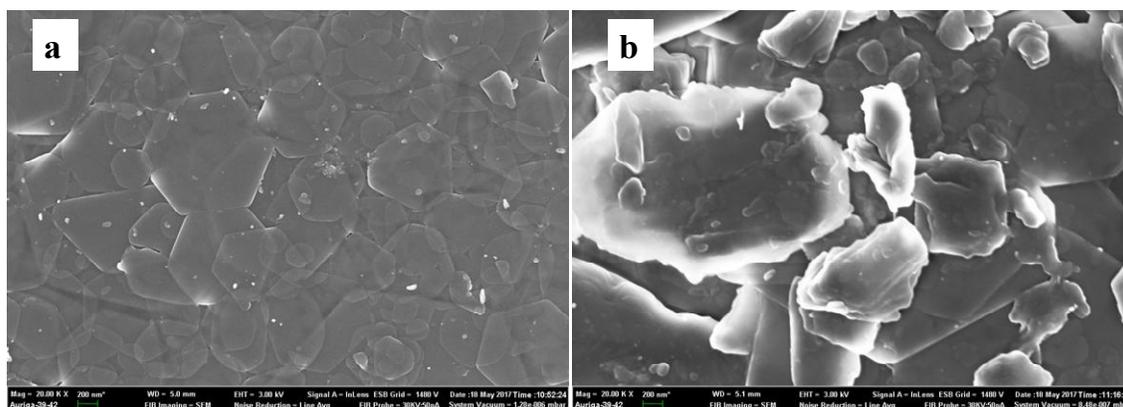


Fig. 3. SEM images of (a) Neat LDH (b) OLDH

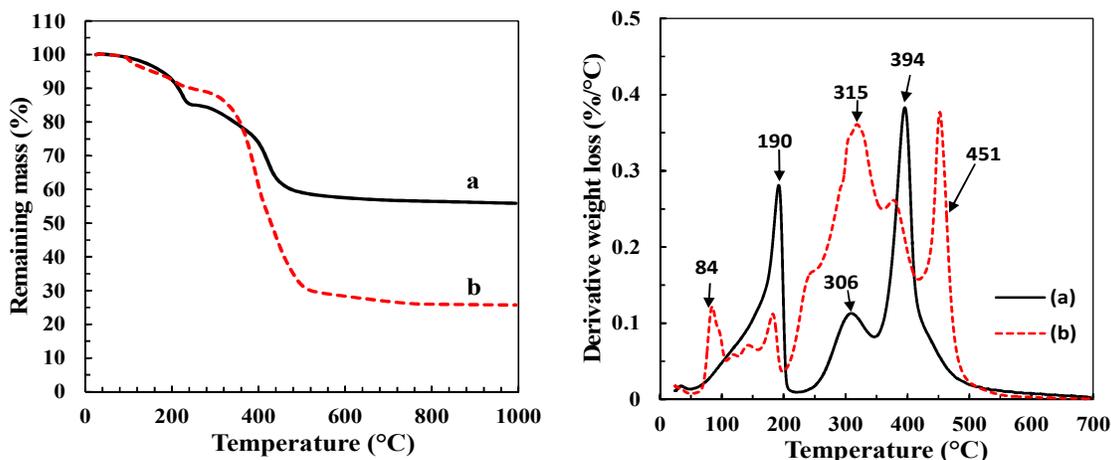


Fig. 4. TGA and DTG curves of (a) Neat LDH (b) OLDH

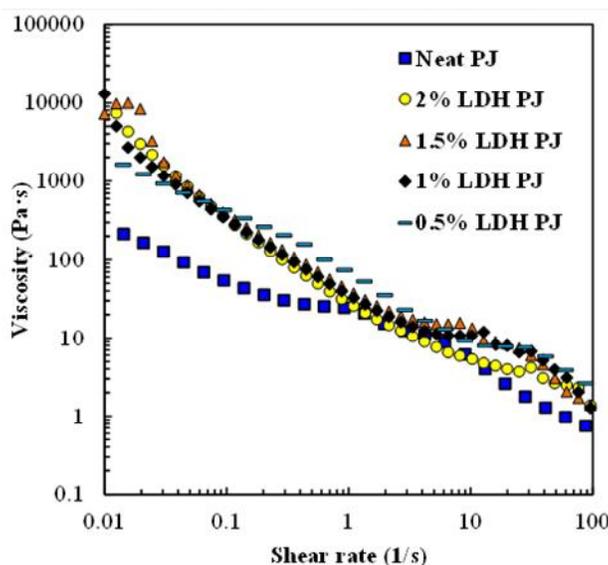


Fig. 5. Steady state shear viscosities of standard PJ and PJ formulations containing varying concentrations of OLDH as a function of shear rate

formulations can be described by a well-known power law (or Ostwald-de Waele)

$$\eta(\dot{\gamma}) = K\dot{\gamma}^{n-1} \quad (1)$$

Where; η is the shear viscosity, $\dot{\gamma}$ is the shear rate, K is the consistency index and n is the flow behaviour index [42]. Generally, Newtonian behaviour is exhibited when n is equals to 1 whereas shear thinning behaviour is less pronounced as n tends to 1. The smaller the value of n , the greater is the degree of shear thinning. The calculated values for n is presented in Table 2 which indicate lower n values for all OLDH containing systems in comparison to standard PJ showing better spreadability of the new formulations on human skin.

It is apparent from Table 2 that the new PJ formulations containing OLDH exhibit a higher magnitude of yield stress in comparison to the commercial PJ and this is attributed to the 3D-network structure imparted by the presence of OLDH that can exhibit a resistance to the flow. During PJ formulation preparation, when molten material is cooled, the 3D network is developed through the interaction of lipophilic OLDH and hydrocarbon phase by sorption mechanism. When sufficient shear stress is applied the 3D network breaks down, leading to shear thinning flow behaviour. The shear viscosity, as well as yield stress of new PJ formulations, increase with increasing the OLDH content up to 1.5 wt% and decline thereafter. This established the critical concentration of OLDH to be 1.5 wt% above

which the structural strength decreases. The standard PJ showed very low shear stress when compared to other formulations with OLDH. The higher yield stress observed for PJ formulations containing OLDH also indicate higher shelf life and storage stability of the products as reported by Brummer et al. [43]. It has been observed that the hydrophobic nature of OLDH has considerably enhanced the stability of PJ for the followed period of 6 months under different storage conditions (results not shown).

Table 2. Calculated flow behaviour index for standard PJ and PJ formulations containing OLDH

Sample I.D	$\eta(\dot{\gamma}) = k\dot{\gamma}^{n-1}$	Yield Stress (Pa)
Neat PJ	0.30	53.12
0.5 % LDH PJ	0.18	68.55
1 % LDH PJ	0.17	132.5
1.5 % LDH PJ	0.1	239.1
2 % LDH PJ	0.05	212.1

To gain some understanding of the microstructure of PJ formulations, dynamic oscillatory shear rheological measurements were conducted in the linear viscoelastic region and the results are presented in Figs. 6 a and b. In oscillatory sweep tests, the measuring system moves back and forth over a range of frequency and amplitude. The given strain and shear stress are used to calculate the storage modulus G' and loss modulus G'' . The storage modulus G' is a value of the stored deformation energy in the system,

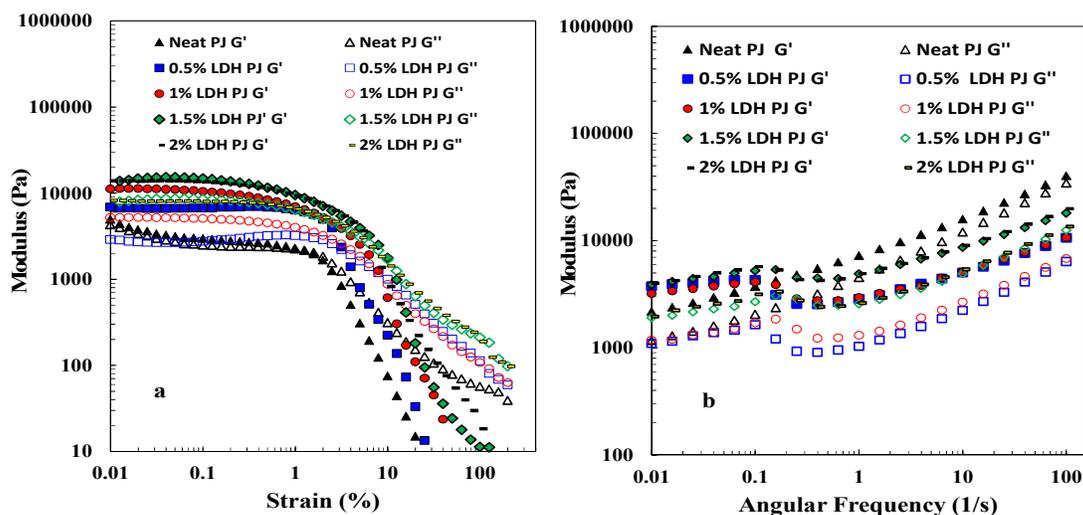


Fig. 6. Dynamic oscillatory rheological modulus of standard PJ and PJ formulations containing varying concentrations of OLDH as a function of a) strain b) angular frequency

typical of elastic (solid part) portion of the sample which gives information about the reversible deformation behaviour and structural stability of the sample. The loss modulus G'' represents the lost deformation energy and therefore characterizes the viscous portion (liquid part) of the sample providing information about the irreversible deformation behaviour. Oscillatory test generally starts with an amplitude sweep where strain is varied between 0.01% and 100% at the constant angular frequency. We can use the plots of G' and G'' against strain to identify the linear viscoelastic strain range (LVE) (where the sample structure is not destroyed by applied strain/deformation). Frequency sweep is done in the LVE range and is used to predict long (low frequencies) and short term (high frequencies) behaviour of the sample. The ratio of G'' and G' is called loss factor ($\tan\delta$) which gives further idea about the sample structure [39].

Fig. 6a compares the storage (G') and loss moduli (G'') of neat PJ with PJ formulations containing various OLDH concentrations. Evidently, for neat PJ, at higher applied strains, G'' predominated over G' indicating fluid-like behaviour of hydrocarbons. In OLDH based systems, at all concentrations except 2 wt.% OLDH, G' is higher than G'' suggesting that the rheological property of PJ is dominated by elastic property imparted by solid phase rather than the viscous property. The LVE range representing the elastic strength of the material is observed to be higher for OLDH systems in comparison to neat PJ which indicates that incorporation of OLDH helped to form an internal structure through 3D network formation. This could mean that higher force is

needed for irreversible deformation which in turn shows higher structural and storage stability of PJ formulations containing OLDH. In frequency sweep plots (Fig. 6b), the critical strain, for all the systems, G' dominates over G'' both at low and high frequencies-typical gel-like (solid-like) behaviour and this shows both long and short term-sample stability of the samples and less chance of separation.

Naime Filho et al. [21] obtained a percolated non-Newtonian flow in silicones by incorporating glycine and alanine modified Mg-Al-LDH. They reported higher storage modulus for silicone-LDH composites with a percolation threshold between 2.5 and 5 wt% of filler loading LDH against unmodified silicone. They interpreted such behaviour by the exfoliation of modified fillers in silicone matrix that forms an extensive network through strong interfacial interaction between the organic anions in LDH and silicone polymer chains. It could be that a similar mechanism occurs in our case with rheological evolution of OLDH containing PJ formulations. Through strong interaction between the organic moieties present on LDH surface, the 3D network structure could be strengthened which further immobilizes the liquid hydrocarbons (normal and iso-paraffins) resulting with significant improvement in storage modulus and viscosity [44]. This is further substantiated by the presence of non-terminal behaviour of the moduli in the OLDH containing PJ at lower frequencies. As the shear rate increases the microstructure can orient with flow direction thus leading to shear thinning behaviour [45]. OLDH, which is hydrophobic and that has surface organic groups can be considered as an excellent shape

anisotropic nanomaterial that is able to stabilize the oil phase via particle assembling and network formation.

In summary, it is identified that OLDH shows great promises as rheology modifier to traditional petroleum jelly formulations offering viscosity enhancement as well as shear thinning behaviour which is directly related to formulation stability, skin feel and spreadability which are crucial for preparation of cosmetic and pharmaceutical products for topical applications. Additional tests on evaluation of sensory properties are underway with the commercial partner.

4. CONCLUSIONS

The objective of the study was to investigate the possibility of employing organically modified layered double hydroxides as a rheology modifier for petroleum jelly formulation through linear and non-linear rheological property measurement. The systematic characterization results from this study indicate that OLDH can act as an effective thickener for PJ formulations. Incorporation of 0.5 to 1.5 % OLDH results in 10-fold increase in viscosity in comparison to the standard reference PJ formulation with significant increase in yield stress. This is attributed to the 3D network formation of PJ hydrocarbons with the LDH particles through the surface organic groups which enhance the resistance to flow of polymer chains. Under mechanical shear, non-Newtonian shear thinning behaviour is observed for PJ formulations containing OLDH which could enhance skin feel and spreadability of the product. Non-linear rheological properties show dominance of solid-like behaviour of the OLDH based formulations. Based on the rheological properties, higher storage stability (shelf life), primary and secondary skin feel on actual application onto human body or skin are predicted for OLDH based PJ formulations.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Chang GS, Koo JS, Song KW. Wall slip of vaseline in steady shear rheometry. *Korea Aust. Rheol. J.* 2003;15(2);55-61.
2. Rose W, Zimmerman AC. US. Patent No. 5,407,678; 1995.
3. Park EK, Song KW. Rheological evaluation of petroleum jelly as a base material in ointment and cream formulations: steady shear flow behavior. *Arch. Pharm. Res.* 2010;33(1);141-150.
4. Wang YP, Wang MC, Chen YC, Leu YS, Lin HC, Lee KS. The effects of vaseline gauze strip, merocel, and nasopore on the formation of synechia and excessive granulation tissue in the middle meatus and the incidence of major postoperative bleeding after endoscopic sinus surgery. *J. Chin. Med. Assoc.* 2011; 74(1);16-21.
5. Presting W, Keil G. Ein Beitrag zur Strukturuntersuchung von Mineralfetten III. Zum Gebrauchswert von Vaselinen. *Chem. Tech.* 1936;8;36.
6. Pena LE, Lee BL, Stearns JF. Structural rheology of a model ointment. *Pharm. Res.* 1994;11(6);875-881.
7. Tarangul EV, US Patent 3852475; 1974.
8. Bekker M, Webber GV, Jacobs C, Louw NR, Montgomery NT, Van Rensburg VJJ. US. Patent Application No. 14/361,204; 2012.
9. Longer MA, Ch'Ng HS, Robinson JR. Bioadhesive polymers as platforms for oral controlled drug delivery III: oral delivery of chlorothiazide using a bio adhesive polymer. *J. Pharm. Sci.* 1985;74(4);406-411.
10. Boylan JC. Rheological study of selected pharmaceutical semisolids. *J. Pharm. Sci.* 1966; 55(7);710-715.
11. Davis SS. Viscoelastic properties of pharmaceutical semisolids I: Ointment bases. *J. Pharm. Sci.* 1969;58(4);412-418.
12. Pandey P, Ewing GD. Rheological characterization of petrolatum using a controlled stress rheometer. *Drug Dev. Ind. Pharm.* 2008;34(2);157-163.
13. Bekker M, Webber GV, Louw NR. Relating rheological measurements to primary and secondary skin feeling when mineral-based and Fischer-Tropsch wax-based cosmetic emulsions and jellies are applied to the skin. *Int. J. Cosmet. Sci.* 2013;35(4);354-361.
14. Arizaga GGC, Satyanarayana KG, Wypych F. Layered hydroxide salts: Synthesis, properties and potential applications. *Solid State Ionics.* 2007;178(15):1143-1162.
15. Bergaya F, Theng BKG, Lagaly G (Eds.), *Handbook of Clay Science. Developments of Clay Science, Volume 1, Elsevier Ltd. Amsterdam.* 2006;1021.
16. Adachi-Pagano M, Forano C, Besse JP. Delamination of layered double hydroxides by use of surfactants. *Chem. Commun.* 2000;1; 91-92.

17. Costa FR, Leuteritz A, Wagenknecht U, Jehnichen D, Haussler L, Heinrich G. Intercalation of Mg–Al layered double hydroxide by anionic surfactants: preparation and characterization. *Appl. Clay Sci.* 2008; 38(3):153-164.
18. Moyo L, Nhlapo N, Focke WW. A critical assessment of the methods for intercalating anionic surfactants in layered double hydroxides. *J. Mater. Sci.* 2008;43(18):6144-6158.
19. Nhlapo N, Motumi T, Landman E, Verryn SM, Focke WW. Surfactant-assisted fatty acid intercalation of layered double hydroxides. *J. Mater. Sci.* 2008;43(3):1033-1043.
20. Focke WW, Moyo L, Labuschagne FJWJ, Hoosen NG, Ramjee S, Saphiannikova M. Anomalous shear viscosity–temperature behaviour of jojoba oil/LDH-stearate suspensions. *Colloids Surf. A. Physicochem. Eng. Asp.* 2014;443:391-397.
21. Naime Filho JF, Leroux F, Verney V, Valim JB. Percolated non-Newtonian flow for silicone obtained from exfoliated bioinorganic layered double hydroxide intercalated with amino acid. *Appl. Clay Sci.* 2012;55:88-93.
22. Kameda T, Saito M, Umetsu Y. Preparation and characterisation of Mg–Al layered double hydroxides intercalated with 2-naphthalene sulphonate and 2, 6-naphthalene disulphonate. *Mater. Trans.* 2006;47(3):923-930.
23. Miyata S. The syntheses of hydrotalcite-like compounds and their structures and physico-chemical properties I: The systems $Mg^{2+}-Al^{3+}-NO_3^-$, $Mg^{2+}-Al^{3+}-Cl^-$, $Mg^{2+}-Al^{3+}-ClO_4^-$, $Ni^{2+}-Al^{3+}-Cl^-$ and $Zn^{2+}-Al^{3+}-Cl^-$. *Clays Clay Miner.* 1975;23:369-375.
24. Miyata S, Kumura T, Hattori H, and Tanabe K. Physicochemical properties of magnesia-alumina, *Nippon Kagaku Zasshi.* 1971;92: 514–519.
25. Itoh T, Ohta N, Shichi T, Yui T, Takagi K. The self-assembling properties of stearate ions in hydrotalcite clay composites. *Langmuir.* 2003; 19(22):9120-9126.
26. Xu ZP, Braterman PS. Synthesis, structure and morphology of organic layered double hydroxide (LDH) hybrids: Comparison between aliphatic anions and their oxygenated analogs. *Appl. Clay Sci.* 2010;48(1):235-242.
27. Eshwaran SB, Basu D, Vaikuntam SR, Kutlu B, Wiessner S, Das A, Naskar K, Heinrich G. Exploring the role of stearic acid in modified zinc aluminum layered double hydroxides and their acrylonitrile butadiene rubber nanocomposites. *J. Appl. Polym. Sci.* 2015; 132(9):41539-41548.
28. Aramendia MA, Borau V, Jimenez C, Marinas JM, Ruiz JR, Urbano FJ. Comparative study of Mg/M (III) (M=Al, Ga, In) layered double hydroxides obtained by co-precipitation and the sol-gel method. *J. Solid State Chem.* 2001; 168:156–161.
29. Wang Y, Wu P, Hou Y, Zhu N, Dang Z. Intercalation of l-alanyl-glutamine dipeptide into layered double hydroxides: configuration stabilization in confined interlayer region. *Ind. Eng. Chem. Res.* 2012;51(34):11128-11136.
30. Bin Hussein MZ, Zainal Z, Yahaya AH. Synthesis of layered organic–inorganic nanohybrid material: an organic dye, naphthol blue black in magnesium–aluminum layered double hydroxide inorganic lamella. *Mater. Sci. Eng., B.* 2002;88(1):98-102.
31. Klopogge JT, Hickey L, Frost RL. FT-Raman and FT-IR spectroscopic study of synthetic Mg/Zn/Al-hydrotalcites. *J. Raman Spectrosc.* 2004;35(11):967-974.
32. Meng Z, Li X, Lv F, Zhang Q, Chu PK, Zhang Y. Structure, molecular simulation, and release of aspirin from intercalated Zn–Al-layered double hydroxides. *Colloids Surf. B Biointerfaces.* 2015;135:339-345.
33. Zou K, Zhang H, Duan X. Studies on the formation of 5-aminosalicylate intercalated Zn–Al layered double hydroxides as a function of Zn/Al molar ratios and synthesis routes. *Chem. Eng. Sci.* 2007;62(7):2022-2031.
34. Hussein SH, Al Ali AQM. Comparative study of Mg/Al-and Zn/Al-layered double hydroxide-perindopril erbumine nanocomposites for inhibition of angiotensin-converting enzyme. *Int. J. Nanomed.* 2012;7:4251-4262.
35. Anbarasan R, Lee W, Soon SI. Modification of nano-sized layered double hydroxides by long-chain organic aliphatic surfactants. *J. Serb. Chem. Soc.* 2008;73(3):321-331.
36. Guo X, Zhang F, Evans DG, Duan X. Layered double hydroxide films: Synthesis, properties and applications. *Chem. Commun.* 2010; 46(29):5197-5210.
37. Cavani F, Trifirò F, Vaccari A. Hydrotalcite-type anionic clays: Preparation, properties and applications. *Catal. Today.* 1991;11(2):173-301.
38. Voyer N, Soisnard A, Palmer S, Martens W, Frost RL. Thermal decomposition of the layered double hydroxides of formula $Cu_6Al_2(OH)_{16}CO_3$ and $Zn_6Al_2(OH)_{16}CO_3$. *J. Therm. Anal. Calorim.* 2009;96(2):481-485.
39. Application notes, Rheology of thickeners in pharmaceuticals: Xanthan, C92IA035EN-A, Anton-Paar, GmbH, Germany; 2011.

40. Xu L, Nakajima H, Manias E, Krishnamoorti R. Tailored nanocomposites of polypropylene with layered silicates. *Macromolecules*. 2009; 42(11):3795-3803.
41. Sochi T. Flow of non-Newtonian fluids in porous media. *J. Polym. Sci. B Polym. Phys*. 2010;48(23):2437-2767.
42. Bird RB, Dai GC, Yarusso BJ. The rheology and flow of viscoplastic materials. *Rev. Chem. Eng*. 1983;1(1):1-70.
43. Brummer R. Rheology essentials of cosmetic and food emulsions. Springer-Verlag, Berlin, Heidelberg. 2006;81-124.
44. Song KW, Chang GS. Steady shear flow and dynamic viscoelastic properties of semi-solid food materials. *Kor. J. Rheol*. 1999;11:143-152.
45. Larson RG. The structure and rheology of complex fluids, Vol. 150. New York: Oxford University press; 1999.