Fatty acid intercalated layered double hydroxides as additives for Jojoba oil and polymer matrices

by

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Declaration

I, Lumbidzani Moyo, the undersigned, declare that the thesis that I hereby submit for the degree PhD in Chemical Technology at the University of Pretoria is my own work, and has not previously been submitted by me for degree purposes or examination at this or any other university.

Pretoria, November 2012

……………………………
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Fatty acid intercalated layered double hydroxides as additives for Jojoba oil and polymer matrices

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Synopsis

Fatty acid intercalated layered double hydroxides were used as additives for Jojoba oil and polymer matrices. The first phase of the study was to intercalate carboxylic acids (C\textsubscript{14} to C\textsubscript{22}). These were successfully intercalated into layered double hydroxides (LDHs), with the formula [Mg\textsubscript{0.7}Al\textsubscript{0.3}(OH)\textsubscript{2}](CO\textsubscript{3})\textsubscript{0.15}·0.5H\textsubscript{2}O. The one-pot synthesis consistently yielded a bilayer intercalated product for the range of acids employed. The intercalated anions had an orientation tilt angle of 55–63°, depending on the length of the fatty acid chain. However, there is an indication that the anion exchange process employed in this study is accompanied by probable dissolution and recrystallisation of the LDH. This is supported by the different growth habits and sizes of platelets observed through scanning electron microscopy (SEM). Moreover, the organo-LDH platelets were found to have varying M\textsuperscript{II}/M\textsuperscript{III} compositions, ranging from 1.65 to 6, indicating that the one-pot synthesis yields an array of mixed metal hydroxides.

Polymer composites, containing 5% and 10 wt.% of stearate intercalated layered double hydroxides (LDH-stearate) and neat layered double hydroxides (LDH-CO\textsubscript{3}), were prepared via melt-compounding to explore the use of LDHs as an additive. The stearate modified starting material was bilayer-intercalated clay. During melt compounding, excess stearates were released and the clay reverted to a monolayer-intercalated form. Comprehensive characterisation and study of the fatty acid-intercalated LDH showed that these organoclays exhibit thermotropic behaviour. This behaviour ultimately leads to the exudation of
excess fatty acid. The exuded stearates were found to have lubricating and plasticising effects on the poly(ethylene-co-vinyl acetate) (EVA) and linear low density polyethylene (LLDPE) matrices. Strong hydrogen bond interactions between the chains of poly(ethylene-co-vinyl alcohol) (EVAL) and the clay platelet surfaces overwhelmed the lubrication effect and caused an increase in the melt viscosity of this matrix. The notched Charpy impact strength of this composite was almost double that of the neat polymer. It appears that this can be attributed to the ability of the highly dispersed and randomly oriented nanosized clay platelets to promote extensive internal microcavitation during impact loading. The creation of a large internal surface area provided the requisite energy dissipation mechanism.

The study also considered fatty acid-intercalated LDH as an argillaceous mineral for potential use as a rheological additive in Jojoba oil. A minimum of 20 wt.% LDH in Jojoba oil formulation was found to be stable, i.e. it did not form separate layers on standing. The viscosity of the neat Jojoba oil demonstrated Newtonian behaviour, whereas the modified LDH/Jojoba oil formulation shear thinned, which is a typical non-Newtonian behaviour. Viscosity as a function of temperature showed complex rheological behaviour for the long chain fatty acids C_{16} to C_{22}. The viscosity increase is assumed to be due to a combination of three events, which include the formation and changes of LDH microstructures within the oil, the loss of excess fatty acids into the oil matrix, and the formation of fatty acid crystal networks. Shear action also induced some delamination of the clay platelets.

**Keywords:** Layered double hydroxides, Intercalation, Fatty acid, Nanocomposites, Thickener
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Preface

The central theme of the study was to explore the nature and properties of fatty acid modified layered double hydroxides (LDHs) and their potential use as additives in polymer matrices and Jojoba oil. The first phase of the project involved intercalating long chain fatty acids, i.e. from C\textsubscript{14} to C\textsubscript{22}, and fully characterising the modified LDH. The stearic acid (C\textsubscript{18}) intercalant was ultimately chosen due to its abundance and availability, its substantially long chain length and its reproducibility during the intercalation trials for the implementation of the stages that followed. The second and third phases entailed the use of stearate modified LDH (LDH-stearate) in the preparation of polymer composites and as an additive in Jojoba oil. The thesis is so structured that these three different phases of the study are presented in self-contained chapters (i.e. Chapters 2–4). The highlight of the work is the improvement of the mechanical properties of LDH-based polymer nanocomposites. LDHs offer an alternative to natural clay minerals such as smectites, which have been traditionally used in clay nanocomposites.

The thesis comprises five chapters, each with its own list of references, and appendices:

Chapter 1 is an introduction to the study, with a brief overview of the nature and history of layered double hydroxides (LDHs) and of the two main areas under review in this study, i.e. LDH-based polymer composites and the possible use of LDHs as argillaceous material in Jojoba oil.

Chapter 2 examines the nature, structure, formulae and preparation techniques for LDHs. It further introduces the reader to intercalation, modification methods and the orientation of intercalated fatty acids. It also gives comprehensive details of the intercalation procedure used and the characterisation of the fatty acid-intercalated LDHs used in this study.

Chapter 3 defines polymer composites and distinguishes nanocomposites from conventional composites. It looks into the different preparation techniques for LDH-based polymer composites. The chapter also reviews the properties observed in the resultant composites. It presents a full characterisation of the LDH-based polymer composites of three different polymer matrices. The composites obtained were fully characterised with
regard to the type of composite, thermal stability, mechanical properties and viscoelastic behaviour.

Chapter 4 examines the anomalous thickening mechanism of LDH-stearate in Jojoba oil as a function of temperature. A brief overview of the colloidal dispersions of LDHs in different media, i.e. aqueous, non-aqueous and emulsions is given.

Chapter 5 summarises the study and the key findings. As the concluding chapter, it provides recommendations on future research in the field and other possible applications of LDHs.

The References provide a record of the literature consulted in the course of this study, which was also used to elucidate the findings of the study.

The Appendices contain complementary and supplementary data generated during the study; these are divided according to the corresponding chapters.
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## List of Acronyms, Abbreviations and Definitions

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<th>Definition</th>
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<tr>
<td>AEC</td>
<td>Anionic exchange capacity – Amount of exchangeable anions available with the crystal structure of an adsorbent material, expressed in meq/100 g</td>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis/analyser</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EVA</td>
<td>Ethylene vinyl acetate</td>
</tr>
<tr>
<td>EVAL</td>
<td>Ethylene vinyl alcohol</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
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<tr>
<td>HT</td>
<td>Hydrotalcite</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma optical emission</td>
</tr>
<tr>
<td>LDH</td>
<td>Layered double hydroxides</td>
</tr>
<tr>
<td>LDH-Be</td>
<td>LDH-behenate</td>
</tr>
<tr>
<td>LDH-My</td>
<td>LDH-myristate</td>
</tr>
<tr>
<td>LDH-Pa</td>
<td>LDH-palmitate</td>
</tr>
<tr>
<td>LDH-St</td>
<td>LDH-stearate</td>
</tr>
<tr>
<td>LDO</td>
<td>Layered double oxide</td>
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<tr>
<td>LLDPE</td>
<td>Linear low-density polyethylene</td>
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<tr>
<td>MFI</td>
<td>Melt flow index</td>
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<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PLLA</td>
<td>Poly(L-lactide)</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl methacrylate</td>
</tr>
<tr>
<td>POM</td>
<td>Polarised optical microscopy</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulphate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TG(A)</td>
<td>Thermogravimetry (Thermogravimetric analysis)</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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# Definitions

<table>
<thead>
<tr>
<th>Term</th>
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<tr>
<td>Anhedral</td>
<td>Refers to poorly formed crystal with no distinct faces</td>
</tr>
<tr>
<td>Delamination</td>
<td>A process in which layers of a multi-layered structure separate</td>
</tr>
<tr>
<td>Exfoliation</td>
<td>A process in which layers of a multi-layered structure are separated into single sheets</td>
</tr>
<tr>
<td>Fatty acid</td>
<td>Carboxylic acid, is an organic compound with a –COOH functional group</td>
</tr>
<tr>
<td>Intercalation</td>
<td>A process in which atoms, ions or molecules are inserted between the layers of a two-dimensional crystal lattice host</td>
</tr>
<tr>
<td>Organo-LDH</td>
<td>Surfactant/fatty acid modified layered double hydroxides</td>
</tr>
<tr>
<td>Peptisation</td>
<td>To disperse a suspension to form a colloid</td>
</tr>
<tr>
<td>Subhedral</td>
<td>Moderately formed crystals</td>
</tr>
<tr>
<td>Thermotropic</td>
<td>Changes in structure as temperature changes</td>
</tr>
<tr>
<td>Euhedral</td>
<td>Fully-faced crystals, well-formed with sharp, easily recognisable crystal faces.</td>
</tr>
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