

The Friction Reducing Properties of Organic Friction Modifier Additives

By

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Declaration of originality:

This thesis describes work carried out at Imperial College London. I declare, to the best of my knowledge, that the work presented in this thesis is my own, except where acknowledged.

Ben Fry

07/07/2020

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Abstract

Organic Friction Modifiers (OFMs) have been used as lubricant additives for over 100 years but the exact mechanism of their friction reducing properties is still uncertain. OFMs are surfactant molecules, with a polar head group and hydrocarbon tail group, which adsorb onto the surface to form self-assembled monolayers. These adsorbed layers reduce friction in mixed and boundary lubrication regimes. This thesis studies the friction reducing properties of OFM additives, which will enable the effective implementation of OFMs within a system and provide potential insight on the design of future OFM additives.

The friction reducing properties of OFM additives are impacted by contaminants within an idealised system. Surface contaminants and contaminants within the base oil were studied to understand the impact these contaminants had on the friction reduction of OFMs. Effective methods were found to remove this contamination to further study the friction reduction of OFM additives.

OFMs are known to adsorb onto a surface, but the link between the adsorption of these additives and their friction reduction is unclear. This thesis studied the adsorption of different OFM additives and has determined a link between the adsorption thickness and the initial friction of these additives.

The mechanism of friction reduction of OFMs with an ester head group was still debated within the literature. This research has found that well adsorbed esters hydrolyse within the contact to form carboxylates on the surface. These carboxylate species dictate the steady state friction of these ester additives.

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'Now to him who is able to do immeasurably more than all we ask or imagine, according to his power that is at work within us, to him be glory in the church and in Christ Jesus throughout all generations, for ever and ever! Amen.'

Ephesians 4 v20-21

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Chapter 1. Introduction

1.1 Introduction

Efficiency in engineering is important. It saves resources and energy. One of the major causes of inefficiency is friction. One of the earliest mentions of this was in a report for the UK government commonly known as the 'Jost Report', which suggested that using advanced tribological solutions can create vast efficiency savings.¹ Most of the losses were caused by wear and reliability of machinery. Since then the challenges have moved into friction reduction as opposed to wear reduction to increase efficiency. Reports by Holmberg et al published in 2012² and again in 2017,³ show that 20% of world energy consumption is used to overcome friction and that global savings of up to 973,000 million Euro, which corresponds to 1.39% of the worlds gross national product (GNP) over the next 15 years, it can be achieved if new tribological technology is implemented within manufacturing. 74 % of this saving comes from reducing friction within machines and equipment as opposed to 5% in 1966. There are several ways to increase friction reduction, such as surface coatings and texturings,⁴ new materials^{5,6} and improving the lubrication fluids.⁷ This thesis focuses on the improvement of lubricating fluids and the use of organic additives within these fluids.

1.2 Boundary Lubrication

The conditions within a lubricated contact can be generalised into different lubrication regimes which can be identified through a Stribeck curve, as shown in Figure 1-1. A Stribeck curve plots the friction coefficient against the change in lubricant viscosity, speed and load on a log scale. This curve can be split into 3 main regions: boundary, mixed and hydrodynamic lubrication. Boundary lubrication (BL) is when the 2 rubbing surfaces are in significant contact with each other, with minimal separation by the lubricant. This region has the highest friction coefficient. It also has the highest wear in a system and thus requires the most protection. Mixed lubrication (ML) is where the lubricant pressure in the

contact is enough to slightly increase the distance between the two surfaces but asperity contact still occurs. The size of this regime is strongly related to the surface roughness, with the rougher the surface the larger the mixed regime. Hydrodynamic lubrication occurs when the film thickness of the lubricant is larger than the surface roughness meaning that the two surfaces are not in contact. This gives the lowest friction value which then increases due to resistance from the lubricant. The lubricant viscosity can play a large effect in this regime.

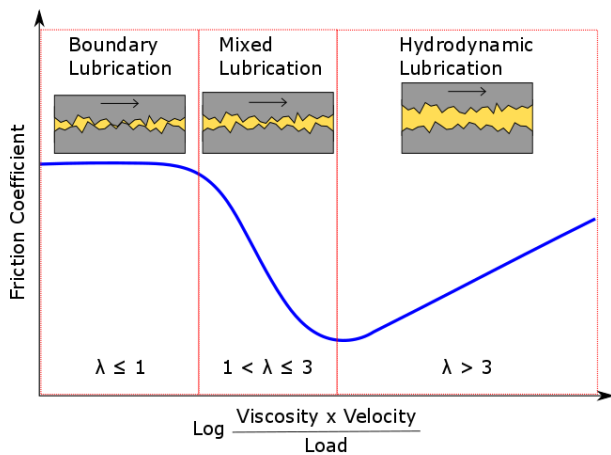


Figure 1-1: A Stribeck curve, showing the lubricating regime of a contact.

The lubricating conditions of a contact can be determined from the ratio of the lubricant film thickness, which can be estimated for a point contact by the Hamrock Dowson formula,⁸ and the composite roughness of the surface, this is known as the λ ratio. Boundary lubrication is when $\lambda \leq 1$, mixed lubrication is when $1 < \lambda \leq 3$ and for hydrodynamic lubrication $\lambda > 3$.

In 2010 it was estimated that 12% of the frictional losses within passenger motor cars originated from hydrodynamic lubrication within the engine² These losses can be reduced through reducing the viscosity of the lubricant within the contact, moving the lubricating conditions on the Stribeck curve towards the left. The consequence of this is more contacts experience mixed and boundary lubrication within an engine. So, improved methods of reducing friction for these regimes are required.

1.3 Engine oil additives

Engine oils are used to protect the engine from damage and to lubricate and reduce friction. They comprise of a base oil and additives within the oil. The base oils are picked for the required thermal and viscous properties for the lubricating conditions. Additives in these oils can be split into 2 general categories, bulk oil additives and surface-active additives. Bulk oil additives, such as antioxidants, viscosity modifiers⁹ and foam inhibitors¹⁰, control the conditions within the bulk solution. Surface active additives, such as friction modifiers,¹¹ anti-corrosion, anti-wear¹² and extreme pressure additives, interact with the surfaces the oils are in contact with. New additives such as ionic liquids have the potential to be used as a multi-functional additives showing both good friction and wear reduction.¹³

Friction modifiers are used to reduce friction when there is surface to surface contact, in the mixed and boundary lubrication regimes. There are 4 main types of friction modifiers; organic, organo-molybdenum, polymer and nano additives.¹¹ Organic Friction Modifiers (OFMs) are surfactant molecules which adsorb to the surface. This adsorbed layer provides low friction within the contact.¹⁴ Molybdenum dithiocarbamate (MoDTC) is used as an organo-molybdenum friction modifier. It has been found to go through a tribochemical reaction under severe conditions to produce MoS₂ sheets which reduces friction within the contact.¹⁵ Polymeric friction modifiers are functionalised polymers which adsorb to the surface and creates a protective boundary film on the surface.¹⁶ Nano additive friction modifiers, such as nano particles, nano rods and nanosheets, reduce friction in the boundary/mixed lubrication regime through several different effects, such as rolling in the contact, mending the gaps in the roughness, creating a protective film and polishing the surface.¹⁷ These additives however can be difficult to synthesise and stabilise within a lubricant solution.

Of those different types of friction modifiers, Organic Friction Modifiers (OFMs) have been around the longest but we still are unclear about exactly how they work. The aim of this work is to gain a better

understanding on the friction reducing mechanism of OFM additives to enable the design of more effective OFM additives.

1.4 Organic Friction Modifiers

Organic friction modifiers, which were originally known as oiliness additives, have been known for around 100 years. These additives are found in vegetable and animal oils but not in mineral oils. As a result, neat mineral oils give high friction when used as lubricants. The friction reducing properties of vegetable and animal fat are due to the inclusion of fatty acids which were successfully isolated in 1918.¹¹ Fatty acids are the first known OFM. Since then, studies have been conducted to understand how fatty acids and other amphiphilic molecules interact with surfaces and reduce friction.

OFMs have polar head groups and hydrocarbon tail groups. Their polar head groups adsorb to the surface while their hydrocarbon tail groups interact with the oil, which allow them to form a self-assembled monolayer (SAM) on the surface. Within the rubbing contact, an OFM layer may in fact be a multilayer.¹⁸ In-situ film thickness measurements have shown that multilayer films of stearic acid (or iron stearate) form in the presence of moisture with the OFM solution when rubbed on a steel substrate.¹⁹ Frequency modulated atomic force microscopy has been used to observe these multilayer films which occur after continuous scanning of palmitic acid solution in hexadecane on a copper surface.²⁰ This layer, as a monolayer or a multilayer, is thought to provide OFMs their friction reducing properties.

The friction reducing properties of a monolayer is thought to be caused by the modes of energy dissipation into the thin film.²¹ The greater the energy dissipation the less the friction reduction the film provides. A common mode of energy dissipation within monolayers are known as gauche defects, which are caused by C-C rotation and bending within the SAM.²² These defects can be formed within sliding contacts by poor packing of the molecules within the layer²³ and weaker interchain van der Waal interactions.²⁴

Many factors affect the nature of the packing of the OFM layer, and hence its effectiveness on friction reduction. These factors, including concentration, head group and tail group properties, which are discussed below.

1.4.1 The Effect of Concentration

In binary solutions, organic friction modifiers start taking effect at a concentration of about 2 ppm and continue to reduce friction until about 2000 ppm.¹¹ This concentration is lower than that used in fully formulated oils, which has been quoted between 0.25%-1% by weight. The high concentration required in commercial lubricants is because OFMs can interact with other additives. Some of these interactions are antagonistic and reduce the friction reducing properties of the OFM.²⁵

As the concentration of an OFM in solution increases, the greater the friction reduction is measured within a contact. At a certain concentration the decrease in friction begins to plateau, this concentration is different for each additive.²⁶ This concentration in aqueous lubricants has been shown to be the critical micelle concentration (CMC). The critical micelle concentration of a surfactant in a solvent, CMC, is the concentration at which the surfactants start forming aggregates in the solution. These micelles are presumed to act as a reservoir of individual surfactants (monomers) in the solution.²⁷ Using water based lubricants, it was found that an increase in the concentration of a surfactant above its CMC did not decrease the friction further.²⁸ This is thought to be linked to the fact that above the CMC, the concentration of the surfactant does not affect the thickness of the SAM formed. When the concentration is below the CMC, the thickness of the SAM decreases as the concentration of the surfactant decreases,²⁹ which also causes the friction to increase.³⁰

Within non-polar solutions various surfactant associates can form. Inverse micelles, have been shown to form within non-polar solutions with the presence of polar contaminants such as water promoting its formation.³¹ The formation of inverse micelles has been shown to promote adsorption onto the surface,³² although there is limited work linking inverse micelle formation to friction reduction. For

carboxylic acid molecules the formation of an inverse micelle is not favourable¹⁸ and can form dimers within solution instead.³³

For all concentrations the adsorption time allowed for the SAM to form changes the nature of the monolayer. The longer the deposition time for the monolayer to form, the more homogeneous the film is. For moderate concentrations (1 mmol dm^{-3}), an SAM formed in about 2 second has a thickness of about 80-90% of its maximum film thickness. A few more hours are required to form a more densely packed/ordered layer and for the displacement of impurities in the monolayer such as solvent molecules.³⁴ At low concentrations ($\mu\text{mol dm}^{-3}$) a complete SAM can form on a surface but this may take up to a week.³⁵

1.4.2 Effect of OFM Tail Group

The tail group of an OFM, especially its length, has been shown to have a large effect on its friction reducing properties. As the length of the chain increases, the friction decreases.^{36,37} This is thought to happen because of the increasing van der Waal forces between chains, which creates a stronger, more densely packed monolayer. This has a significant effect from C1 up to C8, where the van der Waal forces are particularly weak for short chains.

It has been shown that SAMs with an even number of carbon atoms within the linear saturated tail group provide lower friction than SAMs with an odd number of carbon atoms.³⁸ This is known as the 'odd even effect'. This effect also impacts on wettability³⁹ and compressibility⁴⁰ of a SAM. The reason for this effect is the orientation of the terminal methyl group within the monolayer is more varied for odd length tails, allowing more gauche defects within the film.⁴¹

Increasing unsaturation within the tail group increases friction. This is due to the saturated chains forming a more ordered monolayer, which has been shown with the comparison of stearic acid (saturated C18), elaidic acid (E-unsaturated C18) and oleic acid (Z-unsaturated C18).⁴² In situ AFM experiments on mica confirmed that where stearic acid forms islands made of well packed layers,

whereas oleic acid does not, possibly due to its bent tail group causing its inability to form well packed layers.⁴³

In some solvents, the friction decreases with chain length. This is due to chain length matching.¹⁸ Chain length matching is the matching of straight hydrocarbon chains in the OFM to the length of the solvent. Stearic acid has been shown to produce the lowest friction in hexadecane whereas oleic acid, which has a shorter linear section works best in tetradecane.⁴⁴ This is thought to work through the solvent causing greater interactions in the monolayer⁴⁵ but the exact mechanism is still unknown.

The packing density of the SAM has been shown to have an effect on the friction properties of the surface. More densely packed/crystalline films give a lower friction value than less densely packed films.⁴⁶ The level of saturation in the tail influences the packing density of the OFM on the surface with straight chained, saturated or trans-unsaturated, molecules having a denser packing. 'Bent' hydrocarbon chains (cis-unsaturated chains) have a less uniform packing which leads to less adsorption and a less dense film.⁴⁷ This effect is shown in the difference in friction reduction between molecules with saturated and unsaturated tail groups, with straight chained molecules having a generally lower friction than the equivalent bent molecules.⁴⁸

The size of the terminal group of the tail affects the friction. Kim *et al.*⁴⁹ looks at the effect of -CH₂-CH₃, -CH-(CH₃)₂ and -CH₂-CF₃ groups on friction and found that the larger the terminal group the higher the friction, with the -CF₃ group having the highest friction. This is thought to happen because the tail group size was bigger than the crystal lattice size, which hinders the packing of the SAM and reduces its packing density.

It is possible to functionalise the tail of the molecule to alter the physical properties of the SAM. It has been shown that it can alter the wettability of a surface⁵⁰ and adsorption of additives.⁵¹ The difference in terminal group of a similarly densely packed alkylthiol monolayer has been shown to have an impact on the friction of the surface when lubricated with water.⁵²

1.4.3 Effect of OFM Head Group

There are 3 main ways the OFMs will interact with the surface: through physisorption (interaction less than 40 kJ/mol), chemisorption (interactions more than 40 kJ/mol) and chemical reaction (where bonds are formed through the sharing of electrons).⁵³

The first used OFMs were carboxylic acids, with the carboxyl group adsorbing and reacting with the surface. There are 3 different adsorption mechanisms for a carboxylate group, monodentate, bidentate and bridging, as demonstrated in Figure 1-2. Monodentate bonding would be through the deprotonated oxygen onto a surface atom. Bidentate bonding is through both oxygen atoms to the same surface atom. Bridging bonding would bond both oxygen atoms to two neighbouring surface atoms. These can be distinguished through vibrational spectroscopy with each mode of bonding giving a different frequency.⁵⁴ DFT experiments suggest that acid head groups initially physisorb onto an iron oxide surface through bridging over 2 different surface atoms. This is followed by the dissociation of the proton to the lower energy state of a carboxylate salt.⁵⁵ Carboxylic acids provide good reduction in friction but the acidic nature of the chemical promotes corrosion of the contact so other head groups needed to be found.

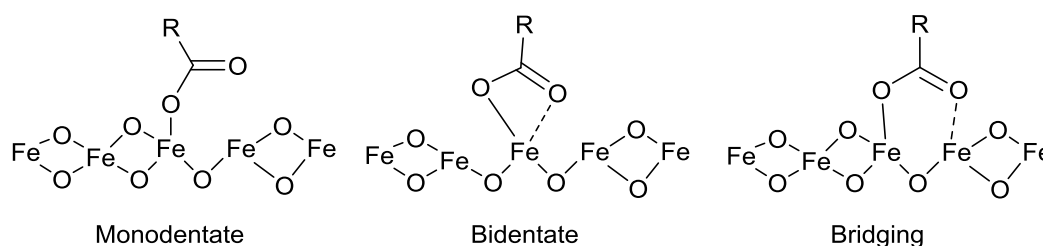


Figure 1-2: The different bonding modes of carboxylic acids onto an iron oxide surface

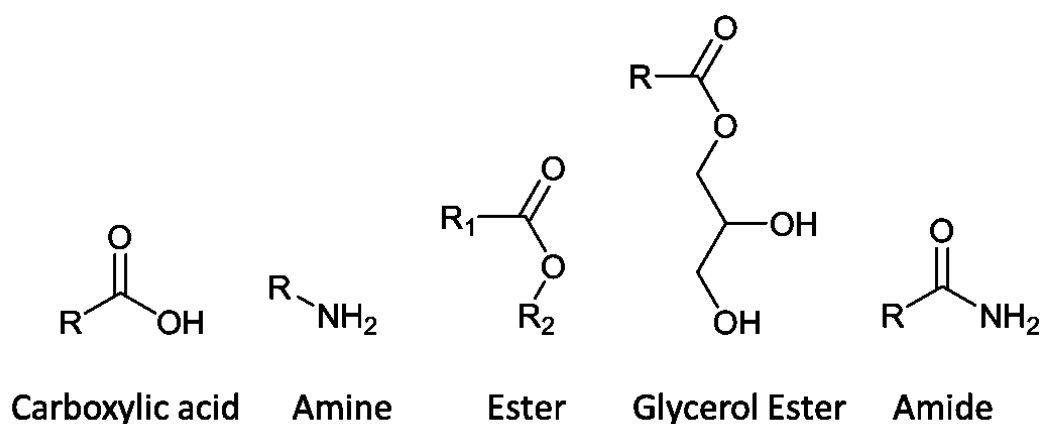


Figure 1-3: The chemistry of common head groups used for OFM additives.

Amines, Figure 1-3, are commonly used to produce low friction, with the lone pair of the nitrogen chemisorbing to the surface. Amines have been shown to have a strong adsorption onto the surface and can create well packed monolayers on steel surfaces.⁵⁶ They are thought to bind to Fe_2O_3 surfaces through the iron (III) atoms over the oxygen atoms on the surface, as shown through XPS analysis.⁵⁷ Unfortunately primary amines in a lubricant have been shown to degrade rubber seals.⁵⁸ So they cannot be used as OFM additives. Other types of amines such as di-branched and tri-branched amines⁵⁹ as well as ethoxylated amines⁶⁰ have been shown to provide effective friction reduction.

Esters such as glycerol monooleate (GMO) are used as commercial OFM additives,⁷ with the glycerol esters having additional functional groups enhancing the friction reduction. GMO has been hypothesised to hydrolyse within the contact and react with the surface like a carboxylic acid.⁶¹ Other esters such as methyl oleate and ethyl stearate have been shown to be less effective for friction reduction than their corresponding acid, potentially down to the lack of OH groups.^{11,26,61}

Amides are another commercially used additive, commonly with an oleyl tail group.⁷ They adsorb onto the surface forming a moderately disorganised film,⁶² and are thought not to dissociate once adsorbed onto iron oxide.⁵⁵

Novel OFM molecules have been synthesised to improve friction reduction. Thermo-cleavable molecules, which are designed to go through ester pyrolysis within the contact to form fatty acids,

have been synthesised. These molecules are believed to provide a greater friction reduction by the controlled release of fatty acid molecules within the contact due to frictional heating.⁶³ Molecules with a sorbitan head group have been tested with friction force microscopy, showing that sorbitan dioleate provides lower friction than GMO and sorbitan monooleate due to its faster rate of adsorption.⁶⁴ The chelating agent amino-PEG2-amine shows greater adsorption and better wear reduction properties than its alkyl substituted derivatives but worse friction reduction due to the lack of an alkyl tail group, showing the balance required between maximising surface adsorption and molecular structure.⁶⁵ Several studies have linked the formation of the adsorbed OFM layer to the layers friction reducing properties. The surface density of a OFM layer is thought to impact the friction coefficient with the maximum coverage providing the minimum friction coefficient.²⁶ The failure temperature of an OFM solution is linked to the desorption of the additive layer on the surface.⁵⁶ The kinetics of adsorption of the OFM additive has been linked to the steady state friction of these solutions through friction force microscopy; solutions containing additives which adsorb quicker on surfaces provide lower friction.^{59,64}

1.4.4 The effect of the substrate chemistry

The substrate the OFM adsorbs onto is another key feature of the friction reduction of OFM additives. If a surface is crystalline and the adsorbed molecules are larger than the crystal lattice size, such as a CF_3 terminal group on an Au (111) surface, then this leads to increased levels of gauche defects within the adsorbed layer increasing friction.⁴⁹

Silicon surfaces are commonly used for the formation of monolayers for MEMS devices.⁶⁶ Silicon has a native oxide layer of SiO_2 on the surface, which forms naturally in air but can be removed through annealing under ultra-high vacuum (UHV).⁶⁷ SiO_2 is relatively inert and would form an amorphous layer a few nm thick on the surface of a crystalline Si wafer.

Steel is an iron alloy mixed with carbon and chromium, which has improved mechanical properties than iron. Bearing steel (AISI 52100) which is commonly used in tribological experiments also contains

a small amount of chromium (1.35-1.6%) within the alloy. The steel itself is highly reactive, and when exposed to oxygen forms a passivation oxide layer on the surface. This layer consists of oxides a few nm thick formed at the metal to air interface, which primarily consists of iron oxide. Iron has two main oxidation states Fe(II) and Fe(III) with the latter the most common form for the oxide (α -Fe₂O₃ haematite). Iron oxide is chemically stable in air but can react with polar groups in oil based solutions. Fe₂O₃ has been shown to be a catalyst for the degradation of hydrocarbons,⁶⁸ and the hydrolysis of esters.⁶⁹

When in humid air silicon surfaces can hydrolyse to form Si(OH)₄ which provides some lubrication to the contact.⁷⁰ Iron oxide surfaces in the presence of water also hydroxylates forming Fe(OH)₃. This iron hydroxide layer still enables adsorption of OFMs through hydrogen bonding⁷¹ but has been shown to produce a slip plane between the metal surface and carboxylic acid head groups, lowering the friction coefficient.⁷² Iron hydroxide has also been hypothesised to cause the deprotonation of a phenol group to form a phenolate anion on the iron oxide surface.⁷³

1.5 Research Questions

After over 100 years of research into organic friction modifiers and there are things that we still do not understand about them. Specifically, the link of the process of OFM adsorption and its effectiveness in friction reduction remains unclear. This work sheds light on this relationship by investigating the effects of (a) OFM chemistry and (b) the interactions between OFMs and other constituents in a rubbing system.

Regarding point (a), while the studies on the link between adsorption and friction reduction of OFM additives are insightful, there are still unanswered questions. Amines have been shown to have a greater and quicker adsorption onto steel surfaces than the corresponding carboxylic acid,⁷⁴ but the latter provides lower steady state friction.⁷⁵ This is also the case with changing saturation of the molecule, with unsaturated fatty acids diffusing quicker and adsorbing faster onto a Fe₂O₃ surface

than a saturated fatty acid but the saturated fatty acid providing lower steady state friction.⁷⁶

Therefore my research question is:

RQ1: 'Is there a link between the adsorption of OFMs with different head groups and tail groups and their friction reducing properties?'

As discussed above GMO is a very commonly used OFM although its working mechanism has only been hypothesized as due to its hydrolysis. Hence my second research question regarding point (a) is

RQ2: 'What is the friction reducing mechanism of GMO? Do esters hydrolyse within a rubbing contact and how does this impact on the friction reduction of the OFM? If esters do hydrolyse within a rubbing contact, can that information be used to design improved OFM additives?'

Regarding point (b), we must remember OFMs are not the only additives in a full formulated oil. Indeed commercial lubricants have multiple additives. In addition, rubbing surfaces and even the lubricant itself, are dirty. Other additives and contaminants may interfere with OFM. Hence my third research question is

RQ3: 'Would surface contaminants and base oil impurities interfere with the performance of OFM? In other word, is there a difference in OFM performance from experiments in "clean" idealised systems compared to systems with known contaminants, such as surface contaminants?'

Taking into the multicomponent nature of commercial lubricant, a simplified system, consist of 2 OFM in a base oil, is used to assess if OFM interaction can be beneficial for friction reduction. My research question here is

RQ4: 'Can the friction reducing performance of OFM additives be enhanced by using a mixture of two different OFM additives? If so, what is the working mechanisms?'

1.6 Thesis Layout

The thesis is set out in the following chapters:

Chapter 2 introduces the methods used to carry out this research, showing the conditions used and a prior literature basis for using these methods.

Chapter 3 discusses the use of ellipsometry for a tribological system. Surface models for the systems used are described and the optical properties of the materials used are explained.

Chapter 4 is the first results chapter which studies the effect of surface cleanliness on OFM friction reduction. As previously described, OFMs can form SAMs on the surface. These surfaces are typically carefully prepared to be clean and free of contamination. Surfaces for tribological experiments are generally cleaned with solvents, which has been shown to leave a residue on the surface.⁷⁷ This study looks at what impact the preparation of a surface has on the friction reduction of OFM additives.

Chapter 5 studies the adsorption of OFM additives. OFMs need to adsorb to the surface to reduce friction. Using ellipsometry and quartz crystal microbalance (QCM) measurements this study wants to link the friction reduction of OFM additives to their adsorption.

Chapter 6 Studies the effect of mixing OFM additive. Ionic liquids are a more recent type of additive which has been shown to provide good friction reduction. An ionic liquid made of two different OFM additives (oleic acid and oleylamine) has been shown to be effective as a lubricant.⁷⁸ This study looks at the impact of mixing two different OFM additives as lubricant additives identifying synergistic effects that the mixtures may have.

Chapter 7 studies the friction reduction of glyceride esters. Glycerol monooleate is a commonly used OFM additive⁷ but the way that it reduces friction is still unclear. This study compares the friction reduction of glycerol mono, di and tri-oleate with that of oleic acid to determine if glyceride esters hydrolyse in the contact to form carboxylic acids.

Chapter 8 studies the impact of base oil impurities on the tribological properties of OFMs. OFM additives have such a large impact on the lubrication properties of oils at low concentrations (0.037 wt% for oleic acid) then there is potential for low concentration polar groups within the base oil to

have an impact also. This study looks at the impurities within a hexadecane solution showing the impact on tribological testing with and without OFM additives.

Chapter 9 studies the friction reduction of glycerate esters. A glycerate ester is formed from the esterification of glyceric acid and a fatty alcohol. With the structure of these glycerate molecules being very similar to that of glyceride esters previously tested, this initial study compares the friction reduction and discussing the mechanism of lubrication of these two types of molecules.

Chapter 10 concludes the thesis, summarising the key findings of the research presented. Possible future work is also discussed.

Chapter 2. Methods

2.1. Introduction

Even at low concentrations (< 0.1 wt%), organic friction modifiers (OFMs) may adsorb and form nanometre thick films on surfaces. Depending on properties of the OFM film, such thin film may provide surface protection and reduce friction in the boundary lubrication regime.

To characterise the properties of the adsorbed OFM films, in situ ellipsometry and quartz crystal microbalance were used. The bulk properties of OFM solutions were characterised using UV-Vis and infrared spectroscopy. Friction tests were conducted in the boundary lubrication regime using a ball on disk tribometer and a high frequency reciprocating rig. Surface analysis of worn surfaces was performed with X-ray photoelectron spectroscopy, atomic force microscopy and scanning white light interferometry.

2.2. Tribometers

2.2.1. Ball on Disk unidirectional test rig

The friction of different OFM additives in the boundary lubrication regime has been studied using a ball on disk tribometer, which showed that the friction of saturated OFM solutions increases with speed whereas unsaturated oleyl tail grouped OFMs friction remain constant with speed.¹⁴ Similar ball on disk tribometers have also been used to show the effect of temperature⁷⁹ and concentration⁸⁰ on the friction reducing properties of OFMs.

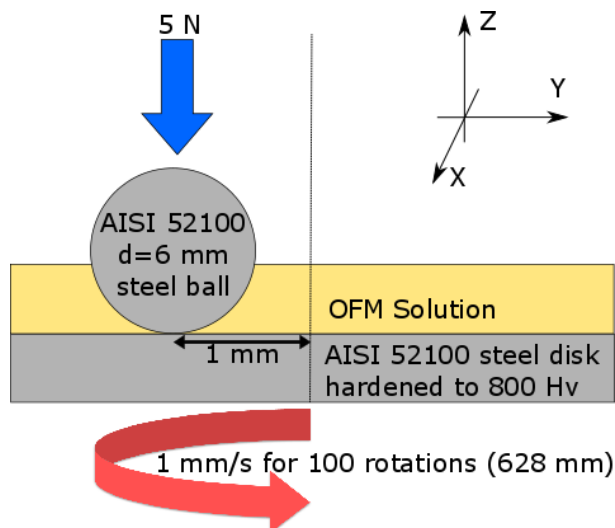


Figure 2-1: Diagram showing the configuration of the ball on disk tribometer used.

Ball-on-disk tribometers use a static ball (or pin) and a moving disk surface. The one at Imperial College London is a UMT-2 originally bought from CETR, but now serviced by Bruker. The tribometer consists of a static ball attached to a load cell, which measures forces in the Z and X (circumferential) direction, as shown in Figure 2-1. The base plate has an ultra-low speed drive, which is able to accurately and smoothly move at speeds as slow as 0.01 RPM. The base plate contains a heating element which can be used for temperature control during the experiment.

A 100 N load cell was used in all cases. The contact was fully flooded, with the holder containing 2 ml of lubricant. Unless stated otherwise, unidirectional friction tests were run at ambient condition, with the test temperature at 23-27 °C, and a sliding speed of 1 mm/s at the contact with a rubbing track radius of 1 mm and a load of 5 N. These conditions give a maximum Hertzian contact pressure of 1.16 GPa and a contact diameter of 90 μm . Using the Hamrock Dowson equation, the minimum film thickness within the contact was estimated to be < 1 nm. Each rotation took 6.28 s and a standard test was 100 rotations. Balls and disks used were made of AISI 52100 steel, with the disk hardened to 800 Hv. The disk had a diameter of 15 mm and the ball with a diameter of 6mm. The roughness (R_a) of the balls and disks was measured using scanning white light interferometry to be 41 ± 3 nm and 6 ± 2 nm respectively. The lambda ratio of film thickness surface roughness $\ll 1$ therefore the friction

tests were run in the boundary lubrication regime. After the test, each ball and disk was rinsed with hexane, dried with compressed air and stored in glass vial for further analysis.

The force measurements were recorded every 0.005 s. The results obtained were averaged from 4 repeats, to reduce the sinusoidal noise obtained (see Figure 2-2). The averaged data was then smoothed using a 15 point moving average for the first 5 rotations and over an entire rotation (1260 points) for the further rotations. The smoothing applied to the friction data can be seen in Figure 2-2.

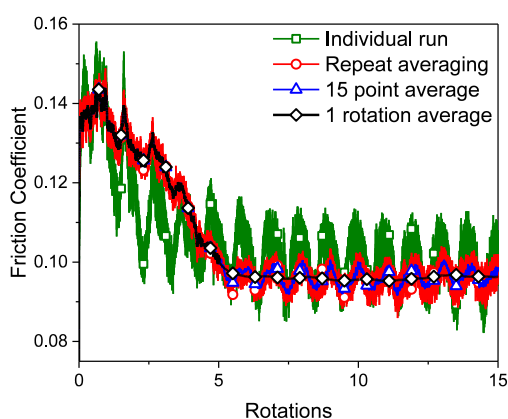


Figure 2-2 A graph showing the different levels of averaging and smoothing of the data from a friction test.

2.2.2. High Frequency Reciprocating Rig (HFRR)

High frequency reciprocating tribometers have been used to investigate the tribological properties of many different solutions as they provide accurate friction and post-test wear data.⁸¹⁻⁸³ The electrical contact resistance (ECR) between the ball and disk during rubbing can be measured simultaneously, with less contact between them resulting in a greater electrical resistance.⁸⁴ A percentage with 0% ECR showing full metal to metal contact and 100% showing no contact. While the use of ECR during a friction test generally has minimal influence on the tribological performance of the test lubricant, it has however been shown to impact the friction reduction properties of pure ionic liquids. This may be due to charging of the surface and hence the surface adsorption of the anion and cation were altered.⁸⁵

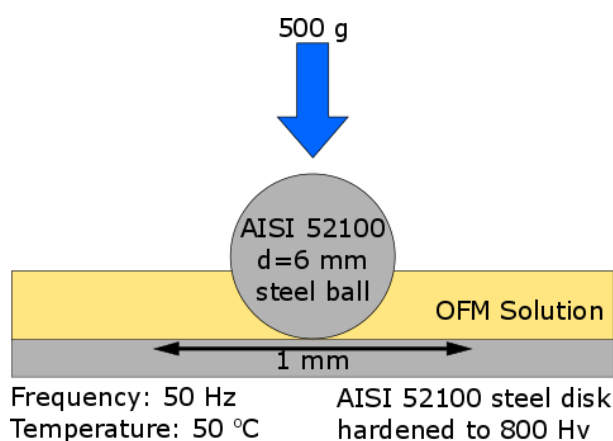


Figure 2-3: Diagram showing the configuration of the HFRR.

A high frequency reciprocating ring (HFRR) uses a static disk and a ball which slides backwards and forwards in a reciprocating motion. The one used at Imperial College is a HFRR 2 from PCS instruments. It consists of a 6 mm diameter ball loaded by hanging weights from the load arm, onto an 8 mm diameter disk, both specimens were made from AISI 52100 steel with the disk hardened to 800 Hv. The contact conditions are the same as the CETR with a load of 5 N, corresponding to the same pressure within the contact. The contact was fully flooded with 2 ml of lubricant used within the holder. The base plate has a heating unit and a thermocouple to regulate the temperature. For the tests in the study, the temperature used was 50 °C. The ball reciprocates at a frequency of 50 Hz and a stroke length of 1 mm, see Figure 2-3. The maximum speed at mid-stroke was 0.157 m/s. The calculated minimum film thickness from the Hamrock-Dowson formula⁸⁶ was about 1.7 nm, which was much smaller than the roughness of rubbing surfaces (roughness measured to be 41 ± 3 nm and 6 ± 2 nm for the ball and disk respectively). So tests were conducted in the boundary lubrication regime. During the test, electrical contact resistance (ECR) is measured.

Friction measurements are taken every second, with the graphed results a moving average over 15 seconds. Worn surfaces were examined using a light microscope. The ball wear scar diameter was obtained from an average of the length of the wear scar perpendicular and orthogonal to the rubbing direction. The disk wear scar width was also measured at the centre of the wear scar. Each result is

an average of more than 3 runs. After the test, each ball and disk was rinsed with hexane, dried with compressed air and stored in glass vial for further analysis.

Comparison between the use of a ball on disk tribometer and an HFRR for different friction modifier additives shows that although both of these tribometers measure friction in the boundary lubrication regime, they may give different trends and friction coefficients for the same set of solutions.⁸⁷ This could be because of the different speeds used in the tests, which has been shown to provide different friction coefficients within the boundary lubrication regime,¹⁴ as well as the difference in the contact motion, with one unidirectional sliding and the other reciprocating.

2.3. Characterisations of adsorbed OFM layers

2.3.1. Ellipsometry

Ellipsometry is a laser based technique used for measuring the optical properties of a surface.⁸⁸ It has been used to measure the thickness of surfactant monolayers on gold^{34,89} and silicon^{90,91} surfaces; and adsorption kinetics and surface layer thicknesses in-situ of many systems, such as proteins^{92,93} and polymers²⁹ in aqueous systems. Ellipsometry has also been applied to quantify the thickness of a ZDDP tribofilm,⁹⁴ as well as the thickness of DLC coatings⁹⁵ and MoS₂ layers in air.⁹⁶ Within a sliding contact lubricated with a base oil, ellipsometry has been used to measure in situ the oil film thickness between the two surfaces with nm accuracy.⁹⁷ Ellipsometry has yet to be applied to examine the adsorption of additives in oil lubricated contacts. This is because base oils and OFM additives have similar bulk refractive indices, which are 1.43 and 1.46 respectively as measured with an Abbe refractometer at 589 nm wavelength. Note also that most ellipsometry experiments were conducted with flat, well characterised surfaces such SiO₂ surface, rather than commonly used metal surfaces such as steel, which are rougher and with less well defined refractive index.

Ellipsometry measures the complex reflection coefficient of the light reflected off a surface. The measurement is based on nulling ellipsometry.^{98,88} With the incident angle and wavelength of the

incident light known, the ratio of the reflected parallel (R_p) and perpendicular (R_s) polarised light is related to values Ψ and Δ using Equation 2-1. This is practically measured at the null point by the angles of the polariser θ_p , and analyser θ_a . Ψ and Δ were then calculated from: θ_p, θ_a .⁸⁸

Equation 2-1

$$\frac{R_p}{R_s} = \tan(\Psi)e^{i\Delta}$$

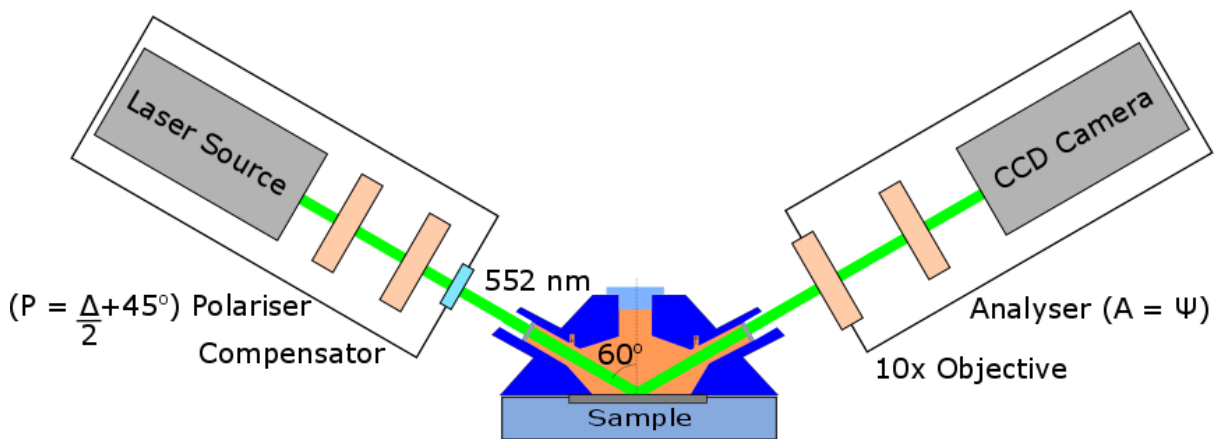


Figure 2-4: Diagram showing the layout of the EP3 imaging ellipsometer, with liquid cell attachment.

In this research, an Accurion Nanofilm EP3 imaging ellipsometer⁹⁸ with a solid-liquid cell attachment was used. The ellipsometer has a PCSA (Polariser, Compensator, Surface and Analyser) setup, as shown in Figure 2-4. In this setup, an elliptically polarised light, which was created by passing light through a polariser, then through a quarter wavelength compensator (fixed at $\pm 45^\circ$), was directed to the sample. The light reflected off of the sample surface was collected through a 10× objective, which then passed through an analyser before it was captured by a CCD camera.

Two types of ellipsometry measurements were conducted, with the angle of laser incidence set at 60° . Spectroscopic (SE) measurements, which took an hour to run, were performed with different wavelengths from 371-1000 nm under no flow conditions. Four zone averaging, with combinations of both positive and negative angles of the polariser (P) and analyser (A), and the quarter waveplate compensator (C, fixed at 45°) (+P, +A, +C; +P, +A -C; -P, -A, +C; and -P, -A, -C), was used for each value

of Ψ and Δ to remove any systematic errors⁸⁸. Kinetic measurements used a 552.2 nm light source, with Ψ and Δ recorded every 10 seconds, using only the condition of +P, +A and +C. Note that the area examined during each measurement was about $500 \times 1000 \mu\text{m}^2$. Results are shown as an average of 2 or more tests, Kinetic measurements are smoothed with a moving average over 50 seconds.

Prior to a test, the liquid cell was immersed in isopropanol and cleaned in an ultrasonic bath for 30 mins, before drying with compressed air. The substrate was immersed in toluene and cleaned in an ultrasonic bath for 30 mins before further cleaning by oxygen plasma for 2 minutes (for Si wafers or steel disks) or UV-Ozone for 30 minutes (Fe_2O_3 crystal).

For liquid cell measurements the test procedure was as follows:

- An initial SE base line of the silicon wafer substrate was taken in air to obtain the thickness of the SiO_2 layer on the surface. This was not needed with the Fe_2O_3 crystal as the substrate used has a constant refractive index.
- Once the test substrate was placed in the liquid cell filled with hexadecane, a kinetic run was used to check the stability of the test system by obtaining a stable base line. Note that refractive index changes with temperature so this was used to check if the temperature has stabilised.
- Once the test system was stable, a SE run was used under no flow conditions to get the base line in hexadecane.
- Under a flowing condition, a kinetic measurement was obtained, first in hexadecane for 10 minutes to obtain a stable baseline, then in flowing the OFM solution for 2 hours.
- After 2 hours, the flow was stopped and the SE measurement was run.
- The cell was rinsed with hexadecane whilst using a kinetic measurement. Often no change was observed over a 30 minute rinse or if a change was measured it was not reproducible.

Kinetic measurements were run with the flow rate of the OFM solution at 1 ml/min. The flow showed little impact on the noise of the measurement for tests at room temperature (Black line, Figure 2-5)

but when at elevated temperature (50 °C red line, Figure 2-5) there is a significant increase in noise. This is due to the refractive index difference between liquid in the liquid cell and the injected fluid, as the injected fluid is at a lower temperature. Currently the set up does not enable the inlet tubing to be heated and control the temperature of the fluid before being injected to the heated liquid cell. As a result, results from kinetic measurements above run temperatures were not attempted further.

The liquid cell has a test volume of 0.7 ml. With a flow rate of 1 ml/min, this means the time for total displacement (presuming an ideal system) of hexadecane by the test OFM solution is 42 seconds or 5 measurements after the start of the kinetic run. The consequence of this is that the initial adsorption kinetics cannot accurately be measured with these conditions.

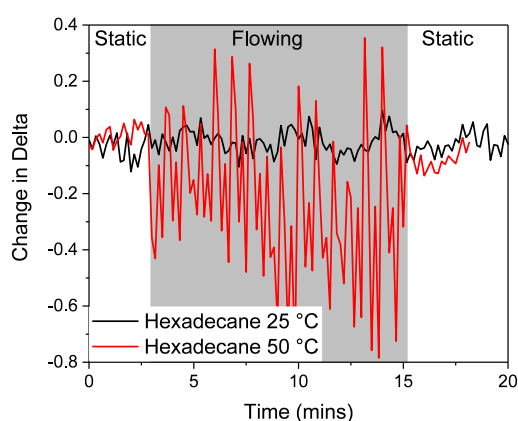


Figure 2-5: The noise of the data from a kinetic ellipsometry run flowing (grey) and static (white) for hexadecane on Fe_2O_3 at 25 °C (black line) and 50 °C (red line).

Modelling of the reflected surfaces were carried out using Accurion's EP4 modelling software. The model is deemed to represent the surface properties of the sample when the values of Ψ and Δ obtained from the model matched the experimental values. To obtain these values the thickness and refractive index of each layer are varied to obtain the optimum fitting. Further details on the analysis and optical models used are given in Chapter 3.

2.3.2. Quartz Crystal Microbalance (QCM)

QCM is a common technique used to measure the adsorption of surfactant additives onto different surfaces and has been used previously for OFM additives from oil based solutions. Lundgren showed the first case of OFM adsorption using this technique, showing the adsorption of differently saturated carboxylic acid molecules from a hexadecane solution.^{99–101} Since then there have been several other publications looking at different aspects of OFM adsorption, including the effects of concentration¹⁰² and OFM head group structure.^{59,64}

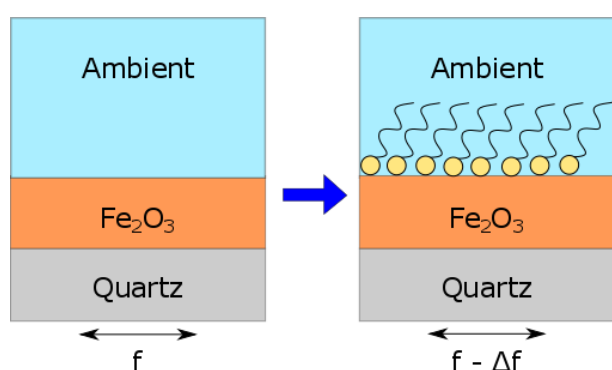


Figure 2-6: Diagram showing the adsorption of surfactant molecules within the QCM.

A QSense quartz crystal microbalance with dissipation (QCM-D) was used to measure the mass and the properties of the OFM adsorbed film. A QCM measures the resonance frequency f of a quartz crystal, which may drop as molecules deposit onto its surface, Figure 2-6. The dissipation of the crystal D is defined as the ratio of energy loss to that of the elastic energy input and may change depending on the properties of the adsorbed layer.¹⁰³ The resonance frequency of the quartz crystal used in this study is 5 MHz in air. The relationship between the adsorbed mass (Δm) and the change in resonance frequency (Δf) is described by the Sauerbrey equation, Equation 2-2.²¹ Note that C is related to the properties of the quartz crystal and in our case = 17.7 mg/m² and O is the harmonic overtone number. Equation 2-2 assumes that the adsorbed layer is relatively rigid (as shown by $\Delta D \sim 0$), and the adsorbed layer is uniform over the surface of the crystal.

$$\Delta m = \frac{C\Delta f}{O}$$

If the film is not rigid ($\Delta D \neq 0$), then the Sauerbrey equation is not valid and the Voigt viscoelastic model,¹⁰⁴ which also calculates the shear viscosity and shear elasticity of the adsorbed film, can be used instead.

SiO₂ and Fe₂O₃ coated quartz crystals were used to measure the adsorption of OFM additives onto these surfaces from a hexadecane solution. Before use, the QCM crystal was rinsed with toluene and isopropanol before UV Ozone cleaning for 30 minutes. The QCM cell and Viton O-ring was rinsed with toluene and isopropanol, before cleaning with oxygen plasma for 2 minutes.

After placing the crystal into the flow cell, the resonance frequencies and dissipations of the various odd overtones (O : 1 - 13) of the crystal were measured in air before hexadecane was injected at a flow rate of 0.35 ml/min at 20°C. Tests were also run at a faster flow rate, which gave similar results, showing that the adsorption process was not transport limited. Hexadecane was run until a stable baseline, defined as Δf in 10 mins < 1 Hz, was achieved before the additive solution was added. Note that this hexadecane baseline, which was stable in short time, showed considerable drift over 2 hours, Figure 2-7. This may be due to the impurities within the hexadecane adsorbing onto the surface as discussed in Chapter 8. Hence with our setup cautions must be taken when examining adsorption results obtained in hexadecane with long test duration. After the test, the system was rinsed with hexadecane, toluene, isopropanol then toluene and hexadecane to remove traces of the OFM from the tubing.

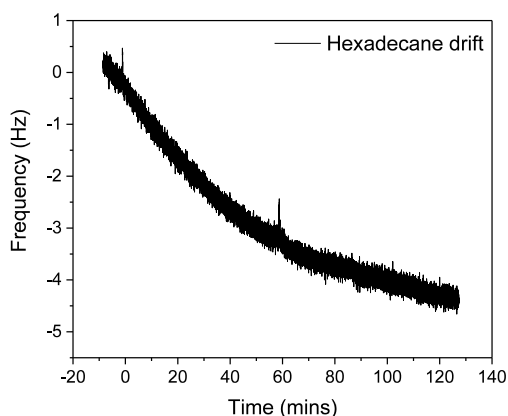


Figure 2-7: The drift frequency of the QCM crystal of hexadecane only over a full 2-hour test.

The test cell has an approximate volume of 0.15 ml. With the flow rate at 0.35 ml/min, the time for total displacement of solution already in the cell by the injection of the test solution (presuming an ideal system) is 26 seconds. This means that initial adsorption kinetics (the first 30s after the injection of the test solution) cannot be reliably measured for this system.

Table 2-1: Viscosity of OFM solutions in Hexadecane as measured using a Stabenger viscometer.

	ρ / kgm^{-3}	η / kgms^{-1}	ρ / gcm^{-3}
Hexadecane	773.0	0.00347	0.7730
1 mM Oleylamine	772.8	0.00347	0.7728
1 mM Octadecylamine	772.8	0.00347	0.7728
1 mM GMO	772.8	0.00347	0.7728
1 mM Oleic Acid	772.8	0.00347	0.7728
10 mM Oleylamine	773.0	0.00348	0.7730

Changes in viscosity and density of test solutions were measured using a Stabenger viscometer at 20 °C. The results in Table 2-1 show minimal change in the viscosity and density of hexadecane solutions containing OFMs at a concentration at or below 1 mM; and small change for solutions with

concentrations above 1 Mm. The QCM results were corrected for the change in liquid loading as shown in Equation 2-3 and Equation 2-4 for frequency and dissipation respectably.

Equation 2-3

$$\Delta f_{liquid\ loading} = -\sqrt{\frac{n}{\pi}} \frac{f_0^{\frac{3}{2}}}{\rho_q v_q} (\sqrt{\rho_l \eta_l} - \sqrt{\rho_s \eta_s})$$

Equation 2-4

$$\Delta D_{liquid\ loading} = \frac{1}{\sqrt{n\pi}} \frac{2f_0^{\frac{1}{2}}}{\rho_q v_q} (\sqrt{\rho_l \eta_l} - \sqrt{\rho_s \eta_s})$$

where ρ_q is the specific density of quartz, η_q is the shear wave velocity in quartz, $v_q = (\mu_q/\rho_q)^{1/2} = 2f_0 h_q$, μ_q is the shear modulus of quartz, h_q is the thickness of the quartz crystal, ρ_l is the density of the liquid containing the adsorbing species, η_l is the viscosity of the liquid containing the adsorbing species, ρ_s is the density of the solvent, η_s is the viscosity of the solvent.¹⁰⁵

Results shown are converted to changes in mass using the Saubery equation because the change in dissipation of the film is small ($D < 1$), Equation 2-2 and are further smoothed using a 15-point moving average.

2.4. Characterisations of OFM solutions

2.4.1. Infrared spectroscopy

Infrared (IR) spectroscopy is a well-known characterisation technique for the understanding the chemical composition of a sample. When IR radiation is passed through a sample certain wavelengths are adsorbed. The wavelengths of IR radiation that are absorbed correspond to the movement of chemical bonds (bond stretching and bending) of molecules in the sample. Only bond movements which change the dipole moment of the molecule absorb IR radiation.

A Perkin Elmer frontier Fourier Transform IR spectrometer in transmission mode was used. Samples were placed between two KBr plates with a known separation of 1 mm, IR radiation from 4000 - 400

cm^{-1} was passed through the plates and the absorption of these wavelengths was measured. The results obtained for the solutions were corrected by subtracting from it the spectrum of cleaned hexadecane. Due to the large path length which is required for the low concentration solutions, the peaks caused by the absorbance of hexadecane were saturated so any peaks overlapping with those of hexadecane cannot be accurately measured, as shown in Figure 2-8.

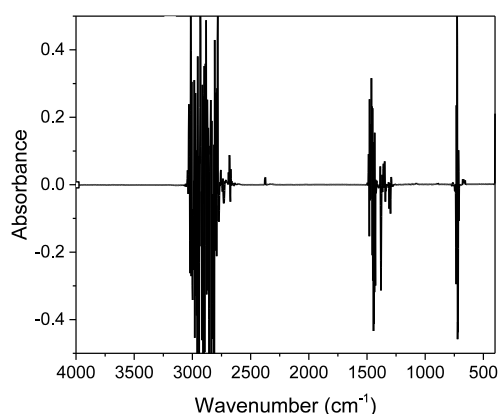


Figure 2-8: The absorbance of a repeated spectra of hexadecane, with the original hexadecane spectra subtracted showing the noise for certain wavenumbers within the baseline.

2.4.2. Spectrophotometry

Spectrophotometry (or UV-Vis spectroscopy) measures the absorption of different wavelengths of light through a solution. The wavelength of light absorbed corresponds to the energy required to excite an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The absorbance of visible light is normally caused by conjugated bonds in organic molecules or heavy metals.

The absorption (A) of light at a certain wavelength is calculated through the Beer-Lambert law (Equation 2-5), which uses measured intensity (I), initial intensity (I_0), extinction coefficient (ϵ), the path length (l) and the concentration of the additive (c).

$$A = \log_{10} \frac{I_0}{I} = \epsilon lc$$

Measurements were taken using a quartz cuvette with a path length of 1 cm. A background was taken of the empty cuvette before each set of measurements. The results were an average of 3 spectra.

2.5. Surface Analysis

2.5.1. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) has been used for the characterisation of OFMs within wear tracks and adsorbed onto different surfaces. The carboxyl peak of stearic acid molecule has been shown to have a shift in the binding energy from 289.2 eV as a free pure acid to 288.9 eV for a surface layer adsorbed onto Fe₂O₃. This peak shift shows the formation of a carboxyl salt on Fe₂O₃ surface, suggesting that stearic acid forms a chemical bond with the oxide.¹⁰⁶ The bonding of an adsorbed hexadecylamine layer from a dodecane solution on a surface of Fe₂O₃ provided insight into how the amine interacts with the surface. The nitrogen band has 2 peaks showing the amines interaction with specific surface sites, which suggests that the amine had greater interactions with the surface Fe atoms over the O atoms.⁵⁷

X-ray Photoelectron spectroscopy (XPS) is a surface sensitive technique which bombards the surface with X-rays, causing core shell electrons to be removed from the molecular orbitals of an atom, as shown in Figure 2-9. The energy of the released electrons from atoms on the top 5 nm of the surface can be measured. This energy, which is related to the environment of the atom the electron originated, is compared to known binding energies to identify what chemical species are on the surface.

A Thermo Fisher K-Alpha system with an X-ray beam energy of 1486 eV was used. A spot size of 400 µm for HFRR test samples and 200 µm for UMT test samples were used. Results were fit using the K-

alpha software. Peaks were fit with the same FWHM for each atomic spectra. Binding energies were normalised from the advantageous C-C peak found at 284.8 eV.

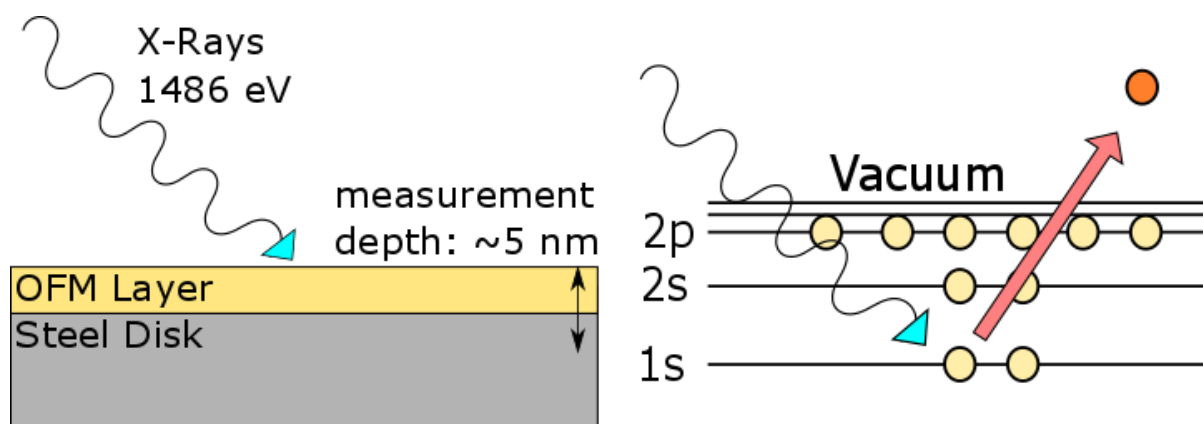


Figure 2-9: A diagram describing X-ray photoelectron spectroscopy (XPS)

2.5.2. Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a technique used for studying surfaces in the nanoscale, which can be performed in air and also in liquid environments. The nanoscale friction measurements of monolayers with mixtures of different chain length organo-silane molecules on Si wafer has been characterised using lateral force microscopy. It was found that 2 component systems with different chain length formed a homogeneous layer that provided lower friction than layers formed of the individual components.¹⁰⁷ Liquid cell AFM has been used to characterise monolayers of fatty acids on a mica surface. It has been shown that a 1 mM solution of stearic acid in hexadecane forms islands of 1.6 nm thick on a mica surface, whereas the unsaturated oleic acid is unable to form islands. This may be due to the inability of the unsaturated tails of oleic acid to form close packed monolayers.⁴³

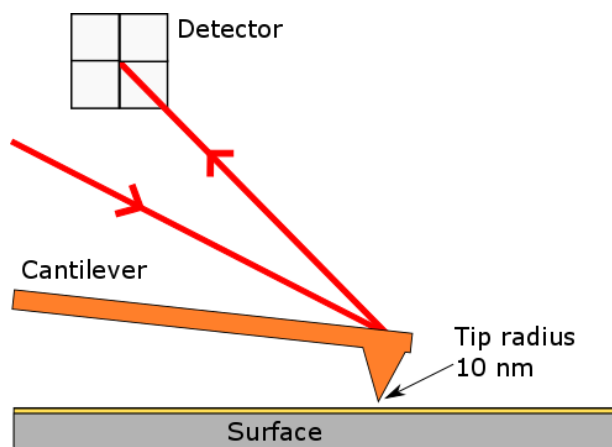


Figure 2-10: Diagram showing the general setup of an atomic force microscope

AFM uses a nanometer sharp tip, which is attached to a cantilever, to scan the surface to measure the topography and physical properties of the surface. The cantilever raster scans across the surface with the deformation of the cantilever measured through a laser reflected off of it into a detector, as shown in Figure 2-10. The 2 main types of AFM scan are tapping mode or contact mode. In tapping mode the tip vibrates with a known frequency, and gently taps the surface measuring the surface topography and also the phase change. The phase is the delay in the oscillation of the vibration of the tip when is tapped against a material. A change in phase can show regions of the surface with different viscoelastic properties. Contact mode AFM (or lateral force microscopy or friction force microscopy) is when the tip is in constant contact with the surface during the raster scan. The twisting of the cantilever can be used to measure the friction force of the surface.

The AFM used was a Veeco Multimode SPM with Nanoscope IV Atomic Force Microscopy (AFM) created by Bruker. The J scanner was used to scan areas up to $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$, using 256 points per line. Tips for use in air were purchased from budget sensors and were for both tapping and contact mode (Tap300AL-G and ContAl-G respectively). Both sets of tips were made of silicon with a tip radius of $< 10\text{ nm}$. The cantilever stiffness was 0.2 N/m for contact mode tip and 40 N/m for the tapping mode tip.

2.5.3. Scanning White light Interferometry

White light interferometry is regularly used to determine the topography of the surface to provide roughness and wear data.^{108–111} Thin film interferometry can also be used to determine the thickness of surface layers. It has been used to determine the separation of a ball and disk in a contact lubricated with OFM additives,¹⁹ and also the change in thickness of ZDDP tribofilms on the surface when mixed with OFM additives.¹¹²

Interferometry uses the reflection of light from a surface and a reflection from a known distance to measure the topography of the surface. The reflected light from the two surfaces will have a different phase, and when combined, causes the formation of constructive and destructive interference. For a white light source, three wavelengths are usually measured (red, green and blue) and the combined interference pattern can be used to estimate the distance the surface is from the lens. When mapped onto a surface, this technique can show the difference in height between the pixels imaged.

The topography of the steel disks and wear tracks were characterised with scanning white light interferometry from Veeco instruments. Measurements were taken using an objective with 20x magnification, measuring an area of 574 x 430 μm^2 . Roughness results were obtained from an area of approximately 100 x 200 μm^2 and were taken at 4 areas of each wear track.

2.6. Summary

Techniques used in this work to study the friction reduction of organic friction modifier additives have been discussed. Procedure and conditions of the carried out test have been stated.

Chapter 3. Ellipsometry for oil based systems

Abbreviations:

A, B, C, D, F, G , are numerical constants used within the refractive index

d , layer thickness

E , energy of the incident light

E_g , bandgap of the material;

E_0 , resonance frequency of the material

k , Extinction coefficient

n , refractive index,

N , complex refractive index

R_s , reflection of perpendicular polarised light

R_p , reflection of parallel polarised light

β , phase thickness

Γ , the dampening

ε , dielectric function of a material

λ , wavelength of the incident light

θ_i , angle of incidence light,

θ_t , angle of refracted light,

3.1 Theory of Ellipsometry

As mentioned in Chapter 2, ellipsometry measures the change in polarisation of light reflected off a surface. The reflection and refraction of light from an interface can be summarised by Snell's law and the Fresnel equation. Snell's law of refraction, Equation 3-1, shows that the angle of the refracted light (θ_t) depends on the angle of the incident light (θ_i) and the refractive indices of the two media the light is traveling through (n_1 and n_2).

Equation 3-1

$$n_1 \sin \theta_i = n_2 \sin \theta_t$$

The Fresnel equations, Equation 3-2 and Equation 3-3, describe the reflectance of an interface,⁸⁸ where R_s and R_p are the reflectance for the s-polarised and p-polarised light respectively.

Equation 3-2

$$R_s = \left(\frac{n_1 \cos \theta_i - n_2 \sqrt{1 - \frac{n_1^2}{n_2^2} \sin^2 \theta_i}}{n_1 \cos \theta_i + n_2 \sqrt{1 - \frac{n_1^2}{n_2^2} \sin^2 \theta_i}} \right)^2$$

Equation 3-3

$$R_p = \left(\frac{n_1 \sqrt{1 - \frac{n_1^2}{n_2^2} \sin^2 \theta_i} - n_2 \cos \theta_i}{n_1 \sqrt{1 - \frac{n_1^2}{n_2^2} \sin^2 \theta_i} + n_2 \cos \theta_i} \right)^2$$

For a multiple layer system, as shown in Figure 3-1, light will be reflected again at the surface layer-substrate interface after traveling through the surface layer. This layer can be characterised by the phase thickness (β), which describes change in phase of the refracted light. β can be found by Equation 3-4 using the thickness of the layer (d), the wavelength of the light (λ), the refractive index of the layer (n_2) and the angle of the refracted light as calculated from Snell's law (θ_2).

Equation 3-4

$$\beta = 2\pi \frac{d}{\lambda} n_2 \cos \theta_2$$

The total reflection of light from the surface (R) can then be characterised from the sum of the reflection of the different layers, as shown in Equation 3-5. The proportion of light that is reflected at each layer (r) are calculated from the Fresnel equation for each interface, with that from the lower interfaces (r_{23}) scaled due to the phase thickness.

Equation 3-5

$$R = \frac{r_{12} + r_{23} e^{-i2\beta}}{1 + r_{12} r_{23} e^{-i2\beta}}$$

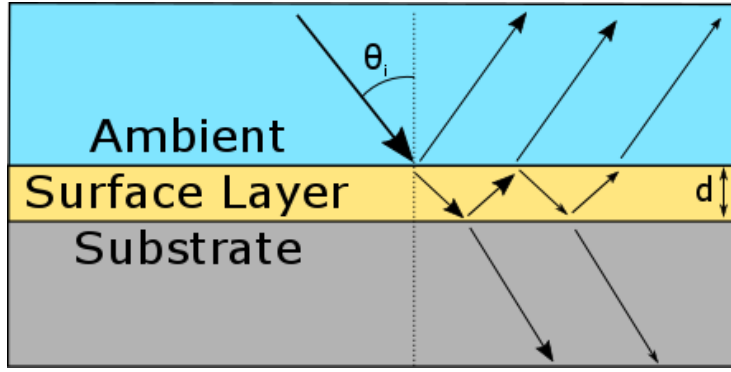


Figure 3-1: A generic optical model, with every layer having a different refractive index.

By applying Equation 3-5 to both the reflected perpendicular (R_s) and parallel (R_p) polarised light, the values Ψ and Δ can then be calculated using Equation 3-6.

Equation 3-6

$$\frac{R_p}{R_s} = \tan(\Psi)e^{i\Delta}$$

The values of Ψ and Δ are measured through the angles of the polariser and analyser at the null point (where the reflection of light is least) with $p = \frac{\Delta}{2} + 45^\circ$ and $A = \Psi$ when $C = 45^\circ$. These values need to be fit into an optical model which includes the optical properties of the surface, the complex refractive index of the surface layers and the layer thickness. The wavelength as well as the angle of incidence of the light source are also required to determine the optical properties of the surface layer. The complex refractive index (N) consists of two parts, the refractive index (n) and the extinction coefficient (k).⁸⁸ Note $\sqrt{\epsilon} = N = n + ik$ where ϵ is the dielectric function of a material. Once the N is known for a material it can be used for successive experiments to determine the thickness of the surface layers.

3.2 Optical Models

Some assumptions are made about the surface to create the optical models:

1. The surface contains multiple distinct layers, which are flat and of uniform thickness. Most surfaces modelled for ellipsometry consist of (a) the ambient environment (for these experiments either air or hexadecane), (b) flat surface layers with a definitive interface between the layers and (c) the base substrate, Figure 3-1. Examples of such systems include a monolayer on Fe_2O_3 or the native SiO_2 layer on a cleaned silicon wafer.
2. The refractive indices of individual layers are constant throughout the layer. If the density or composition of the layer changes throughout the thickness, then a model that consists of multiple layers is required.
3. There is no reflection from the underside of the substrate, either the light is extinguished by the substrate (substrate with a large extinction coefficient) or the reflected beam from the underside of the substrate is not in the measurement area (using a thick transparent substrate). The reflection of light at each interface will contribute to the change in polarisation of the reflected light and thus the Ψ and Δ values.

There are several models which can be used to define the refractive index of a material at a range of wavelengths. Note the refractive index of a material can consist of the summation of multiple optical models in order to properly represent the complex optical properties of certain materials.

The simplest model is to assume that the refractive index does not change with the wavelength of the incident light. This is only true of a vacuum where the refractive index is defined as being 1 but can also be used for other environments where the change in refractive index is negligible, such as air. This model is used for the adsorbed OFM layer.

The Cauchy model is used for transparent materials with a change in n over different wavelengths (λ).⁸⁸ Equation 3-7 shows that 3 parameters (A , B and C) are required to obtain an accurate fit. These values have no physical meaning but have been shown to be an accurate representation of refractive indices of materials with no extinction coefficient.¹¹³ The Cauchy model was used to obtain the refractive index of bulk hexadecane.

Equation 3-7: The Cauchy model

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

The Lorentz oscillator model (Equation 3-8) is used to model dielectric functions (ϵ) of materials, which is linked to the complex refractive index.⁸⁸ E_0 is the resonance frequency of the material, with D as the strength and Γ the dampening. For metals, this equation can be converted into the Drude expression where the resonance frequency (E_0) is 0. The Lorentz oscillator model was used to model the steel substrate.

Equation 3-8: The Lorentz oscillator model

$$\epsilon(E) = 1 + \frac{D}{E_0^2 - E^2 - i\Gamma E}$$

Tauc Lorentz fitting, Equation 3-9, is used to model semiconductors, where E_g is the bandgap energy, F is the oscillation amplitude, E_0 is the energy of the Lorentz peak and G is the broadening.¹¹⁴ This model assumes that there is no adsorption of energies below the bandgap energy E_g , therefore may need to be used in conjunction with other models to get an accurate refractive index over all wavelengths.

Equation 3-9: The Tauc Lorentz model for refractive index.

$$\epsilon(E) = \frac{1}{E} \cdot \frac{F E_0 G (E - E_g)^2}{(E^2 - E_0^2) - G^2 E^2}$$

If a surface is not uniform and consists of two or more different materials then an effective medium layer can be used. An effective medium is a mix of complex refractive index of the substrate and the ambient layer. A Bruggeman effective medium is used to simulate roughness (see Figure 3-2). In this work, a ratio of 50:50 of each layer is used to get a homogeneous refractive index. For a Si surface, the thickness of the effective medium layer is the same as the RMS surface roughness of the surface,

which holds true for roughness values below 4 nm. Above 4 nm, the thickness of the effective medium modelled is thicker than that of the measured RMS roughness value.^{115,116}

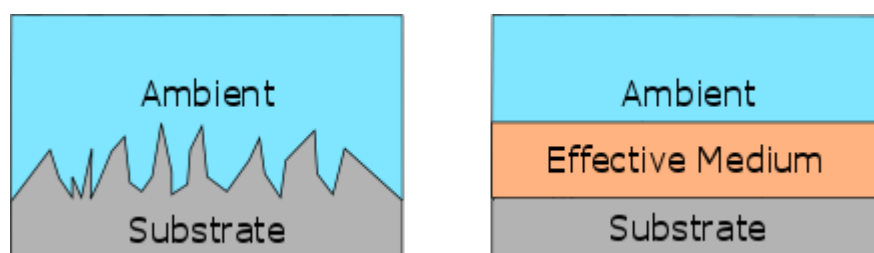


Figure 3-2: An example of how to model a rough surface with an effective medium

3.3 Determining the refractive index

Refractive indices of materials commonly used in ellipsometry, such as air, silicon and SiO_2 , are well-known and can be found in the EP4 software. They can be used for thickness fitting directly. For less commonly used materials; such as bulk hexadecane, Fe_2O_3 , steel disks and the adsorbed OFM layer, these values need to be determined. The following section details the methods used to determine the refractive index of each material.

3.3.1 The refractive index of bulk hexadecane

An open dish was filled with hexadecane (with a depth greater than 5mm) and placed on a hotplate located on the sample stage of the ellipsometer. The height was adjusted so that the reflection of light at the air-hexadecane interface was captured by the camera. When the temperature stabilised, spectroscopic measurements were performed at an angle of incidence of 60° on the air-hexadecane interface. Hexadecane is transparent and known to change refractive index with wavelength,¹¹⁷ therefore the Ψ and Δ values obtained was modelled using a Cauchy model, with the results shown in Figure 3-3 and Table 0-1 found in the Appendix.

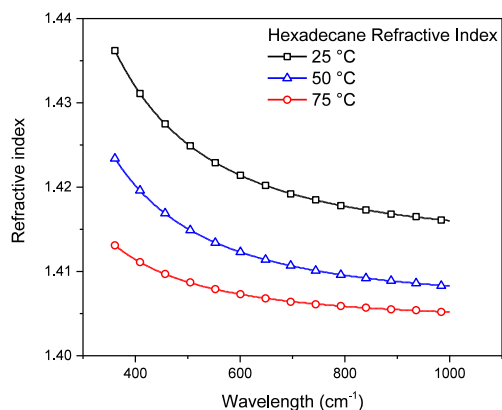


Figure 3-3: The refractive index of hexadecane at different temperatures, extinction coefficient =0.

3.3.2 The refractive index of Iron Oxide

Single crystal α iron oxide with a [0001] orientation was used as the substrate for some of the adsorption experiments. The roughness of the crystal was measured with Atomic Force Microscopy with an average Ra and Rq of < 0.5 nm. This shows that we can model the iron oxide crystal as a flat surface. The refractive index was found by running spectroscopic measurements at different angles of incidence in air, as well as in an ambient hexadecane environment. The Ψ and Δ values were fit using a Lorentz oscillator, and 2 tauc Lorentz oscillators, as shown in Figure 3-4 and Table 0-2 located in the appendix. The Tauc Lorentz oscillators produced a band gap energy of ~ 2 eV, which is similar to the measured band gap of Fe_2O_3 of 2.2 eV, with other bandgap energies higher than the wavelengths measured.¹¹⁴

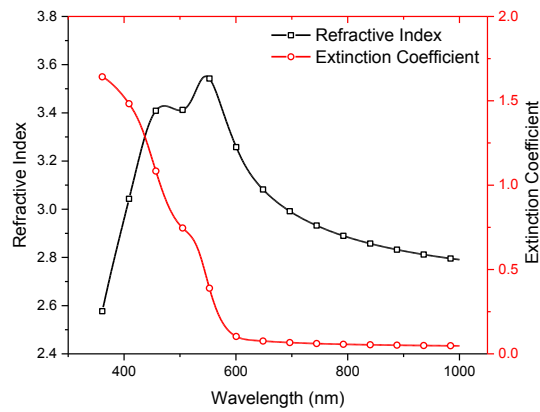


Figure 3-4: The refractive index and extinction coefficient of [0001] Fe_2O_3 crystal

3.3.3 The refractive index of steel disks

Steel disks were used as substrates for adsorption experiments in hexadecane and to measure the thickness of the adsorbed layer on the wear track after a friction experiment. These were discs commonly used for CETR friction test and are made of AISI 52100 steel. The steel has a native layer of oxide on the surface, which will have a different complex refractive index to the bulk steel. It is also rougher than surfaces commonly used for ellipsometry. These factors make these steel disks non-trivial for determining an ideal optical model. The model chosen (shown in Figure 3-5) shows a steel base layer (grey) with an oxide layer (green) and an adsorbed layer (yellow) on the surface. The oxide layer is rough. The effect of surface roughness is modelled as a Bruggeman effective medium layer (orange) between the oxide and the adsorbed layer on the surface. The effective medium layer is assumed to contain 50% iron oxide with the remaining 50 % consisting of the adsorbed layer.

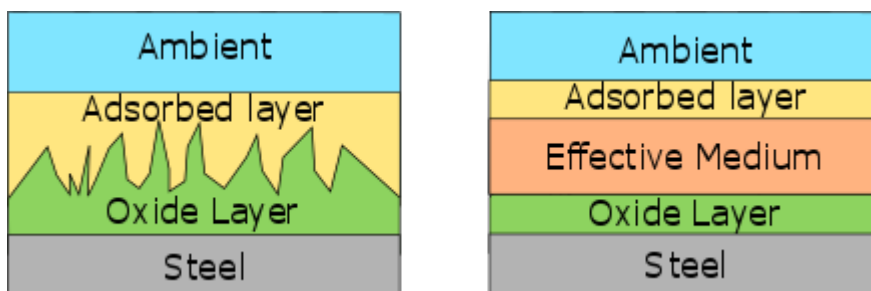


Figure 3-5: The surface model used to fit the obtained Psi and delta values for steel disk.

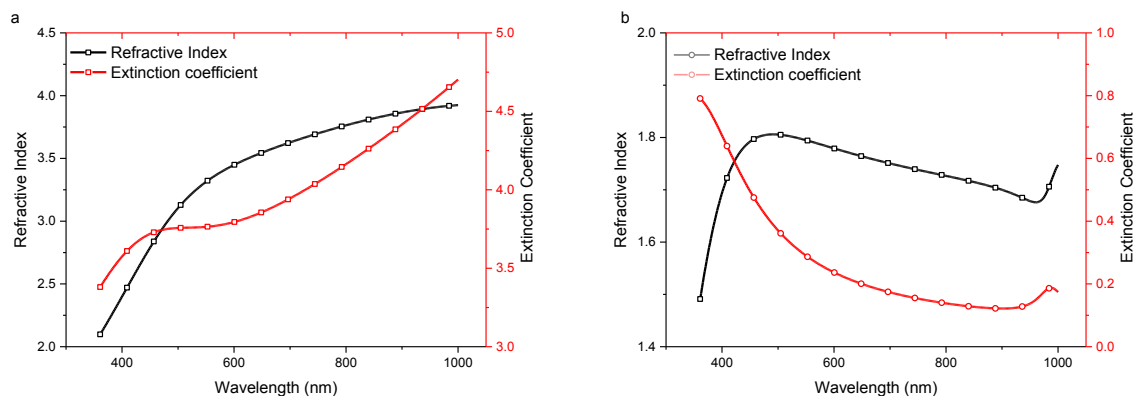


Figure 3-6: The refractive index and extinction coefficient of (a) Steel and (b) the oxide layer on the steel surface

Spectroscopic ellipsometry was performed on several steel disks in air and in hexadecane. Results from all runs were fit at the same time to get an average refractive index for the underlying steel substrate and the oxide layer for all disks, as well as the thickness of the oxide layer, and absorption layer of each individual disk. The steel and the steel oxide layer were both modelled with 3 Lorentz fits, as shown in Figure 3-6 and values shown in Table 0-3 and Table 0-4 in the appendix. The RMS roughness (R_q) of the steel disks were obtained through AFM measurements. At the scale of the size of a pixel of images obtained from the CCD camera in the imaging ellipsometer ($750 \times 750 \text{ nm}^2$), the steel disks had an average R_q of $2.43 \pm 1.22 \text{ nm}$. Similarly wear tracks after 100 rotations had an average roughness of $3.03 \pm 1.18 \text{ nm}$. Results were averages of 2-3 measurements inside and outside of the wear track on multiple disks. The average R_q values were used as a constant thickness of the effective medium for the fitting of steel disks. Fitting values obtained when using the extreme values of the error bars, showed minimal change to the results obtained.

3.3.4 The Refractive Index of Adsorbed OFM Layer

For ellipsometry measurement, the refractive index of thin films is coupled to the thickness of the layer.^{118,119} The consequence of this is that both the refractive index and film thickness cannot be determined from a single experiment. Several papers have avoided this issue by assuming a refractive index of the adsorbed layer, with most selecting the refractive index of the bulk surfactant or

protein.^{89,120–122} The refractive index of an adsorbed film has however been shown to be different to the refractive index of the bulk surfactant. For example Brunner showed that an adsorbed layer of octadecylsiloxane (with a bulk RI of 1.444 as measured with an abbe refractometer) has a refractive index of between that of chlorobenzene and tribromomethane (from 1.524 – 1.596) as found by measuring the Brewster angle of the film adsorbed onto a silicon wafer in these solvents.¹²³

Table 3-1 shows how the measured thickness of an adsorbed layer is affected by its modelled refractive index (1.45 – 1.55) in different ambient environments. This presumes a constant delta value, which corresponds to 2 nm film thickness at RI of 1.45 for all environments, at a constant wavelength of 552.2 nm (the wavelength used for kinetic measurements). In air ($n = 1$), the range of refractive indices has minimal impact on the estimated thickness of the adsorbed layer ($\pm 5\%$). In media with higher refractive indices, the choice of presumed refractive index of the adsorbed layer becomes more important. In hexadecane ($n = 1.43$), the adsorption film thickness drops from 2 to 0.5 nm as the refractive index of the film increases from 1.45 to 1.55. This makes having the correct RI for the adsorbed OFM layer important for having an accurate film thickness measurement in a hexadecane solution.

Table 3-1: The change in film thickness with the refractive index of the OFM layer with different ambient conditions.

RI of adsorbed film	Air (RI = 1)	Water (RI = 1.33)	Hexadecane (RI = 1.43)
1.45	2 nm	2 nm	2 nm
1.50	1.9 nm	1.5 nm	0.75 nm
1.55	1.8 nm	1.2 nm	0.5 nm

When monitoring the adsorption of OFM additives onto Si or Fe₂O₃, changes in both Psi and delta are observed as adsorbed film thickness increases, with the change in delta much greater than the change in Psi. Figure 3-7 shows how the modelled Psi and delta values change with changing film thicknesses for different presumed RI of the film. The change in delta (solid lines) is largely influenced by the

refractive index of the adsorbed layer. The smaller the refractive index difference between the layer and the ambient (hexadecane), the greater the change in thickness with a small change in delta.

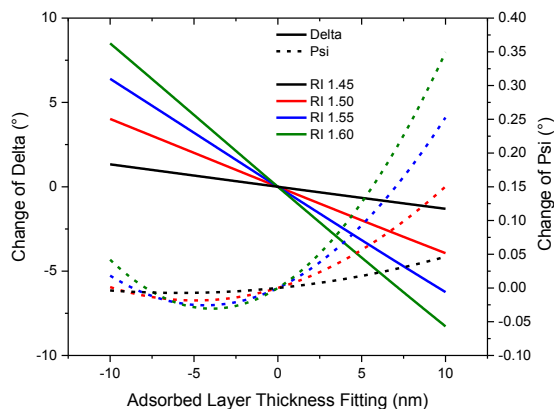


Figure 3-7: The modelled change in Psi (dotted) and Delta (solid) at different refractive indexes for a growth in adsorbed film from hexadecane solution onto a Si wafer.

These combined factors make the determination of the refractive index of the adsorbed layer important for obtaining reliable layer thickness. The method for the determining of the RI of the organic surfactant monolayer is as follows:

1. Si wafer was cleaned using Oxygen plasma for 30s and the thickness of SiO_2 on the wafer was measured by spectroscopic ellipsometry.
2. The cleaned wafer was placed into a solution of 1 mM octadecyltrichlorosilane (ODTS) in toluene to form a stable well-packed layer on the surface. After a 10-minute formation time, the ODTS coated wafer was rinsed with excess toluene. ODTS forms a densely packed covalently bound monolayer on the surface which has a strong absorbate-surface interaction.¹²⁴ This layer was used as it was thought not to be removed by the immersion in hexadecane.
3. The Ψ and Δ values of this coated layer were measured using spectroscopic ellipsometry in air.
4. The same wafer was placed into the solid-liquid cell and the Ψ and Δ values were measured while in a hexadecane environment.

5. Both of these measurements were fit simultaneously to provide the same refractive index and thickness of the ODTS layer in the ambient environment being air ($n=1$) and hexadecane ($n=1.4315$). This was repeated 3 times and the average result showing a refractive index of 1.55 for the adsorbed layer.

This result was used as the value for all the different OFMs tested, as the OFMs all have the same bulk refractive index to that of ODTS (1.46).

3.4 Comparing Results from QCM and Ellipsometry

Since both QCM and ellipsometry examine adsorption behaviour, their results should be related. They are linked most often using De Feijter's equation (Equation 3-10), which relates the adsorbed mass (m) to the thickness of the adsorbed layer (d), the difference in refractive index between the ambient solvent (n_{amb}) and the OFM (n) and the change in refractive index with concentration ($\frac{dn}{dc}$).¹²⁵

Equation 3-10

$$m = d \frac{(n_{amb} - n)}{dn/dc}$$

This works well for protein adsorption in aqueous solutions where $\frac{dn}{dc}$ is large. For OFMs in hexadecane, however where $\frac{dn}{dc}$ is ten times smaller than that of protein in aqueous solutions, the error incurred using De Feijter's equation can be substantial. In this case, the Cuypers method as shown in Equation 3-11⁹² may be used. To convert the thickness of the adsorbed layer (d) to the mass adsorbed on the surface (m), the density of the layer is required (ρ^0). The density is estimated by the ratio of the molecular weight (M) to the molar refractivity (A) of a molecule, along with the partial specific volume of the OFM at 20 °C (V_{20}) and the refractive indices of the pure bulk OFM (n) and pure solvent (n_{amb}). This equation assumes that the adsorbed layer is an ideal mixture between the OFM and the solvent, which has been shown previously to for OFM SAMs.¹⁸ The equation can be simplified if the adsorbed

layer is thought to be purely formed of the adsorbate which reduces the estimated mass on the surface compared to the solvent containing model.

Equation 3-11

$$m = d \cdot \rho^o = \frac{0.3}{\frac{A}{M} - V_{20} \frac{n_{amb}^2 - 1}{n_{amb}^2 + 2}} * \frac{n + n_{amb}}{(n^2 + 2)(n_{amb}^2 + 2)} * d(n - n_{amb})$$

Table 3-2: The values used in the Cuypers equation (Equation 3-11) to convert between QCM and ellipsometry data.

	Bulk OFM Refractive index, n	Ambient Refractive index, n_{amb}	Molar refractivity, A (m ³ /mol)	Molecular weight, M (g/mol)	Partial Specific Volume, V_{20} (m ³ /g)
1 mM Octadecylamine	1.46	1.4315	89	269.51	1.16279E-06
1 mM Oleic Acid	1.46	1.4315	87.1	282.48	1.11732E-06
1 mM GMO	1.46	1.4315	104	356.54	1.06157E-06
1 mM Oleylamine	1.46	1.4315	89	267.51	1.23001E-06
0.1 mM Oleylamine	1.46	1.4315	89	267.51	1.23001E-06
10 mM Oleylamine	1.46	1.4315	89	267.51	1.23001E-06

The values used for the conversion are bulk values. If the refractive index of the adsorbed layer would be used instead of that of the bulk OFM (as calculated in section 3.3.4), this would increase the mass calculated on the surface to be four times greater for all additives tested. The success of this conversion is discussed in Chapter 5 with results shown in Figure 5-13 and Figure 5-14.

3.5 Summary

This section describes how to use ellipsometry for tribological systems. Through understanding of the different optical models and systematic testing, the complex refractive index of tribological materials can be obtained.

Chapter 4. Effect of Surface Cleaning on Performance of Organic Friction Modifiers

The results of this chapter have been published and can be found at the following reference: Fry, B. M.; Moody, G.; Spikes, H.; Wong, J. S. S. Effect of Surface Cleaning on Performance of Organic Friction Modifiers. *Tribol. Trans.* 2019, 0 (0), 1–14.

4.1. Abstract

The performance of surface active additives, such as friction modifiers, depends on their interactions with surfaces. Their effectiveness thus hinges upon the surface conditions. In this work, the effect of cleaning methods of test substrates on the friction reduction capabilities of different organic friction modifier (OFM) additives was investigated. 52100 steel discs and balls were the test specimens. They were cleaned in five different ways. The cleaned surfaces were characterised by using ellipsometry and atomic force microscopy. The tribological performance of stearic acid (STA), octadecylamine (ODA) and octadecanol (ODO) on these surfaces were then tested.

As-received steel surfaces were covered with contaminants which may impede the formation of OFM surface layer. Cleaning these surfaces with solvents cannot completely removed these contaminants, with residue layers remain. Cleaning with oxygen or argon plasma results in cleaner surfaces as compared to those cleaned by solvents only. The impact of the choice of cleaning methods on friction depends on the strength of the interaction between the OFM and the steel surface, which determines the ability of an OFM to displace surface contaminations. Cleaner surfaces result in lower initial friction for STA and ODA. Steady state friction is also affected, but to a smaller extent. It may be because most contaminants remained in the wear track are mechanically removed during rubbing.

4.2. Introduction

Self-assembled monolayers (SAMs) have been shown to form on clean metal surfaces.⁵³ This is well known since the first realisation of SAMs when Zisman et al. created an oleophobic monolayer on a surface after cleaning the surface using a Bunsen burner.¹²⁶ Most papers about the formation of SAMs used gold surfaces due to its chemical inertness.^{89,127} Studies have been conducted on gold surfaces to find which cleaning method gives the most consistent monolayer. Through surface analysis techniques such as contact angle measurements and X-ray photoelectron spectroscopy (XPS), the cleaning methods found most effective are either piranha solution¹²⁸ or UV-Ozone.^{129–131}

Organic friction modifiers (OFMs) are known to self-assemble onto surfaces, with the polar head group adsorbing to the surface and the hydrocarbon tail group interacting with the solution. As a result, friction in the boundary regime is reduced.^{11,14} OFMs are typically used on steel surfaces, the most commonly used engineering surfaces. Steel samples are often received with surfaces covered with corrosion resistant chemicals or coatings, as well as other contaminants from the air. The commonly used corrosion inhibitors vary among samples and suppliers, from pastes which are applied to surfaces, to volatile corrosion inhibitors (VCI).¹³² If these molecules are not completely removed, they prevent OFM molecules from adsorbing on the surface. Note that adsorbed OFMs, with high surface packing density can lead to low friction.^{46,133}

Not all cleaning methods that are effective for gold surfaces can be applied to steel. For example, steel reacts with the piranha solution and oxidises in other aqueous based cleaning solutions. In the literature, steel samples for OFM friction tests are cleaned in several ways. In Zisman's original experiment,¹²⁶ the non-oxidising part of the flame from a Bunsen burner was used to clean various metals. This method has since been found not to give reproducible results. Cleaning steel surfaces with solvents is common practice. While some did not mention the cleaning solvents used,^{112,134} many, however use solvents such as benzene,⁴⁴ acetone^{28,108,135,136} and toluene.^{14,137,138} When cleaning with a solvent, residues, indicative of surface contamination, may remain on the surface.¹³⁹ This may

influence the tribological properties of the surface in dry sliding. Barthel *et al.* examined the impact of several cleaning methods on steel-on-steel dry sliding friction. They found that solvent cleaning left a residue on the surface which results in lower friction whereas UV/ozone cleaning produced a cleaner surface and hence higher friction.^{77,140} This suggests that surface contaminants may lubricate rubbing contacts.

Oxygen plasma^{141–143} or argon plasma^{141–143} can effectively remove surface contaminants and have been used as the final cleaning step of surfaces for tribological tests.^{72,144} Oxygen plasma works by bombarding the surface with oxygen ions, which react and oxidise the surface. This changes organic material into CO₂ and H₂O (which are then removed by the vacuum pump) and inorganic material into oxides. It is a common method for cleaning silicon surfaces.¹⁴¹ Argon plasma works by bombarding the surface with inert argon atoms which etch away the top layer at the surface. Note that long periods of plasma treatment have been shown to promote the growth of a layer of carbon on the metal surface¹⁴⁵ and increase the surface roughness,¹⁴² both of which will prevent the SAM formation on the surface.¹⁴³

It should be noted that surface cleanliness, or in more general terms, surface treatment, also impacts on the interaction between base oils and the surface. NASA researchers have found that surface cleanliness affects the surface wetting. They found that a chlorofluorocarbon (CFC) based cleaning fluid provides the longest bearing lifetime, with UV-Ozone and super critical CO₂ cleaning producing a lower bearing lifetime.¹⁴⁶ The wettability of aluminium is important for the application of paints which act as a protective layer from corrosion. Cold air plasma is used to clean the surface finding that the longer the plasma treatment the greater the wettability of the aluminium.¹⁴⁷ Several different solvents have been tested to measure the changes to wettability of a metal surface, finding that cleaning the surface with hydrogen peroxide provides the smallest contact angle of water with the surface.¹¹¹ Carbon contamination and wettability of bearing steel prepared with different cleaning methods have also been studied. It was found that the using fluorinated hydrocarbons in a vapor degreaser (Soxhlet

cleaner) results in surface with the least contamination, leading to increase surface wettability.¹⁴⁸ The wettability of a lubricant is important for elastohydrodynamic lubrication, as it affects lubricant entrainments and lubricant flow in the contact. Since this work focuses on the use of additives on boundary lubrication regime, and that all tested lubricants wetted tested rubbing surfaces well, the effect of surface cleanliness on lubricant wettability is neglected in this study.

There is a common consensus on the importance of surface conditions on the properties of the OFM adsorbed layer. The variation of cleaning methods among tribological studies makes the comparison of results from different studies difficult. This paper investigates how cleaning methods of steel substrates affect the friction reducing properties of OFM additives. More specifically this paper examines the effects of the cleaning process on (1) the cleanliness of steel surfaces; (2) the formation of OFM adsorbed layers on steel; and (3) the effectiveness of OFMs.

4.3. Materials

Three commonly used model OFM additives, stearic acid ($\geq 99\%$), octadecylamine ($\geq 99\%$) and octadecanol ($\geq 99\%$) were all used as received. The different head groups have shown different bonding to the surface with acid > amine > alcohol.¹⁴⁹ They are referred as STA, ODA and ODO respectively in this study. The structures of these molecules are shown on Figure 4-1. The base oil, hexadecane ($> 99\%$, Sigma Aldrich), was used as received. 1 mM OFM solutions (w/w 0.037%, 0.035% and 0.035% for STA, ODA and ODO respectively), as well as 0.1 mM and 0.01 mM stearic acid solutions were prepared by stirring at 60 °C.

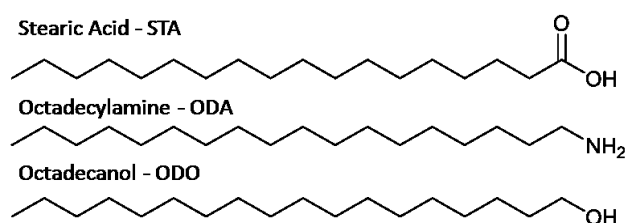


Figure 4-1: Chemical structures of stearic acid, octadecylamine and octadecanol.

Analar toluene ($\geq 99.5\%$), acetone (99.6%) and hexane (99%), were used as received without further purification. AISI 52100 6 mm diameter steel balls and AISI 52100 15 mm diameter steel disks hardened to 800Hv, were used for friction tests. The ball and the disk have a measured roughness (R_a) of 41 ± 3 nm and 6 ± 2 nm respectively.

4.4. Experimental Methods

4.4.1. Cleaning of the Substrates

Steel substrates were cleaned in six ways. In any experiment, both the ball and the disk cleaned in the same way. The six cleaning methods are:

1. No Cleaning; the ball and the disk were used as received.
2. Acetone Cleaning; the ball and the disk were sonicated in acetone for 30 minutes then rinsed with acetone.
3. Toluene-acetone cleaning; the ball and the disk were sonicated in toluene for 30 minutes then rinsed with acetone.
4. Toluene cleaning; the ball and the disk were sonicated in toluene for 30 minutes then rinsed with toluene.
5. Oxygen plasma cleaning; the ball and the disk was first cleaned by the toluene cleaning process (Method 4), then was cleaned with oxygen plasma for 30 seconds.
6. Argon plasma cleaning; the ball and the disk was first cleaned by the toluene cleaning process (Method 4), then was cleaned with argon plasma for 30 seconds.

They are summarised in the effect of plasma cleaning.

Table 4-1. Method 1 investigates if cleaning is necessary. Methods 2 – 4 examine the effectiveness of different solvent cleaning methods commonly used in literature. Finally, methods 5 and 6 study the effect of plasma cleaning.

Table 4-1: Summary of the different cleaning methods studied.

Method	Sonication solvent	Rinsing solvent	Plasma
1 No cleaning	-	-	-
2 Acetone cleaning	Acetone	Acetone	-
3 Toluene-acetone cleaning	Toluene	Acetone	-
4 Toluene cleaning	Toluene	Toluene	-
5 Oxygen plasma cleaning	Toluene	Toluene	Oxygen
6 Argon plasma cleaning	Toluene	Toluene	Argon

4.4.2. Friction Measurements

Friction tests were carried out with tribometer with a ball on disk setup. Tests were run at 5 N with the sliding speed fixed at 1 mm/s. The radius of the rubbing track on the disc was 1 mm, thus each disc rotation corresponded to a sliding distance of 6.28 mm. A total sliding distance of 628 mm (100 rotations) was applied to all tests. The tests were carried out at room temperature (23-27 °C). Each result presented is an average of 4 measurements, with the error values for the first and 97th rotation shown in Figure 6.11. Note that friction coefficients after the fifth rotations are data averaged over 1 full rotation. Friction traces obtained in this work are divided into two stages. Results taken from the first 10 rotations and less give short time friction and corresponds to the short time performance of OFMs. The steady state friction coefficients are obtained from results after the tenth rotation.

4.4.3. Surface Characterisation

Surface characterisation was conducted in ambient conditions. An Atomic Force Microscopy (AFM) was used to examine the surface topography of the cleaned steel disc surfaces (see section 5.2 in Chapter 2). Most images, unless otherwise stated, were obtained with a scan size of $10 \times 10 \mu\text{m}^2$ and a scanning frequency at 0.5 Hz. At least 3 tests were performed for each condition. The thickness of surface contamination layer was estimated in a $3 \times 3 \mu\text{m}^2$ area, with a $1 \mu\text{m}^2$ square scratched away

by the AFM tip at high loads. The step created by the scratch test was used to estimate the thickness of the contamination layer.

Roughness measurements were performed using a white light interferometer, with an area of $200 \times 100 \mu\text{m}^2$ inside the wear track. The results shown are averaged over four measurements.

Ellipsometry measurements were taken of the discs using an imaging ellipsometer (see section 3.1, Chapter 2; and also Chapter 3). Spectroscopic ellipsometry measurements were taken at an incident angle of 60° using 44 wavelengths from 371 nm to 1000 nm. For all samples, the model consists of 5 layers in the following sequence: air as the top most layer with infinite thickness, followed by the contamination layer, an effective medium layer made of 50:50 contamination and oxide, an oxide layer, and the steel substrate at the bottom, as shown schematically in Figure 4-2. More information about the refractive indices of the layers and fitting details are given in Chapter 3.

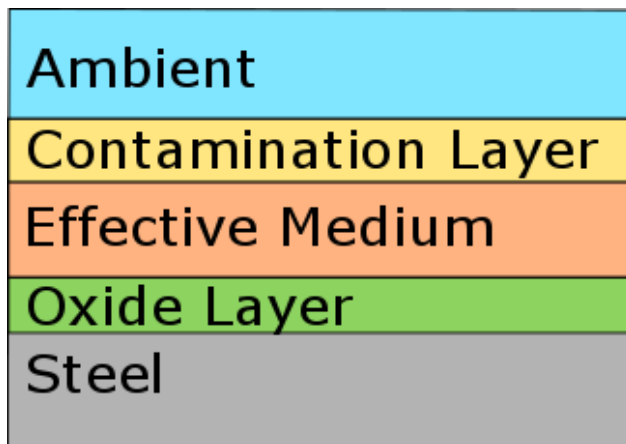


Figure 4-2: Schematic of the five-layer model used to estimate the thickness of the contamination layer by spectroscopic ellipsometry.

4.5. Results

4.5.1. Effectiveness of Various Cleaning Methods

Organic solvents are commonly used for cleaning steel surfaces. The appropriateness of the selected solvent would depend on the type of contaminants on the steel surface. As received steel samples are covered with corrosion inhibitors, and other contaminants due to handling. The two solvents used in

this study, acetone and toluene, have relative polarities of 0.355 and 0.099 respectively.¹⁵⁰ More polar solvents are more able to dissolve polar additives.

Surfaces of the as-received and cleaned substrates were examined with AFM as shown in Figure 4-3. The as-received steel disk (Figure 4-3a) has particulates all over its surface. These particulates, with mean height and diameter of about 4 and 95 nm respectively, are relatively homogeneous in size and cover about 5 % of the surface area. A thin contamination layer underneath the particulates can also be seen. This contamination layer contains micron sized pinholes. The depth of these pinholes is about 2 – 4 nm, suggests that a nm thick contamination layer exists.

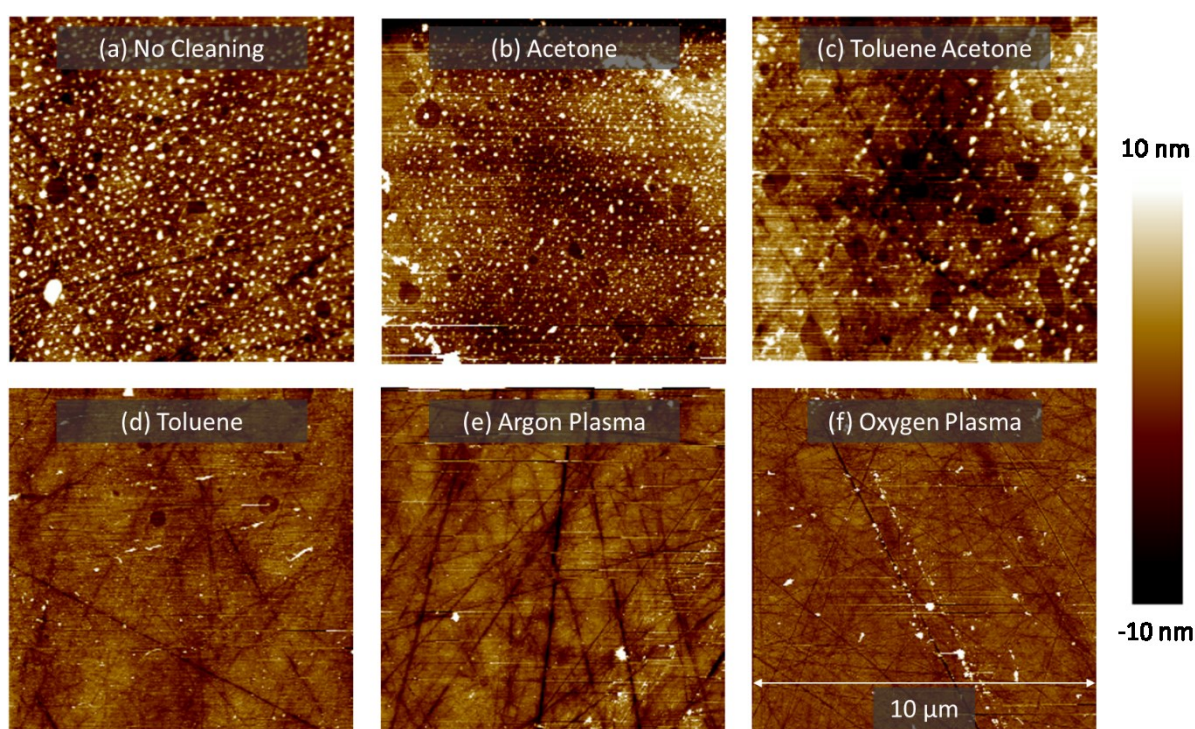


Figure 4-3: Topographical images of steel disks that have been subjected to, (a) no cleaning (b) acetone cleaning, (c) toluene acetone cleaning, (d) toluene cleaning, (e) argon plasma cleaning and (f) oxygen plasma cleaning.

The substrates that were cleaned with acetone (Figure 4-3b and Figure 4-3c) show an increase in the coverage of contaminant particles on their surfaces (see Table 4-2). Note the surface coverage of the contaminants on the surface sonicated with toluene and then rinsed with acetone (Figure 4-3c) is lower than that cleaned by just acetone alone (Figure 4-3b). While the thickness of the contamination layers of these surfaces and that of the as-received surface are similar, particulate size changes after

cleaning in both cases. This may be due to the breaking up, re-adsorption and re-arrangement of particulates on the surface during rinsing and sonication. Interestingly, surfaces cleaned with toluene only (Figure 4-3d) are cleaner, with fewer particulates (Table 4-2). These results suggest that using acetone is not effective and potentially may contaminate the steel surfaces. Cleaning the toluene-cleaned surface with argon (Figure 4-3e) or oxygen (Figure 4-3f) plasma removes most of the particulates, as well as some of the contamination layer. The contamination layers can be scratched away with an AFM tip, potentially exposing the steel surface (scratch tests). The thickness of the contamination layer, estimated by measuring the step produced by the removed materials, together with results from spectroscopic ellipsometry, are shown in Table 4-2. The thickness of the effective medium and iron oxide layers for fitting data from ellipsometry are shown in

Table 4-3. The thickness of the contamination layer are higher for all solvent-cleaned disks, with toluene acetone cleaning showing the thickest contamination layer through ellipsometry and AFM scratch tests. Plasma cleaned surfaces are much cleaner than the solvent cleaned surfaces, with both ellipsometry and AFM results showing minimal contaminations.

Table 4-2: Thickness measurements of the contamination on the surface after different cleaning methods.

	Size of particulates			Thickness of the contamination layer		
	AFM			AFM		Ellipsometry (nm)
	Mean height (nm)	Mean diameter (nm)	Area covered (%)	Pinhole depth (nm)	Scratch test (nm)	
No Cleaning	4.2	95	5.0	2.8 - 4.8	1.8 – 2.3	1.9 – 6.1
Acetone	3.8	92	10.6	1.9 - 5.3	1.7 – 2.3	3.6 – 3.7
Toluene Acetone	3.4	127	8.5	1.9 – 4.3	2.9 – 3.1	4.8 – 5.1
Toluene	2.6	68	1.3	2.3 – 3.8	1.2 – 2.6	2.8 – 3.8
Argon Plasma	2.6	79	0.5	-	0.0 – 1.4	0.7 – 1.0
O2 Plasma	3.8	79	1.1	-	0.0 – 2.3	0.4 – 1.6

Table 4-3: The thicknesses of the layers on the steel disk measured through fitting of the spectroscopic ellipsometry data.

Layer Thickness (nm)	No Cleaning	Acetone	Toluene Acetone	Toluene	Oxygen Plasma	Argon Plasma
Contamination	1.9 - 6.1	3.6 - 3.7	4.8 - 5.1	2.8 - 3.8	0.4 - 1.6	0.7– 1.0
Effective medium	2.43	2.43	2.43	2.43	2.43	2.43
Oxide	5.0 - 5.2	4.9 - 5.1	4.8 - 5.0	4.8 - 5.9	4.80 - 5.1	2.6 - 5.0

In summary, solvent cleaning, particularly using toluene, is effective in the removal of particulate contaminants. The removal of contamination layers, however, requires plasma treatment. Since surface cleanliness affects the properties of OFM surface layers, it is hypothesized that friction coefficients results from the use of OFM depends on the chosen cleaning procedure.

4.5.2. Effect of Cleaning on OFM Performance: Change of OFM Head Group

Three different head groups were chosen as OFM additives. The effectiveness of 1 mM stearic acid in hexadecane (1 mM STA) in reducing friction of steel-steel contacts is shown in Figure 4-4. The solvent cleaned samples (yellow asterisks, red triangles and blue inverted triangles for acetone only, toluene then acetone, and toluene only samples respectively) and as-received sample (green squares) have similar friction coefficients during the first 3 rotations. Friction is the highest ($\mu \sim 0.22$) during the first rotation. It drops gradually in the first three rotations, after which it remains relatively constant ($\mu \sim 0.08$). With plasma-cleaned samples (pink stars and black diamonds, Figure 4-4), 1 mM STA gives constantly low friction throughout the tests. Note that all steel samples regardless of cleaning processes have similar steady state friction coefficients. (see insert in Figure 4-4). Thus the effect of cleaning procedures on the effectiveness of STA is only apparent to short time friction.

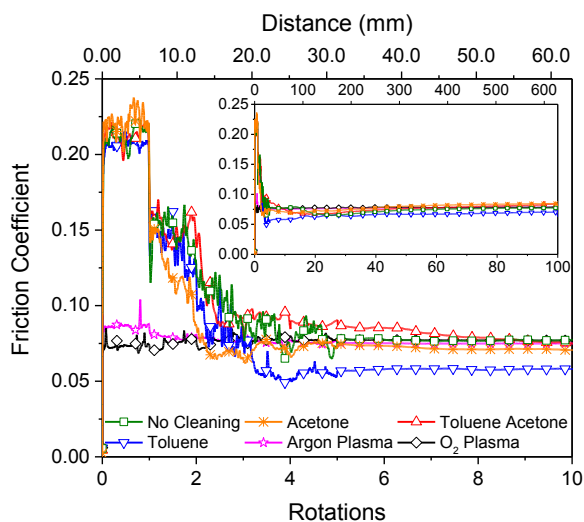


Figure 4-4: The effect of cleaning method on the friction of steel-steel contact lubricated by 1 mM stearic acid solution.

Similar conclusions can be made when 1 mM Octadecylamine in hexadecane (1 mM ODA) is used, see Figure 4-5. Plasma cleaned samples (pink stars and black diamonds, Figure 4-5) maintain $\mu \sim 0.08$ throughout the test. For solvent-cleaned samples, the transition from initial high friction state ($\mu > 0.17$) to lower steady state friction ($\mu \sim 0.08$) occurs more quickly than the case of 1 mM STA and takes only one rotation. The steady state friction among solvent-cleaned samples varies. Samples cleaned with acetone, together with the as-received sample having the highest friction, while acetone-toluene cleaned and toluene cleaned samples exhibit lower friction. Plasma cleaned samples have the lowest friction. Our results show that substrate cleaning procedures impacts on both long and short time effectiveness of ODA, with cleaner substrates result in lower steady state friction.

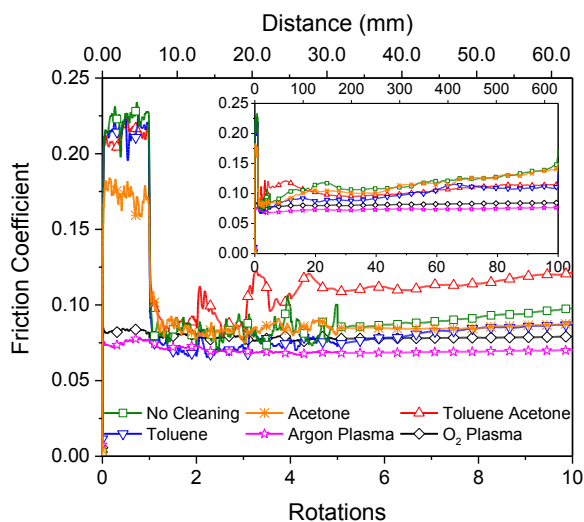


Figure 4-5: The effect of cleaning method on the friction of steel-steel contact lubricated by 1mM octadecylamine solution.

Steel-steel contacts in 1 mM Octadecanol in hexadecane (1 mM ODO) have higher friction than those observed with 1 mM STA and 1 mM ODA. 1 mM ODO gives similar friction coefficients for all samples regardless of cleaning methods initially (see Figure 4-6), with the plasma-cleaned samples ($\mu \sim 0.20$) giving slightly lower μ than the solvent-cleaned ones ($\mu \sim 0.24$). Coefficients of friction are initially relatively constant, they then increase with the number of rotations (see insert, Figure 4-6), signifying damage to the surface. Acetone-cleaned samples (yellow asterisks) see a rise in friction coefficient from the 10th rotation and reaches a high constant friction stage ($\mu \sim 0.5$) by the 40th rotation (rubbing distance ~ 240 mm). All other samples exhibit a more gradual increase in friction coefficient and did not stabilise by the end of the tests. These observations suggest that ODO is an ineffective OFM in our test conditions.

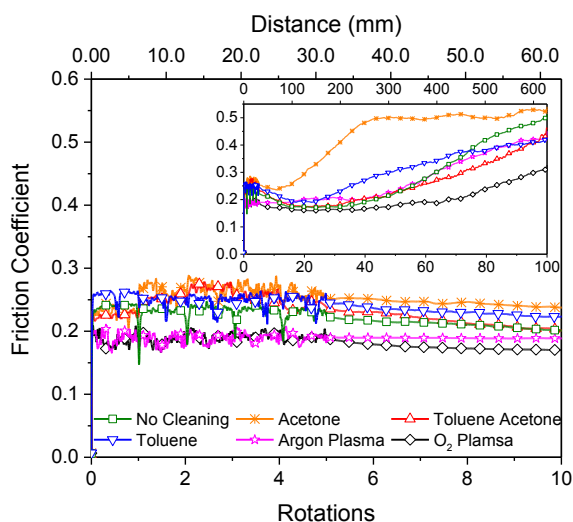


Figure 4-6: The effect of cleaning method on the friction of steel-steel contact lubricated by 1mM octadecanol solution

4.5.3. Effect of Cleaning on OFM Performance: Change of OFM Concentration

To investigate if the sensitivity of the effectiveness of OFM to the substrate cleaning procedures depend on the concentration of OFMs in lubricants, solutions with 0.01, 0.1 and 1 mM stearic acid (STA) in hexadecane were used to lubricate toluene-cleaned and oxygen plasma-cleaned substrates. Regardless of cleaning methods, the transition from the initial high friction state to the lower friction steady state takes longer and the steady-state low friction coefficient increases with decreasing STA concentration (Figure 4-7 and Figure 4-8). Note that for 0.01 mM STA, the friction coefficient increases eventually after a period of constant friction coefficient. The increase in μ at this stage is accompanied by damage to the rubbing surfaces. Plasma cleaning results in surfaces with lower initial friction and a shorter transition from initial high friction state to lower steady state friction. The lowest friction coefficient achieved for STA in this study is about 0.08. This is achieved more readily for the plasma cleaned surface (0.1 mM) than the solvent cleaned surface (1 mM), see green diamond lines in Figure 4-7 and Figure 4-8.

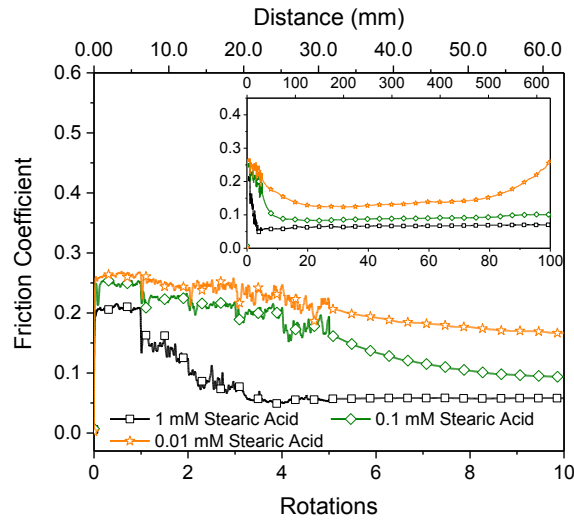


Figure 4-7: The effect of additive concentration on the friction of toluene-cleaned steel-steel contact lubricated by stearic acid solution.

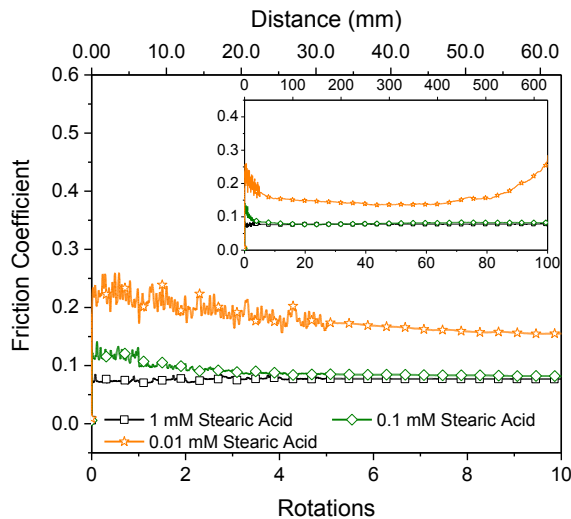


Figure 4-8: The effect of additive concentration on the friction of oxygen plasma cleaned steel-steel contact lubricated by stearic acid solution.

Having low friction can be important for managing wear of rubbing contacts. Figure 4-9 shows how roughness of resulting wear tracks after 100 rotations, shown as S_a taken from interferometric images (shown in Figure 4-10), is related to the friction at the 97th rotation. As expected, higher friction coefficients correspond to rougher surface. This is primarily dictated by the chemistry of OFMs, with ODO (blue symbols) always has high friction coefficients and high wear track roughness and STA (olive symbols) always has low friction and low roughness in this study (Figure 4-9a). The impact of cleaning process is most clearly obtained using ODA (red symbols, Figure 4-9b), with as received (red square)

and acetone-cleaned (red asterisk) samples having significantly higher roughness than argon plasma cleaned samples (red star) where the wear tracks were barely visible.

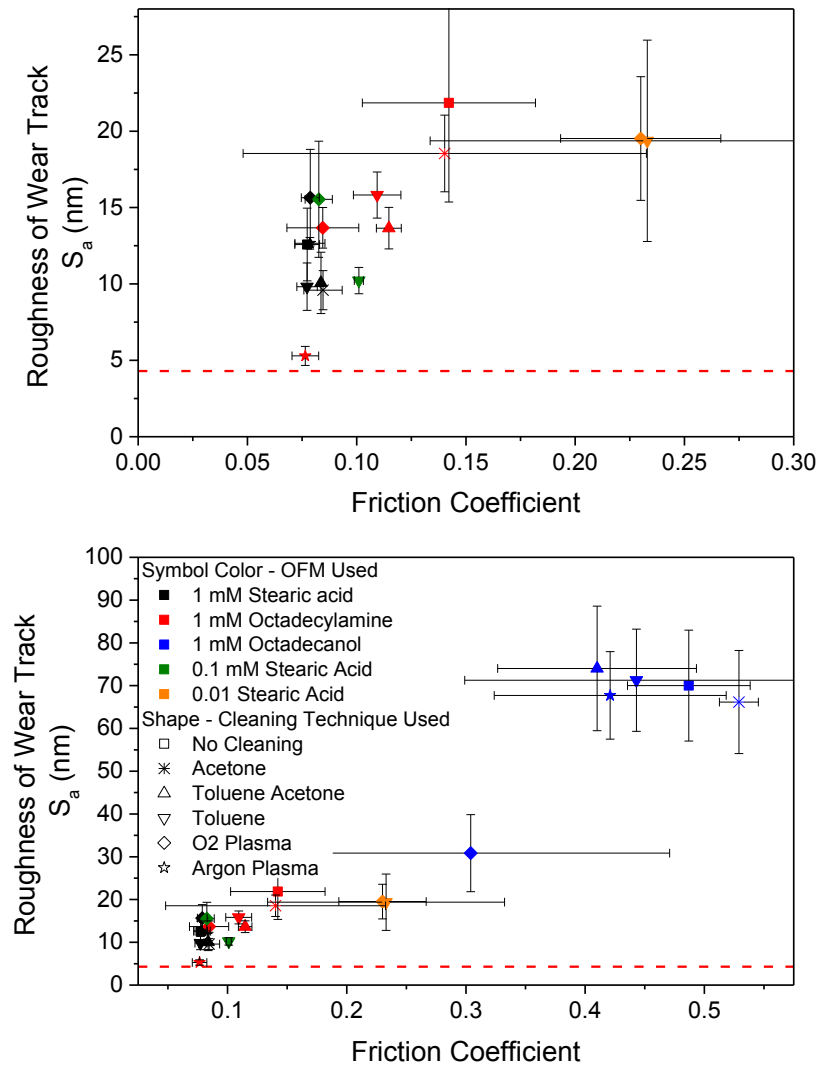


Figure 4-9: The relationship between the roughness of the wear track and the steady state friction coefficient obtained from OFM solutions, (a) excluding and (b) including data from octadecanol. The red dashed line shows the roughness of the disc outside of the contact area.

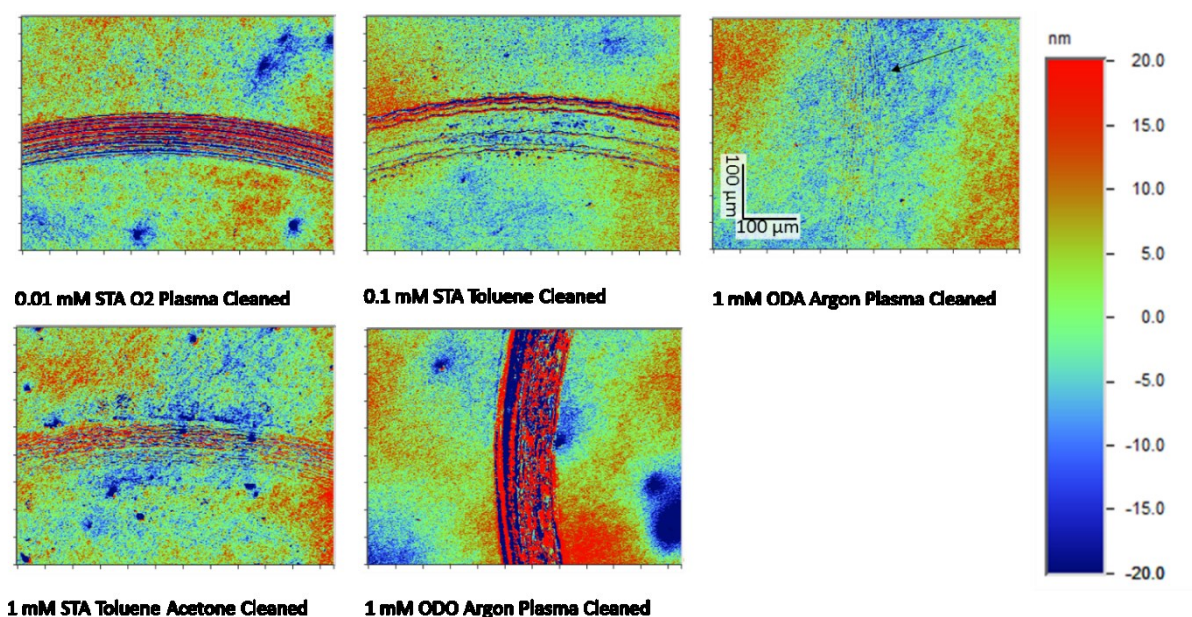


Figure 4-10: Representative WLI images of the wear track on the disk for the 5 different OFM additives tested.

4.6. Discussion

The friction coefficients obtained with stearic acid (STA), octadecylamine (ODA) and octadecanol (ODO) at the 1st and the 97th rotations of friction tests are presented in Figure 4-11. Together with results discussed in previous sections, important observations regarding the effects of cleaning procedures of steel surfaces on cleanliness of steel surfaces and the effectiveness of OFM are summarised below:

- (1) Solvent cleaning is not effective in removing surface contaminants. Toluene can remove particulates in this study. Plasma-treatment is necessary to effectively remove surface contaminants.
- (2) The effect on OFM chemistry has a greater influence than the choice of cleaning procedures on the effectiveness of OFMs in steady-state friction coefficients (solid symbols, Figure 4-11).
- (3) The choice of cleaning procedure impacts on initial friction coefficients (shown as open symbols, Figure 4-11), and the transitions from initial high friction state to steady state lower friction state.

- (4) The concentration required of the OFM for low friction is greater for toluene-cleaned surfaces than for plasma-cleaned surfaces.

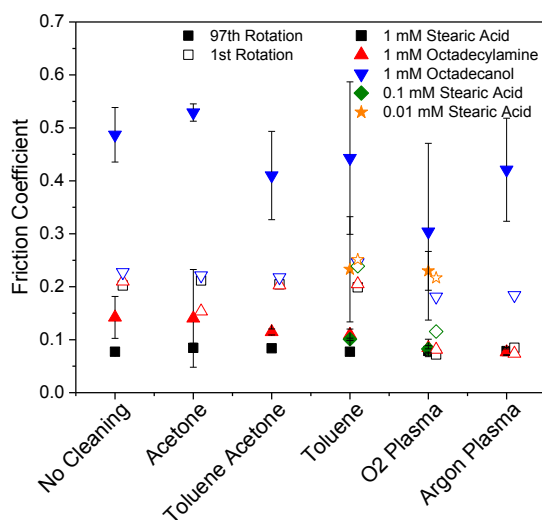


Figure 4-11: Summary of the friction at the 1st and 97th rotation of different samples

The effectiveness of OFMs is commonly linked to the quality of the self-assembled OFM layers, and hence the surface conditions. It is thus perhaps surprising that the influence of cleaning procedures is limited to the initial friction experienced by the steel-steel contacts. Additionally, while the amount of surface contaminants depends on the choice of solvents, all solvent-cleaned surfaces behave similarly, and have similar friction coefficients at the first rotation (see Figure 4-11).

4.6.1. Surface Cleanliness Affects Adsorption of OFMs

For OFMs to reduce friction and surface damage of a steel-steel contact, the OFM needs to interact with the steel surface directly. In a friction test, this can be achieved by (1) the OFM molecules displace the surface contaminants; and (2) mechanical removal of contaminants due to rubbing. The former is governed by the strength of the interaction between the additive and the surface, and will likely be relevant at the very start of the rubbing test. The latter is driven by the applied shear stress, and is likely to be relevant to subsequent rubbing. This leads to our observation that the choice of cleaning method impacts more on the initial high friction state than on the steady state friction.

1 mM of OFMs in hexadecane were given 2 minutes to adsorb on steel surfaces before the friction test began. The friction coefficients obtained during the first rotation, μ_1 , for as-received and solvent cleaned samples were similar. Note that while the amount and the morphology of particulate contaminants differ, a sufficient amount of surface contaminants, in the form of a contamination layer (~2 nm thick), remain on all solvent cleaned samples. On the other hand, plasma cleaned samples do not have this contamination layer and show a lower μ_1 of 0.08 for STA and ODA (Figure 4-4 and Figure 4-5). The results obtained using 0.01, 0.1 and 1 mM STA (Figure 4-7 and Figure 4-8) in hexadecane show similar μ_1 with toluene-cleaned samples, while μ_1 decreases with STA concentration for plasma-cleaned samples. This suggests that the displacement of surface contaminants by the OFM, and hence the availability of surface binding sites, are crucial in determining the effectiveness of OFM. As a result, the existence of the contamination layer, rather than the OFMs, determines the friction of the first rotation.

The decrease in friction after the first rotation, as seen for STA and ODA for as-received and solvent cleaned samples, is likely due to the mechanical removal of the contamination layer during rubbing. The formation of surface OFM layers then follows. STA takes three rotations to produce constant low friction whereas ODA takes one rotation. The transition will depend on (1) the ease of contaminant removal and (2) the adsorption and the surface rearrangement kinetics of the OFM additives. ODO shows no transition as it only weakly adsorbed and cannot provide surface protection. Hence its performance is not affected by the removal of contaminants.

4.6.2. Surface Contamination Affects the Steady State Friction Coefficient

The steady state friction coefficient, μ_{ss} , for this discussion, is taken as the friction coefficients at 97th rotation μ_{97} . The OFM chemistry governs the long-time friction. STA, which strongly binds with steel surface, gives low μ_{ss} . ODO, which only weakly interacts with steel, has high μ_{ss} . The inability of ODO to protect steel-steel rubbing surfaces is evident by the increase in friction coefficient with rubbing distance due to increased surface roughness (see insert in Figure 4-6). For ODA, μ_{ss} changes slightly

with the cleaning method, see Figure 4-5. The cleaner the surface, the lower the resulting friction. This shows STA is more effective than ODA in removing surface contaminants. Note that surface contaminants, such as corrosion inhibitors, may have a similar amine binding group as ODA.

Using plasma cleaned surfaces, STA and ODA have similar friction coefficients that are relatively constant during the whole tests. After the tests, it is observed that test solutions form beads on the discs, suggesting that the disc surfaces were oleophobic. This shows that plasma cleaning results in a sufficiently clean surface for OFM to form densely adsorbed layers quickly. This is in agreement with work done by Zisman in the 1940s showing both additives have the same friction with clean surfaces (cleaned by Bunsen burner) due to the formation of well packed, oleophobic monolayers.¹²⁶ As long as the quality of surface layers is sufficient to offer protection to the steel surface, the coefficient of friction remains roughly constant. Note that this applies to STA and ODA which have strong interaction with steel and is not the case for ODO. Using ODO gives rise to weakly bound surface layer which does not provide protection for the surface, and friction increases with time even if plasma-cleaned surfaces were used.

4.7. Conclusions

Organic friction modifiers (OFMs) are used to reduce friction in mixed and boundary lubrication regime. In this study, we examined how the choice of cleaning process impacts on the effectiveness of OFMs. Using stearic acid, octadecylamine, and octadecanol, our results show that depending on OFM chemistry, how steel test specimens were cleaned affects the friction reduction of OFM additives.

The surface of as received sample is covered with particulate contaminants below which is a thin, a few nm thick, contamination layer. This thin layer cannot be removed by cleaning with solvents but is removed by oxygen or argon plasma treatment. The choice of cleaning methods has a large impact on the initial friction where the friction is dictated by the ability of OFM molecules to displace contaminants on the surface. Where there is minimal contamination, after plasma cleaning, the

friction is determined by the chemistry of OFM, i.e. the strength of interaction between the OFM and the surface of the steel disk. For solvent-cleaned samples, most of the contamination is rubbed off after the first rotation and the OFM chemistry dictates the friction thereafter.

The steady state friction of strongly adsorbing additives, such as stearic acid, is not affected by the choice of cleaning methods. The cleaning method however significantly affects the onset of surface damage, where friction rises significantly, when the OFM interacts weakly with the surface such as for octadecanol. For 1 mM octadecylamine, its friction depends on the cleanliness of the surface due to its intermediate surface interaction strength. Our work shows that there is a range of additive affinity and concentration where cleaning process does impact the results. Care must be taken when comparing results and trends from different studies where different cleaning methods have been used. When considering the working mechanism of OFM, the process of surface contamination removal should be taken into account.

Chapter 5. Adsorption of Organic Friction Modifier Additives

The results of this chapter have been published and can be found at the following reference: Fry, B. M.; Moody, G.; Spikes, H. A.; Wong, J. S. S. Adsorption of Organic Friction Modifier Additives. *Langmuir* **2020**, 36 (5), 1147–1155.

5.1. Abstract

This chapter studied the relationship between the adsorption of OFMs and their friction and wear reducing properties in a rubbing contact. The effect of molecular structure was investigated by using OFMs of various tail saturation and head group chemistry. OFM tested were oleic acid, octadecylamine, oleylamine and glycerol monooleate.

The thickness of an OFM adsorbed layer in hexadecane, examined in-situ by spectroscopic ellipsometry and quartz crystal microbalance (QCM), depends on the molecular structure and the concentration of the OFM. As expected, saturated, linear chain gives the thickest film. A critical OFM layer thickness of about 0.6 nm is necessary to achieve low initial and maximum friction. The thicker OFM layers are accompanied by narrower wear tracks, which are rougher than the wider, smoother wear tracks formed with thinner OFM layers. The interplay between the thickness of the OFM layer and wear track surface roughness results in all OFM layers having similar steady friction. This shows that the apparent effect of OFM depends on the stage of rubbing test: initially on friction; and then subsequently on surface damage.

Despite OFMs and the base oil having similar refractive indices, ellipsometry was found to be a suitable technique for examining the adsorption of OFM additives from an oil based solution, and showed reasonable correlation with QCM results.

5.2. Introduction

The tribological properties of OFM SAMs have been widely studied. By keeping the average area per molecule constant ($21.6 \text{ \AA}^2/\text{molecule}$ for thiols on gold¹⁵¹), changing the length of the tail group of a thiol results in a change in friction on gold surface in air, as measured through friction force microscopy (FFM). Below a critical chain length of C12, friction is high. Further increase in chain length however has a minimal effect on friction. This critical chain length was said to be linked to the van der Waals force among tail chains in the monolayer, above which the force was sufficient to prevent the formation of gauche defects which causes an increase in friction.²⁴

The density of the tail groups of thiols on gold can be changed by using thiols of different molecular structures (1 head group, 1 tail group; 2 head groups, 1 tail group; 2 head groups and 2 tail groups), resulting in a packing density of $21.6\text{--}33.75 \text{ \AA}^2/\text{molecule}$. It was found that a less densely packed layer has a higher friction.⁴⁶ Packing density has also been shown to be linked to the molecular tilt. The larger the tilt as observed in a more sparsely packed layer, the less the van der Waals forces are in the monolayer.¹⁵² Both of these factors change the height of the monolayer, and the friction.

Some of the findings about thiol described above apply to OFMs adsorbed from a solution onto a surface. The effect of the tail length of OFM additives was studied by Hardy which found that a C12 chain was needed to achieve low friction.³⁷ Jahanmir however later concluded that the optimum OFM tail length depends on the test conditions.³⁶ The effect of chain packing observed with thiol is not as clear with OFM molecules. Previous quartz crystal microbalance (QCM) measurements showed that the packing density of oleic acid on steel coated QCM crystals was $100 \text{ \AA}^2/\text{molecule}$.⁹⁹ Various amine based friction modifiers have also been shown to have an adsorption density of over $100 \text{ \AA}^2/\text{molecule}$.⁵⁹ This suggests that OFM molecules are significantly more loosely packed than a thiol monolayer.

Molecular dynamics (MD) simulations of OFMs adsorbed on iron and iron oxide surfaces have shown that a higher surface coverage leads to lower friction^{133,153–155}. A recent combined experimental and

simulation study has suggested that, although friction decreases with increasing OFM coverage, complete coverage of the surface is not necessary for an effective friction reduction.¹⁰² It has been suggested that surface coverage may have a stronger effect than tail length on friction of OFMs. This is because the thickness of the OFM layer may change during rubbing. The height of a palmitic acid layer in hexadecane on a copper surface has been shown using frequency modulated atomic force microscopy (FM-AFM) to grow from 2.5 nm to about 20 nm during continuous scanning.¹⁵⁶ Polarised neutron reflectometry (PNR) showed that the adsorbed film had an initial thickness of 1.4 nm, which then formed a multilayer (reaches 5.9 nm) when under a constant pressure of 3MPa.²⁰ Colloidal probe AFM measurements (with a Hertzian maximum pressure of 210 MPa) of a palmitic acid layer on copper showed a reduction in friction without a change in layer thickness within a pre-scratched area.²⁰ They suggested that rubbing may change the additive layer other than its height.

While intuitively the adsorption of OFM additives should play a significant role in friction properties of OFM layers, there is increasing evidence showing that the OFM layers may change during rubbing. This poses the question of whether the importance of adsorption behaviour of OFMs on friction remains as rubbing progresses. The aim of this research is to study the relationship between the adsorption and the friction reducing properties of OFM additives at the initial rubbing stage and when steady state friction coefficient is established. In this work, two in-situ techniques were used to measure the adsorption of the OFM additives on silicon; QCM, which has previously been shown to measure the adsorbed mass of OFM molecules;^{57,100} and spectroscopic ellipsometry, a technique which is used for oil based adsorption measurements for the first time. These results were correlated to the friction reduction properties of OFM in the boundary friction regime.

5.3. Materials

Four OFM additives (see their molecular structures in Figure 5-1) were chosen to examine the effects of surface-OFM interactions and tail structures of OFM on the tribological performance of OFMs. They were octadecylamine, oleylamine, oleic acid and glycerol monooleate. All were $\geq 99\%$ in purity,

purchased from Sigma Aldrich and used as received. The base oil was hexadecane (99%, Sigma Aldrich) which was cleaned through a column containing activated alumina, silica gel and 3 Å molecular sieves. 1 mM solutions were prepared by stirring OFMs in cleaned hexadecane at 60 °C for 2 hours. These corresponded to w/w 0.035%, 0.035%, 0.037% and 0.046% for octadecylamine, oleylamine, oleic acid and glycerol monooleate respectively. 0.1 mM and 10 mM oleylamine solutions (w/w 0.0035% and 0.35% respectively) were also prepared.

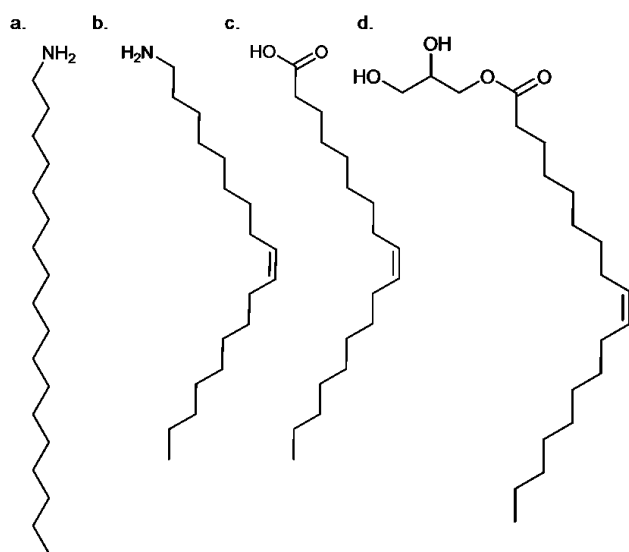


Figure 5-1. The structures of the OFM molecules tested, (a) octadecylamine, (b) oleylamine, (c) oleic acid, (d) glycerol monooleate (GMO)

Silicon wafers (100 orientation), used for friction and ellipsometry measurements, were purchased from Pi KEM. Borosilicate 6 mm glass balls for friction measurements were purchased from PCS instruments. SiO₂ sputter coated QCM crystals were purchased from q-sense. Analar toluene ($\geq 99.5\%$), analar isopropanol ($\geq 99.5\%$), analar acetone ($\geq 99.5\%$) and hexane (99%), for cleaning and rinsing, were all purchased from Sigma Aldrich and were used as received.

5.4. Experimental Methods

5.4.1. Friction measurements

Si wafers were cut to size of $15 \times 15 \text{ mm}^2$ and cleaned in the same way as the ball, by using toluene in an ultrasonic bath for 30 minutes. These were then dried and then cleaned with oxygen plasma for 2 minutes before being assembled into the holders for the ball and disk.

Friction tests were carried out with a CETR Universal Mechanical Tester (CETR-UMT-2). The rubbing contact consisted of a stationary glass ball against a rotating silicon wafer. At the start of the test, the ball and the disk remained stationary within the lubricant for 2 minutes to allow the OFM adsorbed layer to form. The test was then carried out with an applied load of 5 N, giving a maximum Hertzian pressure of 1.07 GPa. The sliding speed at the contact was 1 mm/s, the radius of the disc rotation was 1 mm, thus each disc rotation corresponded to a sliding distance of 6.28 mm. A total sliding distance per test was 628 mm (100 rotations). All tests were carried out at room temperature (23-27 °C). Each result is an average of 4 measurements.

Rubbed disks were rinsed with hexane and the morphology of the wear tracks were examined using a Veeco scanning white light interferometer.

5.4.2. Ellipsometry

In this study, an Accurion Nanofilm EP3 imaging ellipsometer⁹⁸ with a solid-liquid cell attachment was used. An optical model (Figure 5-2), which consisted of an adsorbed layer on top of a silicon oxide (SiO_2) layer, was created. Modelling of the reflected surface was carried out using Accurion's EP4 modelling software. Details of the modelling are provided in Chapter 3.

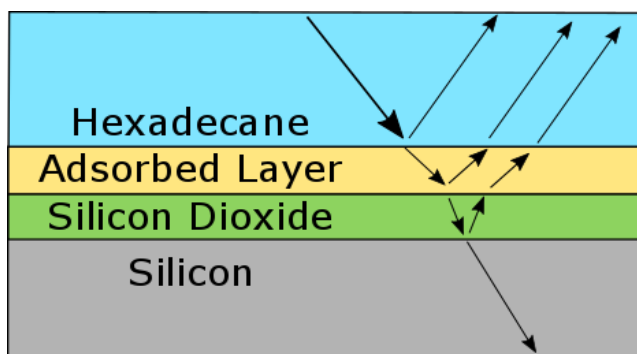


Figure 5-2. The optical model used to fit Ψ & Δ to calculate the thickness of the adsorbed layer in hexadecane.

A piece of Si wafer ($25 \times 10 \text{ mm}^2$) was cleaned with toluene and oxygen plasma, in a similar way to those for friction tests, with the test procedure explained in Chapter 2 Section 3.1. Two types of ellipsometry measurements were conducted, with the angle of laser incidence set at 60° . Spectroscopic (SE) measurements were performed with 40 different wavelengths from 371-1000 nm. Kinetic measurements used a 552.2 nm light source, with Ψ and Δ recorded every 10 seconds. Note that the area examined during each measurement was about $500 \times 1000 \mu\text{m}^2$. Results presented are average of at least two tests. The kinetic measurements shown are representative of the behaviour of each OFM solutions.

5.4.3. Quartz Crystal Microbalance

A QSense quartz crystal microbalance with dissipation (QCM-D) was used to measure the mass and the properties of the OFM adsorbed film. A QCM crystal was rinsed with toluene and isopropanol before UV Ozone cleaning for 30 minutes. The resonance frequencies and dissipations of the various odd overtones ($O: 1 - 13$) were measured in air before hexadecane was injected at a flow rate of 0.35 ml/min at 20°C . At least two tests were conducted for each OFM solutions.

The results from ellipsometry and QCM were compared using the Cuyper's method⁹² as described in chapter 3 section 3.

5.5. Results

5.5.1. Change of OFM additive structure

The four OFMs chosen in this study, octadecylamine, oleylamine, oleic acid and glycerol monooleate, have different structures, as shown in Figure 5-1. Octadecylamine and oleylamine are straight and bent chained molecules respectively with amine head groups; oleic acid and glycerol monooleate are bent chained molecules with a carboxylic acid and a glycerol ester head groups respectively. They adsorb onto the SiO_2 surface to different extents, as shown in Figure 5-3. The adsorbed mass of the OFM detected by the QCM measurements (Figure 5-3a) show that as soon as the OFM solutions are injected into the flow cell (at time = 0), a large initial adsorption onto the SiO_2 surface is observed. For all OFMs, the rates of adsorption decrease and then stabilise at much lower rates within 10 mins. The rate of decrease in the adsorption rate depends on the structure of the OFM. After 30 minutes of adsorption (and the same after 2 hours as shown in Figure 5-4), oleic acid (orange circles) adsorbs the least on the SiO_2 surface followed by oleylamine (red diamonds). 1 mM GMO (black inverted triangles) results in higher adsorbed mass compared to the other unsaturated OFMs. This may be partly due to its higher molecular weight. The straight chained octadecylamine (blue squares) results in the highest adsorbed mass, which stabilises quickly.

When OFM solutions are injected into the liquid cell during kinetic ellipsometry measurements, Δ drops, with the greatest reduction in Δ occurs immediately after the injection of OFM solutions (Figure 5-3b). Note that a reduction in Δ is related to an increase in adsorbed film thickness. Octadecylamine (blue squares) forms the thickest films with oleic acid (orange circles) the thinnest. Oleylamine (red diamonds) gives a slightly thicker film than oleic acid. Its change in Δ is around 1/4 of that of octadecylamine film, similar to what is observed in terms of adsorbed mass with QCM experiments. In general, changes in OFM adsorbed film thicknesses, as shown in kinetic ellipsometry measurements (Figure 5-3b), confirm results from QCM measurements. The most noticeable difference between the

QCM and ellipsometry results is the adsorption behaviour of the 1 mM GMO solution (black inverted triangles) which shows a similar change in Δ to oleylamine (red diamonds).

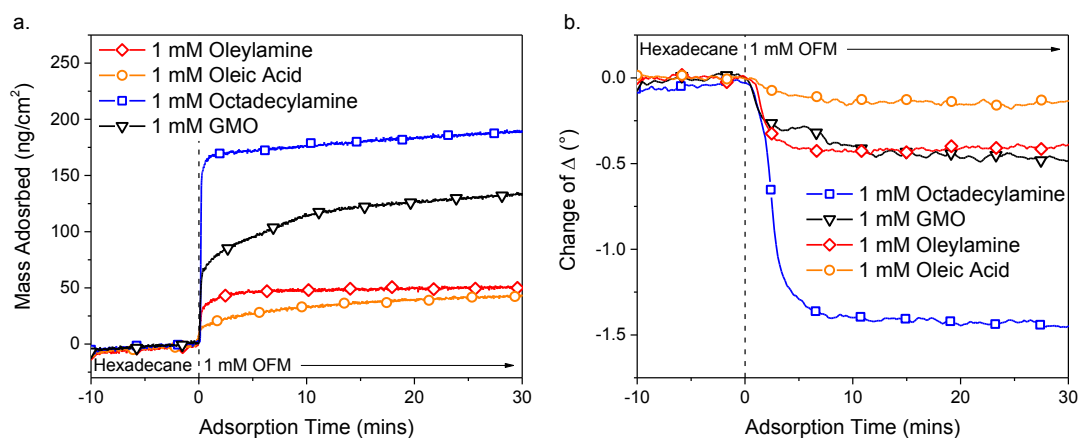


Figure 5-3. The adsorption of 1 mM OFM additives from hexadecane on SiO2 examined with (a) QCM; and (b) ellipsometry. Injection of OFM solution at adsorption time = 0.

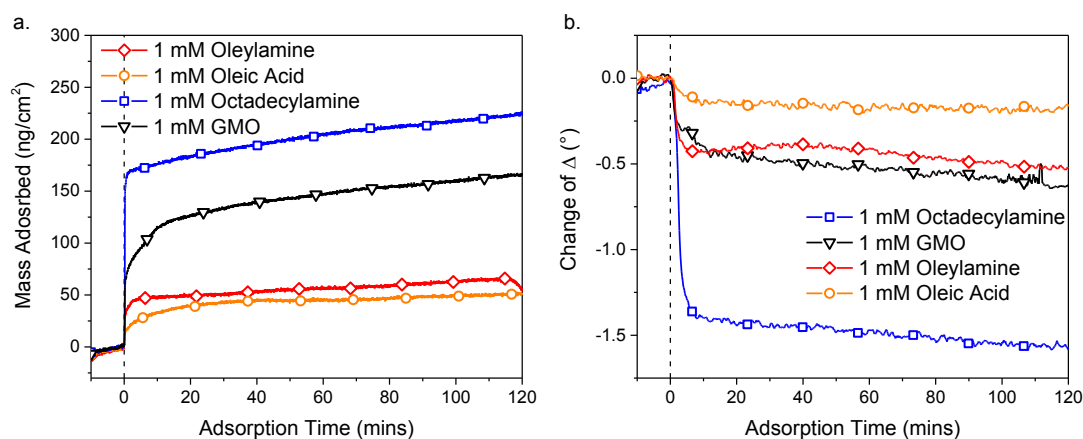


Figure 5-4: Adsorption of different OFM additives measured by (a.) QCM and (b.) ellipsometry for 2 hours of adsorption.

The effect of OFM additives in hexadecane on the friction of glass-silicon contacts is shown in Figure 5-5 and Figure 5-6. There is a clear difference in the friction coefficients of these five solutions during the first rotation of rubbing: pure hexadecane (green triangles) and 1 mM oleic acid solution (orange circles) have similarly high friction coefficients. The solutions of 1 mM oleylamine (red diamonds) and GMO (black inverted triangles) provide lower friction coefficients. The saturated chain of octadecylamine (blue squares) gives the lowest friction coefficient. Based on the results from QCM

and ellipsometry experiments, OFMs that adsorb more quickly result in lower friction coefficients at the first rotation.

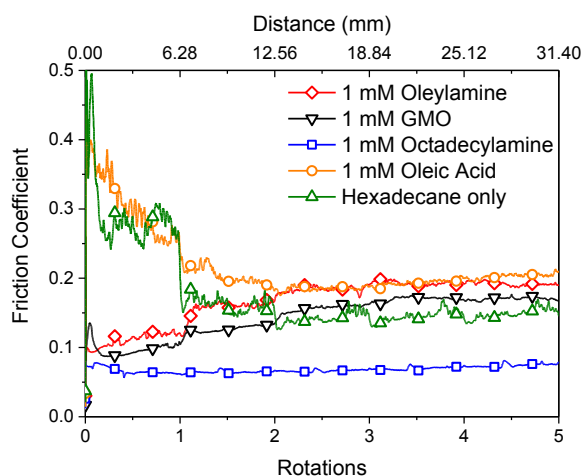


Figure 5-5. The friction coefficients of different OFM solutions in a glass on Si contact.

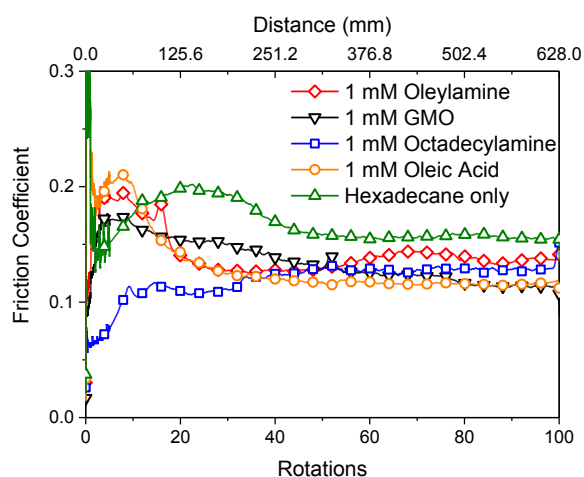


Figure 5-6: Friction of different OFM additives over 100 rotations. Glass ball rubbed against Si wafer.

After the first rotation, the friction coefficient of 1 mM octadecylamine (blue squares) remains constant in the first 5 rotations. Changes in friction coefficients are however observed for all other solutions, particularly 1 mM oleic acid (orange circles) and neat hexadecane (green triangles). At the 100th rotations (see Figure 5-6), all solutions have friction coefficients within the range of 0.1 to 0.15, with all OFM solutions have a lower friction coefficient than neat hexadecane.

5.5.2. Change of additive concentration

The amount the additive adsorbs onto the surface may change with the concentration of the additive in the solution, as shown in Figure 5-7 for oleylamine. Both QCM and ellipsometry measurements show that the initial adsorbed mass of oleylamine increases with its concentration. The 0.1 mM solution (pink stars) has the slowest initial adsorption kinetics although after 30 minutes, its adsorbed layer has similar mass and thickness to those of 1 mM oleylamine (red triangles). After 2 hours adsorption time, Figure 5-8, QCM results see that 10 mM oleylamine solution has the greatest adsorbed mass on the surface, with 1 and 0.1 mM oleylamine showing a similar increase in adsorbed mass. For ellipsometry 0.1 mM oleylamine has the smallest change in delta, whereas 1 and 10 mM oleylamine show a similar drop in delta from the kinetic measurements.

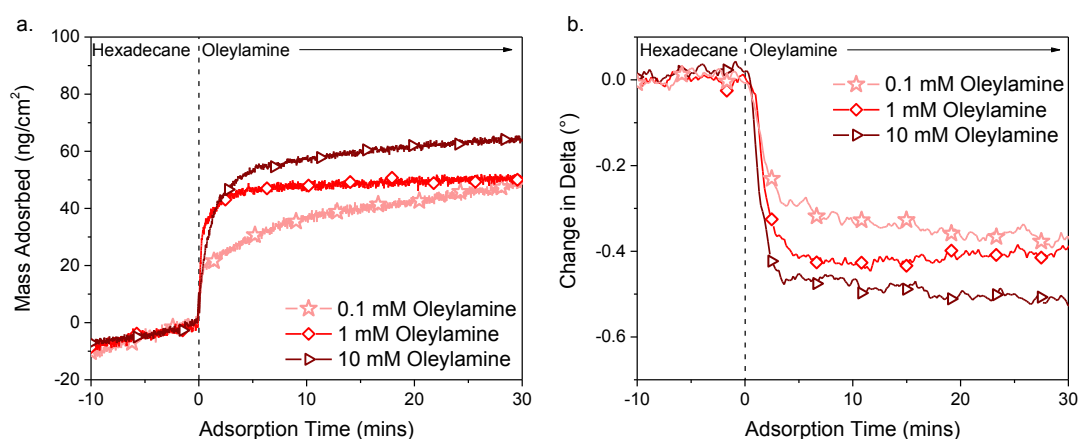


Figure 5-7. The change in adsorption of 10, 1 and 0.1 mM of oleylamine solution on SiO₂ surface as measured through a) QCM and b) ellipsometry. Injection of OFM solution at adsorption time = 0.

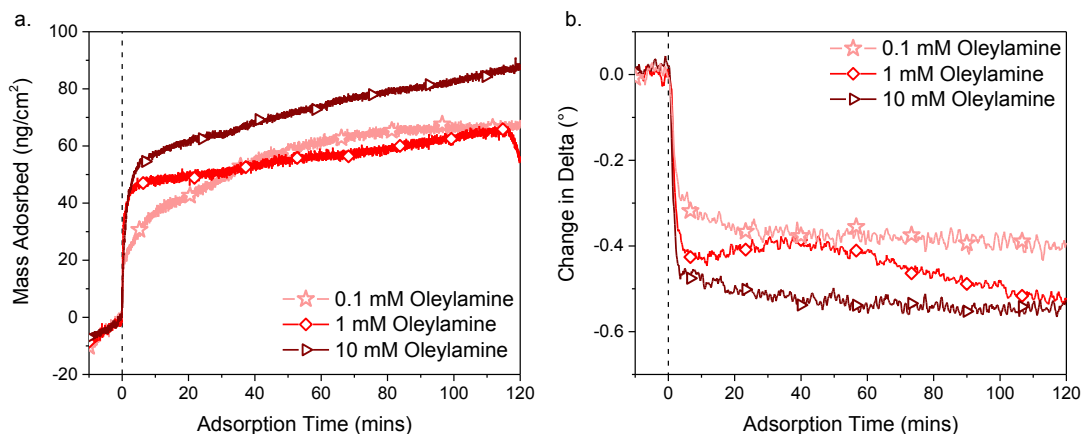


Figure 5-8: Adsorption of different concentration of oleylamine in hexadecane observed by (a.) QCM and (b.) ellipsometry for 2 hours of adsorption.

The concentration of OFM affects the friction reduction properties of the solution as shown in Figure 5-9. For the first rotation, 0.1 mM oleylamine (pink stars) only provides a slight friction reduction compared to neat hexadecane (green triangles). Increasing OFM concentration gives a lower friction coefficient during the first rotation only. These results support that OFM adsorption governs initial friction behaviour. At the 100th rotations (see Figure 5-10), all solutions have friction coefficients within the range of 0.12 to 0.15.

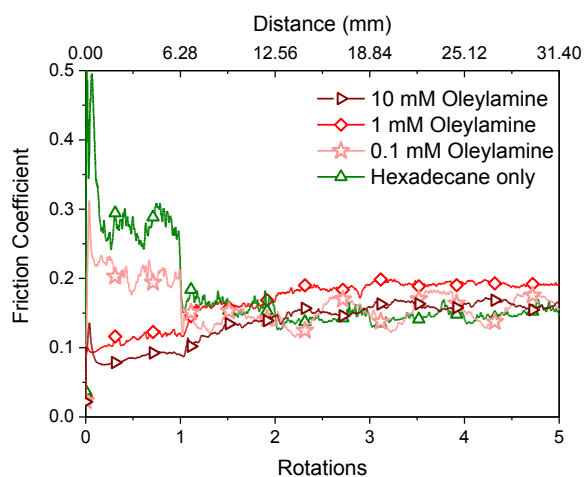


Figure 5-9. The change in friction reducing properties of Oleylamine at different concentrations in a Glass on Si contact.

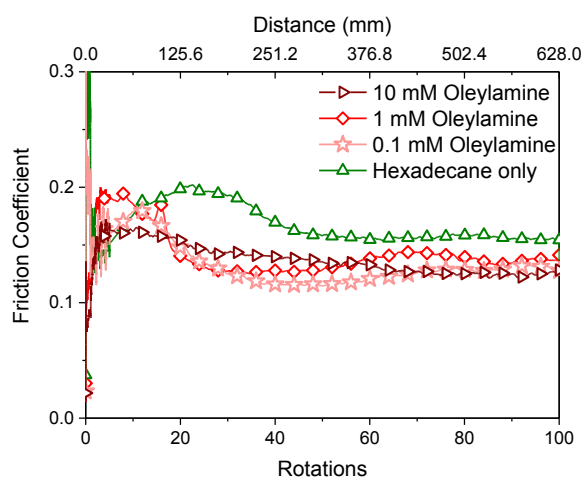


Figure 5-10: Friction coefficient of different concentration of oleylamine in hexadecane over 100 rotations. Glass ball rubbed against Si wafer.

5.5.3. Wear of the disk

Wear tracks on the silicon wafers after 100 rotations of rubbing were examined through scanning white light interferometry (as shown in Figure 5-11). The amount of surface damage is characterised by the width of the wear tracks, shown in Figure 5-12. The lower the initial friction, the smaller the width of the wear track (Figure 5-12a). Interestingly this trend is not observed for the steady state friction acquired at 100th rotation as shown in Figure 5-12b.

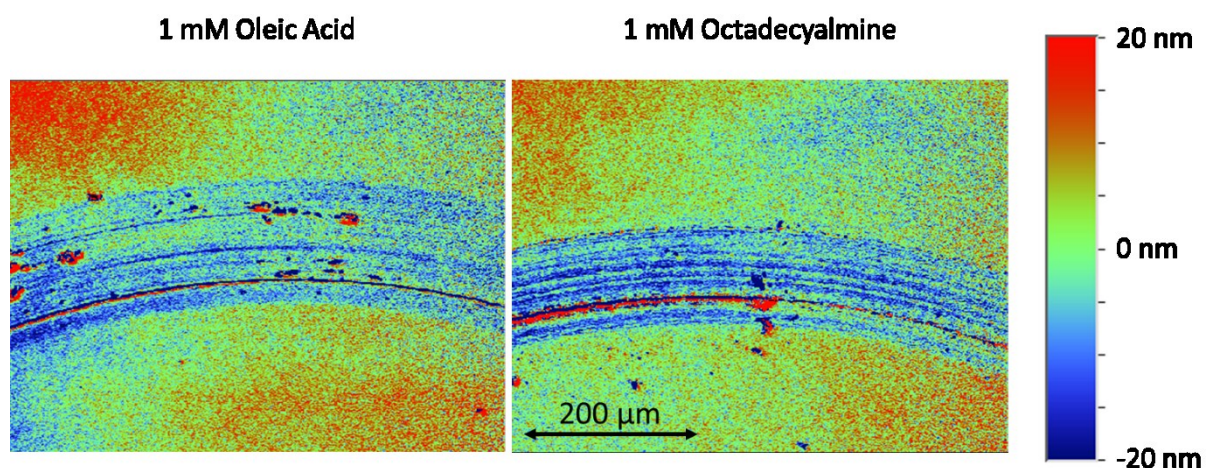


Figure 5-11: Representative images of wear scars on Si wafers formed in 1 mM oleic Acid and 1 mM octadecylamine solutions.

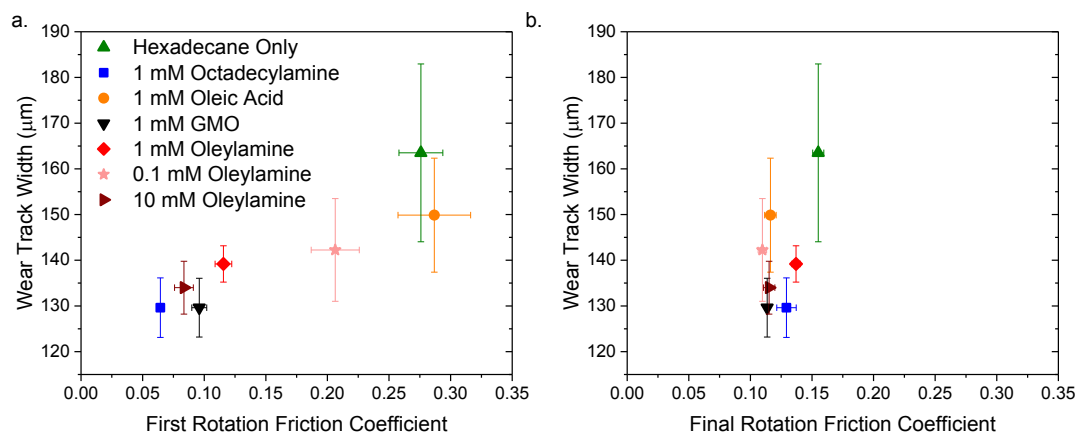


Figure 5-12. The correlation between the width of the wear track on the Si wafer and the a) friction of the first rotation, b) friction of the 100th rotation.

5.6. Discussion

The different OFM solutions are measured to adsorb to the surface with differing adsorption heights/densities. The ability for the OFM to adsorb to the surface could be related to the monomer concentration of the OFM within the solution. This has previously been the case for surfactants in aqueous systems where there is minimal increase in surface adsorption when the bulk concentration goes above the CMC, as there is no further increase in monomer concentration within the solution.²⁸ The solubility of these additives would also contribute to their adsorption properties, with the more soluble OFMs having a smaller difference in affinity for the surface compared to the solution. An alternative way to test these additives would be to test them all at concentrations just below the CMC of each additive. This would aim to keep constant the monomer concentration as well as the affinity of the OFM for the solvent. The disadvantage of this is that fatty acids in oil based solutions have been shown to form dimers within the solution and not inverse micelles,³³ meaning oleic acid could not be tested by this method.

5.6.1. Using ellipsometry for OFM adsorption kinetics in hexadecane

Both the ellipsometry and the QCM experiments show oleic acid, oleylamine, octadecylamine and GMO in hexadecane adsorb on silicon wafer to various extent. The thickness of the OFM layer on the QCM crystal after an adsorption time of 10 minutes can be estimated by its adsorbed mass using

Cuyper's method (Chapter 3 Section 3). This matches that from ellipsometry reasonably well, as shown in Figure 5-13. A similar conclusion can also be made after an adsorption time of 2 hours (see Figure 5-14). This shows that spectrometric ellipsometry can provide useful information on OFM adsorption in organic solvents where the solvents and the pure additives have similar refractive indices.

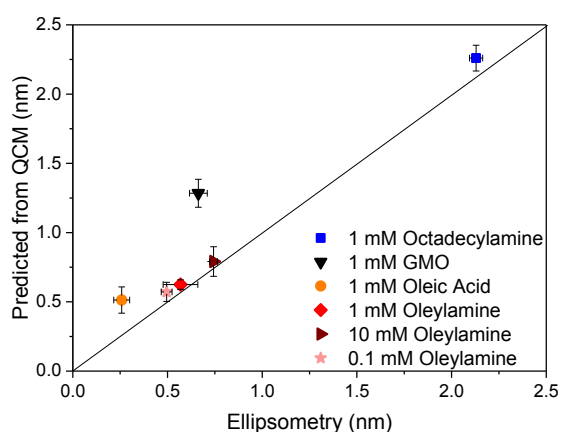


Figure 5-13. Comparison of adsorbed film thickness on SiO₂ obtained from QCM and ellipsometry measurements. Adsorption time = 10 minutes.

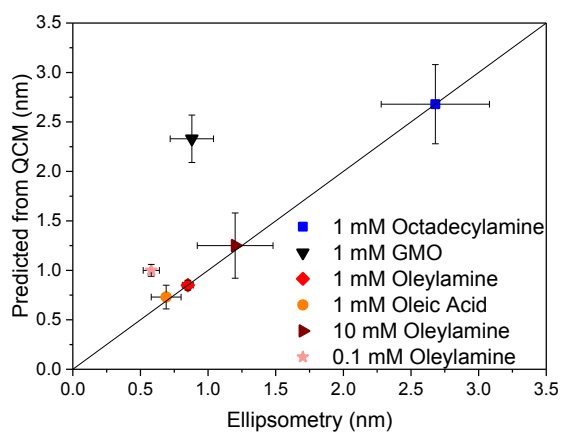


Figure 5-14: Comparison of thicknesses of adsorbed layers from different OFM additives on SiO₂ estimated based on results from QCM and ellipsometry, adsorption time of 2 hours.

The outlier after 10-minute adsorption time in Figure 5-13 is 1 mM GMO (black inverted triangle), with its thickness estimates from QCM results higher than that from the ellipsometry. GMO has a larger

head group than the other OFMs tested, this could mean that an adsorbed layer of GMO has a different refractive index to the one used based on octadecyl trichorosilane monolayer, as mentioned in Section 3.3.4. If this is the case, this result suggests that the adsorbed layer of GMO has a refractive index lower than that of the other additives (which would increase the fit layer thickness for the measured change in Δ).

Interestingly, 0.1 mM oleylamine (pink Stars, Figure 5-14) also shows a greater adsorption height from the QCM measurements than the ellipsometry measurements after a 2-hour adsorption time. This height, as measured with QCM, is also greater than that of 1 mM oleylamine, which is contrary to the expected adsorption isotherm where the adsorbed mass should increase with concentration.¹⁵⁷ It has been suggested that QCM measures the true sensed mass, whereas ellipsometry would measure the adsorbed mass.¹⁰⁰ Assuming a uniform layer with a fixed refractive index, the true sensed mass would include the mass of the trapped solvent in the adsorbed layer, whereas the adsorbed mass would only measure the averaged amount of OFM on the surface. It is possible that when the concentration of the OFM solution is low (as in the case of 0.1 mM oleylamine) or due to the molecular structure of the OFM (as for GMO), a higher fraction of the adsorbed layer is made of trapped solvent, perhaps due to its low relative packing density.¹⁵⁸ As a result, the OFM adsorbed layer may appear thicker from the QCM measurement. Since GMO is more polar than other OFMs tested, polar contaminants such as water may also be incorporated into the adsorbed layer more readily.

5.6.2. Linking adsorption and friction properties of OFM

The relationship between the friction coefficient of the first rotation given by these OFM layers and the thicknesses of their surface adsorbed layers after 10 min is shown in Figure 5-15 (for results based on the thickness of OFM adsorbed layer after 2 hours of adsorption, see Figure 5-16). In this study the thinnest adsorbed layers are formed with 0.1 mM oleylamine (pink stars) and 1 mM oleic acid (orange circles) and are around 0.2 – 0.5 nm. They result in high friction ($\mu > 0.2$). When the adsorbed OFM layer reaches a critical height of about 0.6 nm, which is the case for 1 mM oleylamine (red diamonds)

and 1 mM glycerol monooleate (black inverted triangles), μ is around 0.1. Further increase in the adsorbed film thickness only has a very small effect on friction reduction, as seen with 1 mM octadecylamine (blue squares) which has a thickness of about 2.2 nm and μ is around 0.065. The results in Figure 5-15 suggest that the thickness of the adsorbed layer influences the friction coefficient of the first rotation in boundary lubrication regime.

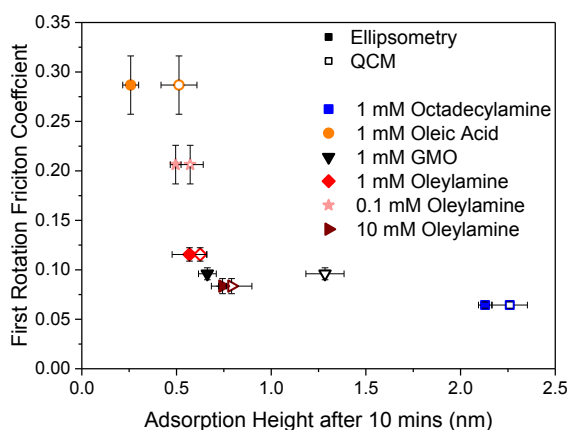


Figure 5-15. The relationship between the thicknesses of adsorbed layers of different OFM additives after 10 minutes of adsorption through QCM (open symbols) and ellipsometry (closed symbols) and the friction coefficient of the first rotation.

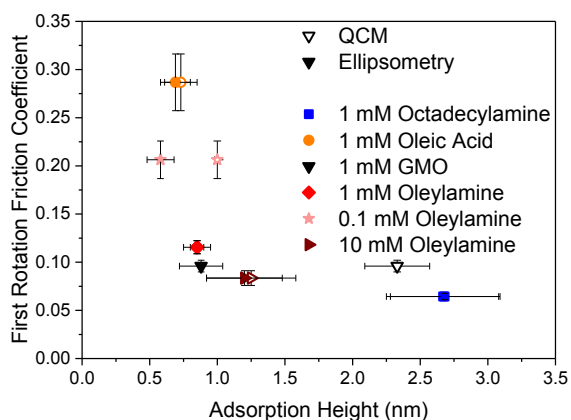


Figure 5-16: The relationship between the thickness of adsorbed layer formed by different OFM additives after 2 hours of adsorptions estimated by QCM (open circles) and ellipsometry (squares) and the friction coefficient of the first rotation.

The adsorbed film thickness is governed by the chain length and the surface coverage of OFM, with the latter related to head group chemistry, molecular structure and bulk concentrations. Indeed octadecylamine, which is a fully saturated straight chain molecule that can be packed densely easily, have the thickest layer while the adsorbed layer that are formed by low concentration OFM solution has the thinnest film. Assuming that the OFM adsorbed layers are monolayers, the surface area occupied by an OFM molecule can be estimated, as shown in Figure 5-17. For these conditions a critical surface OFM density could be found at around $100 \text{ \AA}^2/\text{molecule}$. This value represents tail densities and is suggested to be linked to an increased van der Waals forces in the monolayer.¹⁵² Films more densely packed than $100 \text{ \AA}^2/\text{molecule}$ provide a slight reduction on the friction coefficient. After a 2-hour adsorption time, this critical density is reduced to around $70 \text{ \AA}^2/\text{molecule}$ as seen in Figure 5-18.

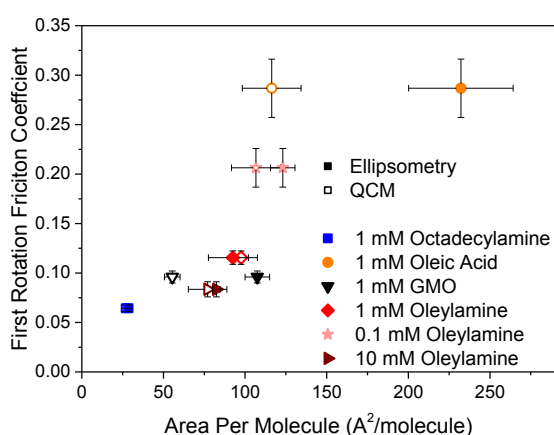


Figure 5-17. The relationship between OFM surface densities at 10 minutes adsorption time as calculated through results by QCM (open symbols) and ellipsometry (closed symbols) and the friction reduction of the first rotation.

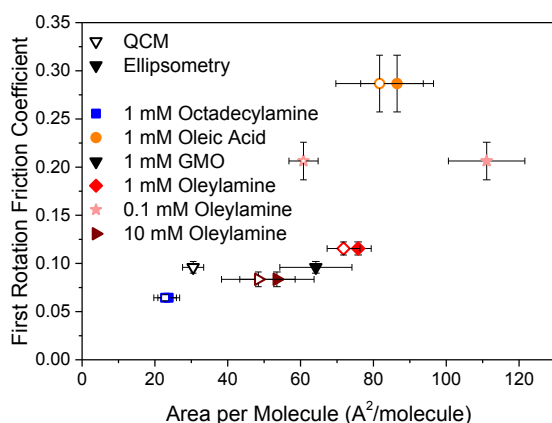


Figure 5-18: The relationship between OFM surface densities after 2 hours of adsorption as calculated through results by QCM (open circles) and ellipsometry (squares) and the friction reduction of the first rotation.

The critical adsorption height / density found could be caused by surface concentration at which multilayer formation occurs. Multilayers have previously been shown to have little improvement to the friction reducing properties of surfactants¹⁵⁹ and thus the small friction reduction is caused by an increase in the density of the base layer. This hypothesis is shown to be incorrect by initial AFM measurements of the silicon surface within a liquid cell, suggesting that the adsorbed layer is flat and homogeneous on the surface with no evidence of a multilayer film.

The discussion so far has focused on the initial friction observed during the first rotation of the friction test. Except for 1 mM octadecylamine which has a densely packed adsorbed layer on the surface, the friction coefficients for other OFM solutions change within the first 5 rotations. By the 100th rotation, all additives have a steady state values of about $\mu = 0.11 - 0.15$ (see Figure 5-6), which is lower than that of neat hexadecane. Note that the thicknesses of OFM adsorbed layers observed in QCM and ellipsometry measurements does not change substantially with time (see Figure 5-4 for data after adsorption for 2 hours). This suggests that factors other than surface adsorption may play a role in determining steady state friction coefficients.

The surface of a silicon wafer, used as the rubbing surface in this study, has a thin layer of SiO₂ (20-50 Å). During the run-in period, the SiO₂ layer may be removed during rubbing, resulting in a pure Si surface instead.¹⁶⁰ Hence the friction coefficient may change as the interaction of the OFMs with the

Si surface may be different to that with SiO₂. Note the parameters used for the optical model (as described in Figure 2 and Chapter 3) cannot be used to fit surface properties of wear track successfully. This provides qualitative support that the surface properties of the silicon wafer are altered due to rubbing. Sliding may also alter the structure of the adsorbed surface layer through shear removal, molecular ordering, or pressure induced multilayer formation as hypothesised by Hirayama et al.²⁰ Tribochemistry may also be a factor in this change of friction coefficient. For example, GMO is thought to potentially hydrolyse to form oleic acid within a sliding contact¹¹ or even break down further as it does on Ta-C DLC coatings.¹⁶¹ Our observations are most likely due to a combination of these factors.

The friction coefficient of the first rotation, as shown in Figure 5-12, is positively correlated to the wear track width, as well as the maximum friction coefficient experienced during the friction test, see Figure 5-19. Our results show that an increase in wear track width, signifies increased wear, is linked to the maximum friction coefficient of the tribopair. Interestingly, the wider wear tracks, as observed with thinner OFM layers, have lower surface roughness (see Figure 5-20). This may be due to the better protection provided by thicker OFM layers, preserving the rougher surface topography of the ball produced when friction is the highest. From this result, one could infer that the failure of the lubricated contact (where friction rapidly increases due to detrimental wear) would occur earlier for systems with a thinner adsorbed layer, longer tests are required to confirm this hypothesis.

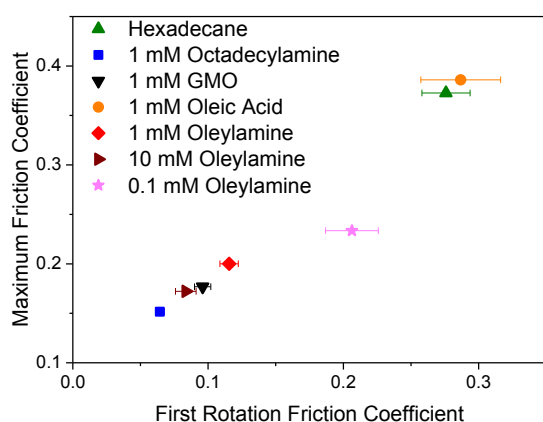


Figure 5-19: The correlation between the friction coefficient of the first rotation and the maximum friction coefficient measured during the test.

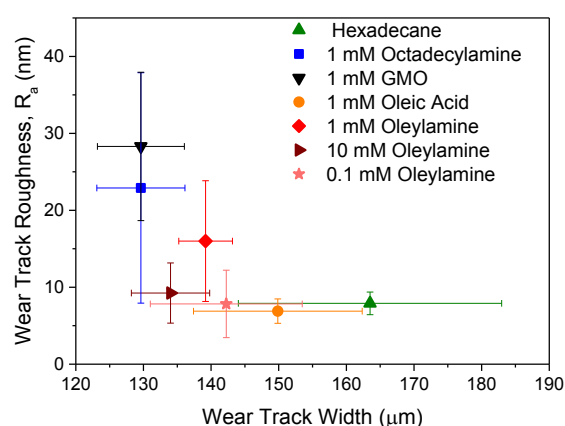


Figure 5-20: The relation between the roughness of the wear track and the wear track width.

5.7. Conclusion

In this work, ellipsometry and quartz crystal microbalance were used to examine the adsorption of OFM additives on silicon in hexadecane. The results were then correlated with the effectiveness of OFM in reducing friction in a glass-silicon contact under the boundary lubricant regime.

We show that ellipsometry is a suitable technique for measuring the growth of OFM films in oil based solutions on smooth surfaces of SiO_2 . These results match those obtained through a quartz crystal microbalance relatively well. Depending of the molecular structures of OFMs, OFM layers differ in thicknesses and hence their surface coverage.

The properties of OFM adsorbed layers govern the initial friction of a glass-silicon rubbing pair. Octadecylamine forms a thick layer that leads to low initial friction while thin oleic acid layers and oleylamine layers result in high friction. GMO forms an adsorbed layer of intermediate thickness even though its friction coefficient is comparable to that of octadecylamine. These results suggest a critical thickness of about 0.6 nm is necessary to provide low initial friction. Note that rougher test surfaces or more severe contact conditions may require higher critical thickness for effective OFM layers.

The thicker OFM layers result in narrower, rougher wear tracks than the wider, smoother tracks observed with thinner OFM layers. It is likely that the roughness of wear track changes as rubbing progresses and a wear track is at its roughest when the maximum friction is achieved. Since the thinner OFM layers are linked to a higher maximum friction, it is possible at the time the maximum friction is reached, the wear track associated with thinner OFM layers are rougher. The thicker OFM layer may however be better in preserving the surface topography: as such, after 100 rotations of rubbing, the wear track with the thinner OFM layer is smoother than that with thicker OFM film. The differences in surface roughness counter the effect of the properties of OFM layer on the wear track which eventually lead to all OFMs giving similar friction coefficients at the 100th rotation. This shows that the impact of the properties of OFM adsorbed layers extend beyond the initial friction to the subsequent surface damage.

Chapter 6. Interactions between Organic Friction Modifier Additives

The results of this chapter have been published and can be found at the following reference: Fry BM, Chui MY, Moody G, Wong JSS, Interactions between organic friction modifier additives, *Tribology International* (2020).

6.1. Abstract

The interactions of different additives in engine oils can create synergistic or antagonistic effects. This paper studies how mixing different organic friction modifier additives affects friction reducing properties of lubricants in the boundary lubrication regime. Amines of different degree of saturation were mixed with either glycerol monooleate (GMO) or oleic acid in hexadecane. The model lubricants thus formed were characterised with Fourier-transform infrared spectroscopy. Friction tests in reciprocating motion using ball-on-disc steel-steel contacts were conducted to examine the tribological performance of these lubricants. Worn surfaces were examined using X-ray photoelectron spectroscopy. Oleic acid and oleylamine, a primary amine. Were found to form a partial ionic liquid, providing synergistic friction reduction. This positive interaction reduces with increasing degree of saturation of the amine. No synergistic effect was observed between GMO and oleylamine, suggesting that GMO does not hydrolyse into a carboxylic acid within a rubbing contact in the presence of amine.

6.2. Introduction

Fully formulated lubricants contain multiple additives, some of which may interact with OFMs. The interactions between OFMs and zinc dialkyldithiophosphates, an extreme pressure (EP) additive, have been shown to be synergistic^{60,112} or antagonistic¹⁶² depending on the chemistry and concentration of the OFM additives. Antagonistic effect has been observed between a sulphur based EP additives and OFMs due to competitive surface adsorption.¹⁶³ Mixing GMO with an overbased calcium

sulphonate detergent also produced antagonistic effects when measuring the lifetime for parts in the hydroforming process.¹⁶⁴ Various OFM additives were added to a continuously variable transmission (CVT) lubricant: oleic acid provided no improvement in friction reduction and removed the detergent from the surface, while GMO improved friction reduction but reduced wear protection when added into the CVT oil.¹⁰⁹ In cases where multiple friction modifiers were used, no synergistic effect was observed between GMO and oleylamide, but synergistic interactions were observed when GMO is mixed with a polymeric friction modifier.⁸⁷

Ionic liquids (ILs) are molten salts which are liquids below 100 °C. ILs have been shown to have promising tribological properties.¹⁶⁵ They can also be used as additives in lubricating oils.¹⁶⁶ Much of the literature on oil soluble ILs studies phosphorous ILs, which are effective antiwear and friction modifier additives.^{81,83,167–170} Protic ionic liquids (PILs) are ionic liquids which form through a simple Brønsted acid-base reaction, with the most heavily researched PILs being amine based.¹⁷¹ Even in pure form, PILs are not fully ionic, with the level of proton transfer from the acid to the base depends on the structure of the reacting species. One study showed that the proton transfer is more complete with primary amines compared to tertiary amines.¹⁷² This is caused by the level of hydrogen bonding that can occur within an ionic liquid, which then impacts on the physicochemical properties of the IL.¹⁷³ Mixing OFMs and PILs has been shown to improve the tribological properties of the lubricant. It is thought that the IL may enhance the hydrogen bonding within the OFM adsorbed layer, giving rise to lower friction.¹⁷⁴

A PIL formed by mixing oleylamine and oleic acid has been shown to be non-corrosive and provide good friction and wear reducing properties as a pure ionic liquid.⁷⁸ Note that both oleylamine and oleic acid are used individually as OFM additives.¹¹ Thus it is hypothesized that a synergistic effect exists when they are used together as lubricant additives. This study tests this hypothesis. Since it has been suggested that GMO breaks down to oleic acid during rubbing,¹⁷⁵ the effect of mixing oleylamine and GMO in a lubricant is also investigated. The performance of oleylamine, a primary amine, will be

compared to that of a secondary and two tertiary amines to shed light on the interactions between amine, oleic acid and GMO and their effects on friction.

6.3. Materials

All chemicals were $\geq 99\%$ purity and were purchased from Sigma Aldrich. Hexadecane was cleaned through a filter of activated alumina, molecular sieves and silica gel before use. All other chemicals were used as received. All tests were conducted with 1 mM OFM solutions in hexadecane. The OFM additives tested, as shown in Figure 6-1, were oleic acid, glycerol monooleate (GMO), oleylamine (OA), diocylamine (DA), trihexylamine (TA) and dimethylhexadecylamine (DM16) and their concentrations are 368 ppm, 461 ppm, 346 ppm, 312 ppm, 348 ppm and 348 ppm respectively if only one OFM is used in the solution. Two types of OFM solutions were prepared: a single-component system, consisting of only one type of OFM in hexadecane; and a two-component system, consisting of two types of OFMs in hexadecane.

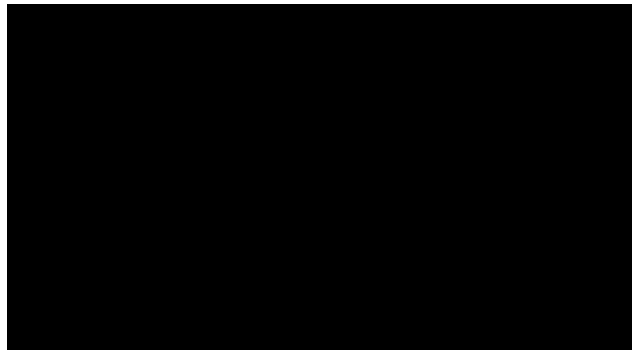


Figure 6-1. Structures of the OFM additives tested, (a) oleic acid, (b) glycerol monooleate (GMO), (c) oleylamine (OA), (d) dimethylhexadecylamine (DM16), (e) dioctylamine (DA), (f) trihexylamine (TA).

A 1 mM single-component solution was prepared by adding the additive to hexadecane, which underwent magnetic stirring for 3 hours at 60 °C. A two-component solution was prepared by mixing equal volumes of two 1 mM single-component solutions at 60 °C for 1 hour. Hence the concentration of individual components in a two-component solution was 0.5 mM. Test solutions have similar viscosities to that of hexadecane (1.72 mPa·s at 50 °C).

Oleic acid and GMO are both commonly tested OFM additives. A primary (oleylamine, OA), a secondary (dioctylamine, DA) and two tertiary (trihexylamine, TA and dimethylhexadecylamine, DM16) amines were tested to examine how the structure of the amine affects its effectiveness in friction reduction. All chosen amines have similar molecular weights. OA has previously been suggested to form an ionic liquid with oleic acid.⁷⁸

6.4. Methods

A ball-on-disc geometry, consisted of a stationary steel disc and a steel ball undergoing linear reciprocating motion, was adopted for friction tests. Both the balls (diameter = 6 mm) and the disks (diameter = 8 mm) were made of AISI52100 steel, with the latter hardened to 800 Hv. They cleaned with toluene, followed by cleaning with oxygen plasma for 1 minute to remove any surface residue, as found in Chapter 4.

Friction tests were carried out on a high frequency reciprocating rig (HFRR) from PCS instruments. The tests were run with a stroke distance of 1 mm, frequency of 50 Hz, at a temperature of 50 °C. An applied load of 500 g was used. Each test was run for 3 hours. The friction coefficients and electrical contact resistance (ECR) experienced by the contact were recorded throughout the test. Three tests were conducted for each condition.

After each test, the ball and the disk were rinsed with hexane before the wear scars were examined with a light microscope. Roughly circular wear scars were observed on the steel balls and their diameters were obtained as the average of the width along the two axes parallel and orthogonal to the rubbing direction. Ex-situ chemical analysis was performed on the wear scars of the steel disks using X-ray photoelectron spectroscopy (XPS). A Thermo Fisher K-Alpha system with an X-ray beam energy of 1486 eV was used. The spot size of the X-ray beam was 400 μm . An average over 20 scans and 40 scans were applied to the C_{1s} spectra and the lower intensity N_{1s} spectra respectively.

Chemical analysis of the OFM solutions was carried out with transmission infrared spectroscopy using a Perkin Elmer Frontier FTIR system. A liquid cell with KBr plates and a 1 mm PTFE spacer were used. A spectrum of pure hexadecane was removed from spectra of OFM solutions to show the impact of the OFM on the carboxyl peaks (1766 and 1713 cm^{-1}) and the primary amine peak (1620 cm^{-1}). Other potentially relevant peaks were not measured due to the noise caused by the absorption of the solvent.

6.5. Results

6.5.1. Tribological performance of OFMs

6.5.1.1. Single-component systems

The friction coefficients from single-component OFM solutions and the diameters of the resulting wear scars are compared to those from pure hexadecane, as shown in Figure 6-2a and Figure 6-2b respectively. For pure hexadecane (black squares), the friction coefficient increases slowly from ~ 0.2 to ~ 0.33 . The behaviour of the OFM solutions can be divided into two groups. 1 mM GMO (green triangles), oleic acid (red asterisks) and OA (orange diamonds) have stable low friction coefficients. Among the three, GMO has the lowest friction coefficient of 0.11. This is followed by oleic acid and OA, which both have an oleyl tail group. The second group consists of secondary and tertiary amine, whose friction coefficients are initially stable, then increase gradually. DA (blue circles), a secondary amine, shows relatively low initial friction (~ 0.15) for the first 30 mins of the test. Its friction coefficient then fluctuates substantially and its average increases with time. TA (brown stars), a tertiary amine, shows an initially stable friction coefficient of about 0.19 for 40 mins before rising to ~ 0.3 . Interestingly, while the coefficient of friction (~ 0.15) of the less sterically hindered tertiary amine, DM16 (purple inverted triangles), is lower than TA initially, it increases rapidly after $t = 60$ mins and has the highest friction of all single-component OFM solutions after 90 mins of rubbing.

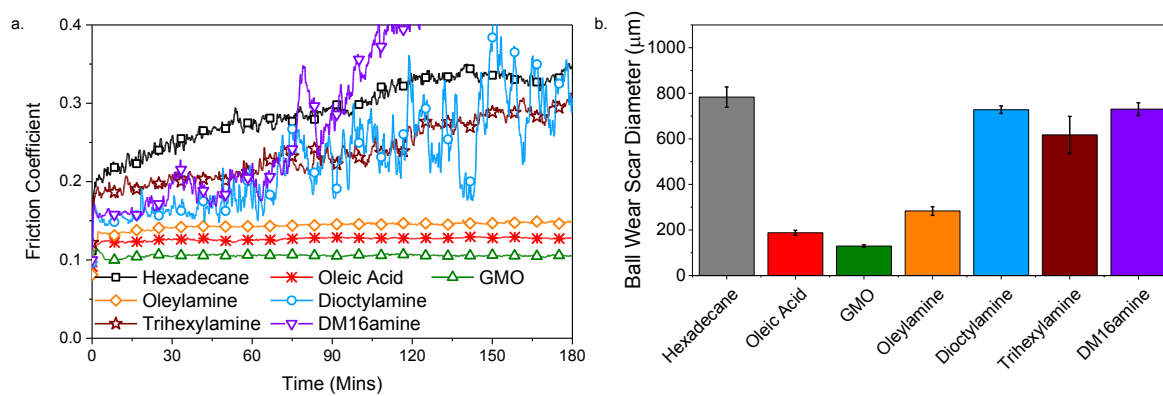


Figure 6-2. For single-component OFM solutions: (a) the averaged friction traces; and (b) the diameter of the wear scar on the ball after friction tests.

Single-component OFM solutions that give low stable friction also have smaller wear scars on steel surfaces (Figure 6-2b, Figure 6-3 and Figure 6-4). The amount of wear on the steel balls are quantified (Figure 6-2b). GMO gives the smallest wear scar, followed by those from oleic acid and OA. DA and DM16 produce larger wear scars than TA. This is also reflected by the friction test results, with DA having large friction fluctuations while DM16 sees its friction increases rapidly.

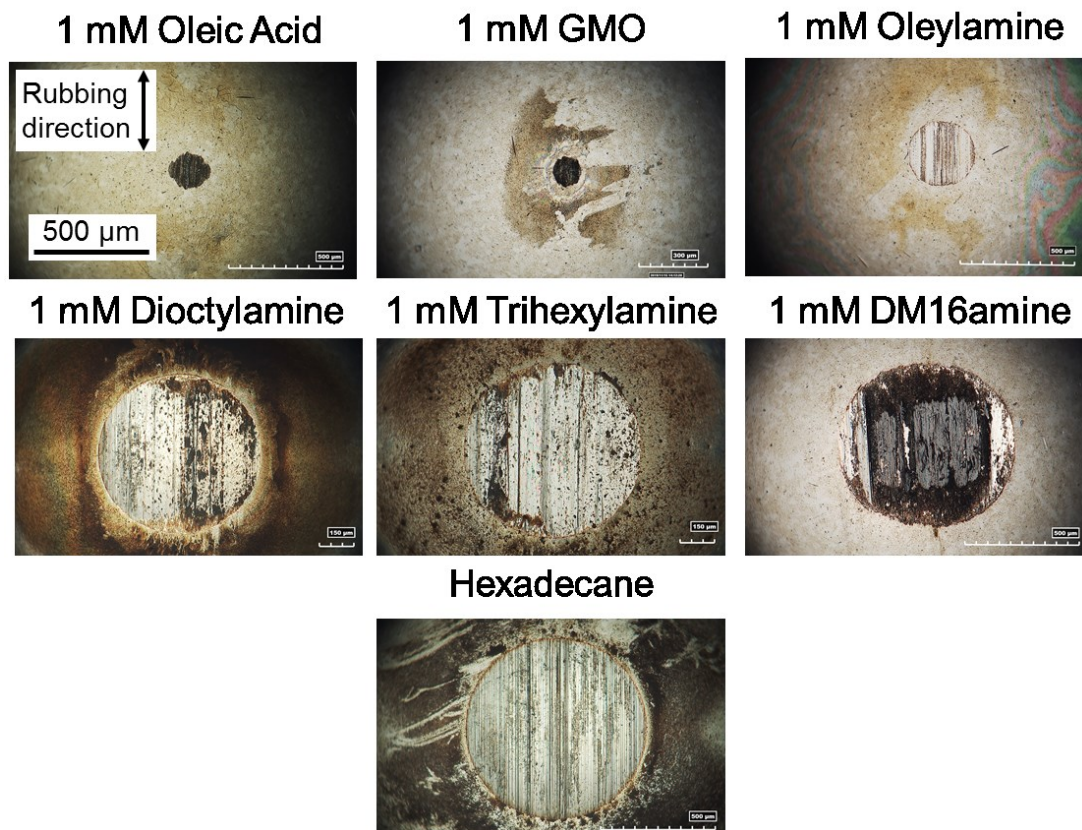


Figure 6-3: Optical micrographs showing representative wear scars on steel balls lubricated by various OFM solutions.

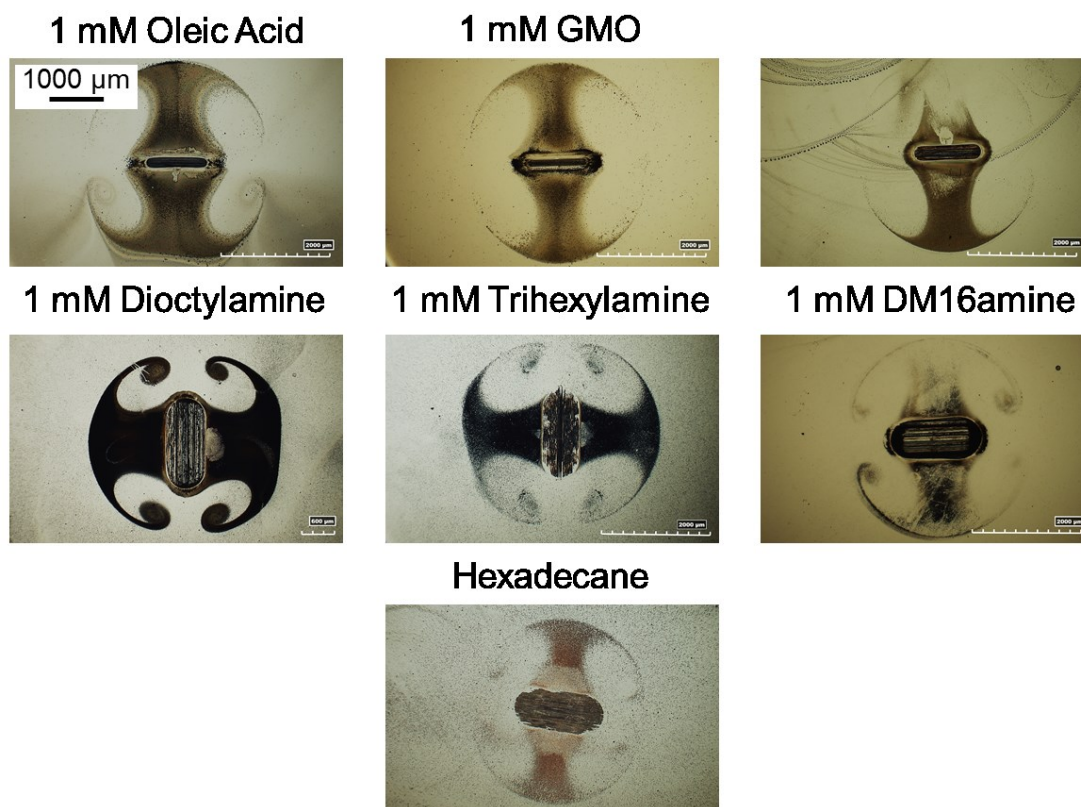


Figure 6-4: Optical micrographs showing representative wear scars on steel disks lubricated by various OFM solutions.

6.5.1.2. Two-component systems: effect of mixing two OFMs

The effect of mixing GMO with amines on friction is shown in Figure 6-5. Results from 1 mM single-component solutions of GMO (black squares, ~ 0.105) and OA (orange diamonds, ~ 0.145) are also included for comparison. None of the 4 amines tested enhance the friction reduction performance of GMO. Mixing GMO with a primary amine (GMO-OA, red inverted triangles) gives a friction coefficient in between those of single-component GMO and OA solutions. This suggests that both additives contribute to friction reduction and they do not interact. A similar effect is seen when GMO is mixed with DA (GMO-DA, blue circles), with the friction coefficient being between those of the two individual additives. The GMO-TA solution (brown stars) shows a slightly higher friction coefficient than that of the GMO solution, while the GMO-DM16 solution follows a similar friction trace to that of the GMO solution. These results suggest that the addition of tertiary amines have little effect, i.e. GMO dominates the performance of these two-component solutions.

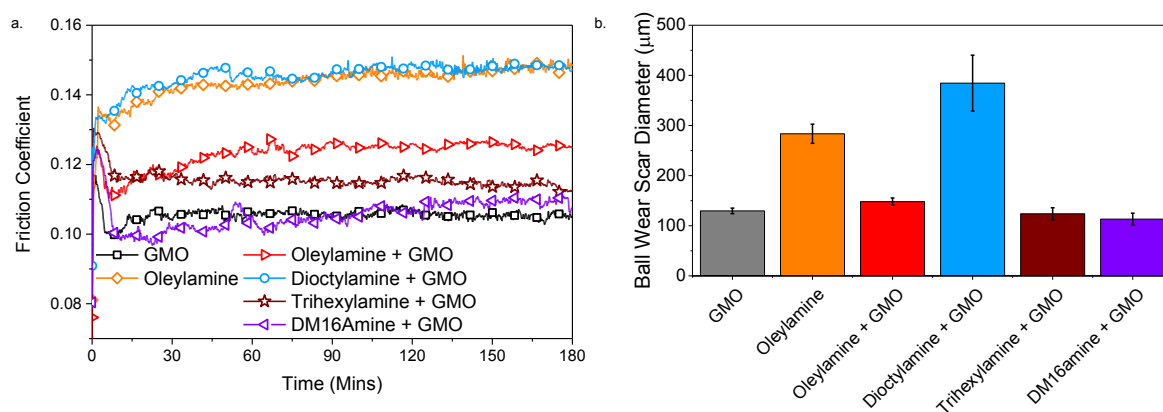


Figure 6-5. The effect of mixing GMO with amines: (a) the averaged friction traces; and (b) the diameter of the wear scar on the ball after friction tests.

When two-component GMO-amine solutions were used, GMO controls the size of the wear scar in most cases (Figure 6-5b, Figure 6-6 and Figure 6-7). The GMO-DA solution is the exception. The diameter of its wear scar on steel ball is in between those of single component GMO and DA solutions and is roughly half of that from the DA solution.

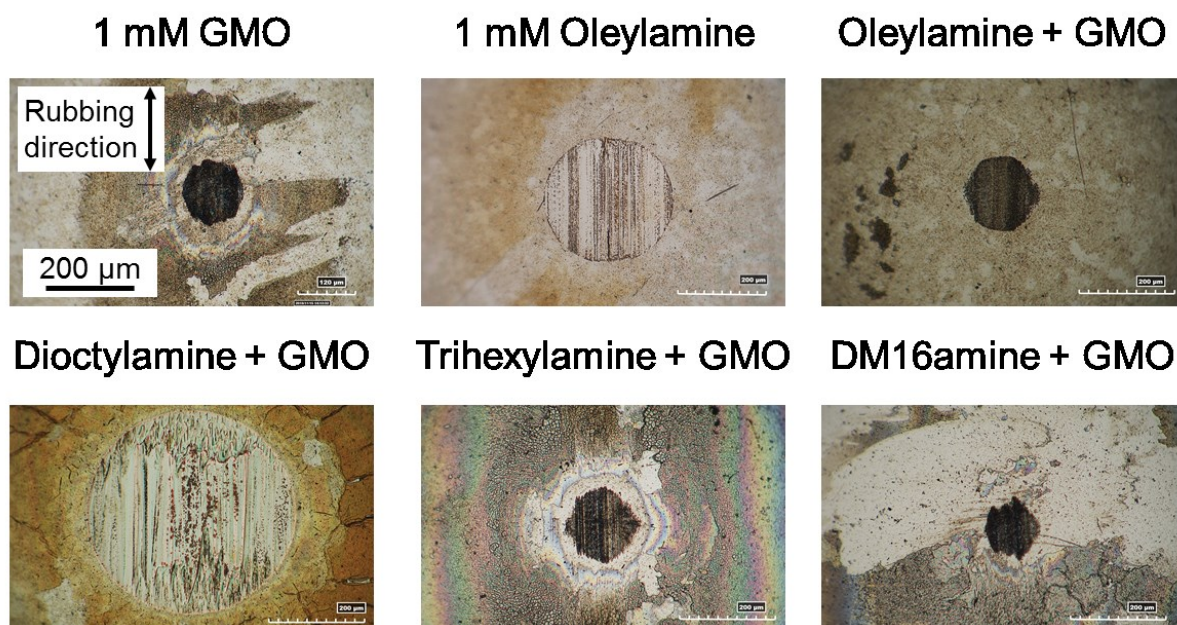


Figure 6-6: Optical micrographs showing representative wear scars on steel balls lubricated by GMO mixtures with different amines.

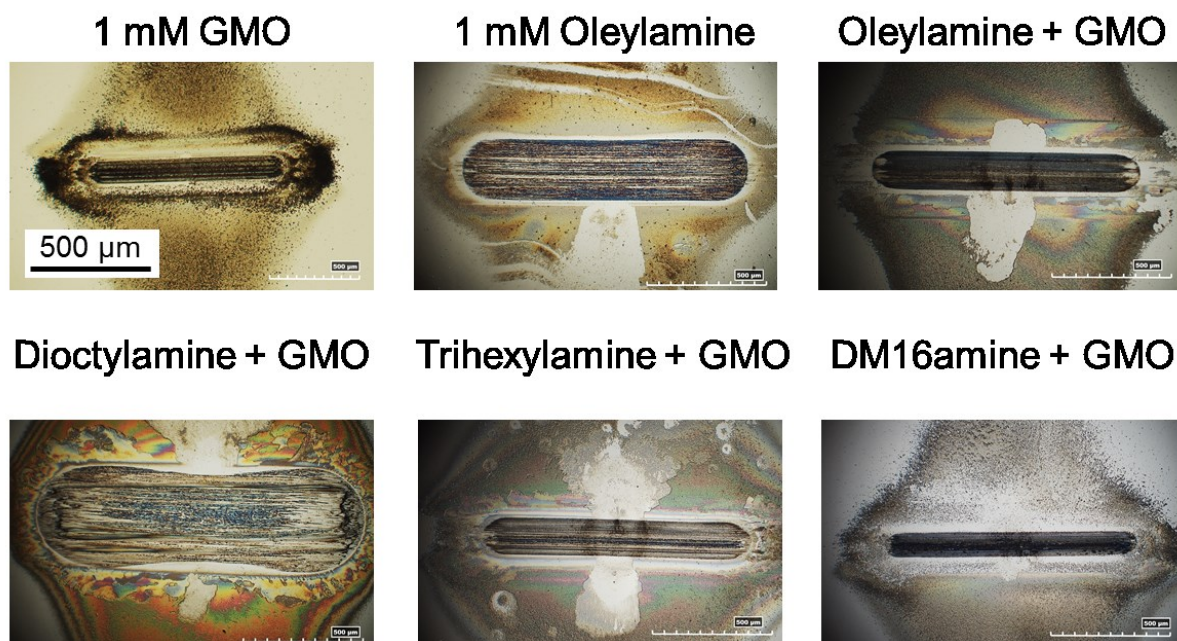


Figure 6-7: Optical micrographs showing representative wear scars on steel disks lubricated by GMO mixtures with different amines.

The effect on mixing oleic acid with amines on friction is shown in Figure 6-8a. Results from 1 mM single component solutions of oleic acid (black squares ~ 0.12) and OA (orange diamonds, ~ 0.145) are also included for comparison. All oleic acid-amine solutions show similar (as in the case of oleic

acid-DM16 solution, purple triangles) or improved performance in friction and wear reducing capabilities compared to 1 mM oleic acid solution. Oleic acid-DA (blue circles) and oleic acid-TA (brown stars) solutions show a $\sim 10\%$ drop in friction coefficients compared to 1 mM oleic acid solution. Note that oleic acid-OA solution (red inverted triangles) gives the greatest reduction in friction coefficient, from 0.12 to 0.07.

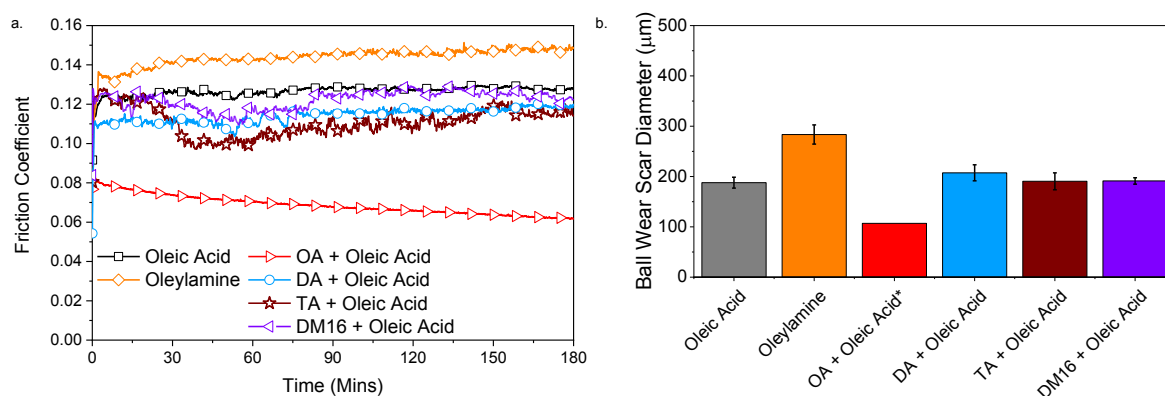


Figure 6-8. The effect of mixing oleic acid with amines: (a) the averaged friction traces; and (b) the diameter of the wear scar on the ball after friction tests.

Since the friction coefficients of most of the oleic acid-amine solutions are similar or only slightly lower than to that of oleic acid solution, it is not surprising that they produce wear scars of similar size, Figure 6-9 and Figure 6-10. The exception is oleic acid-OA solution which gives the lowest friction. It gives no visible wear scar on the disks and only small wear scars are seen on some of the balls.

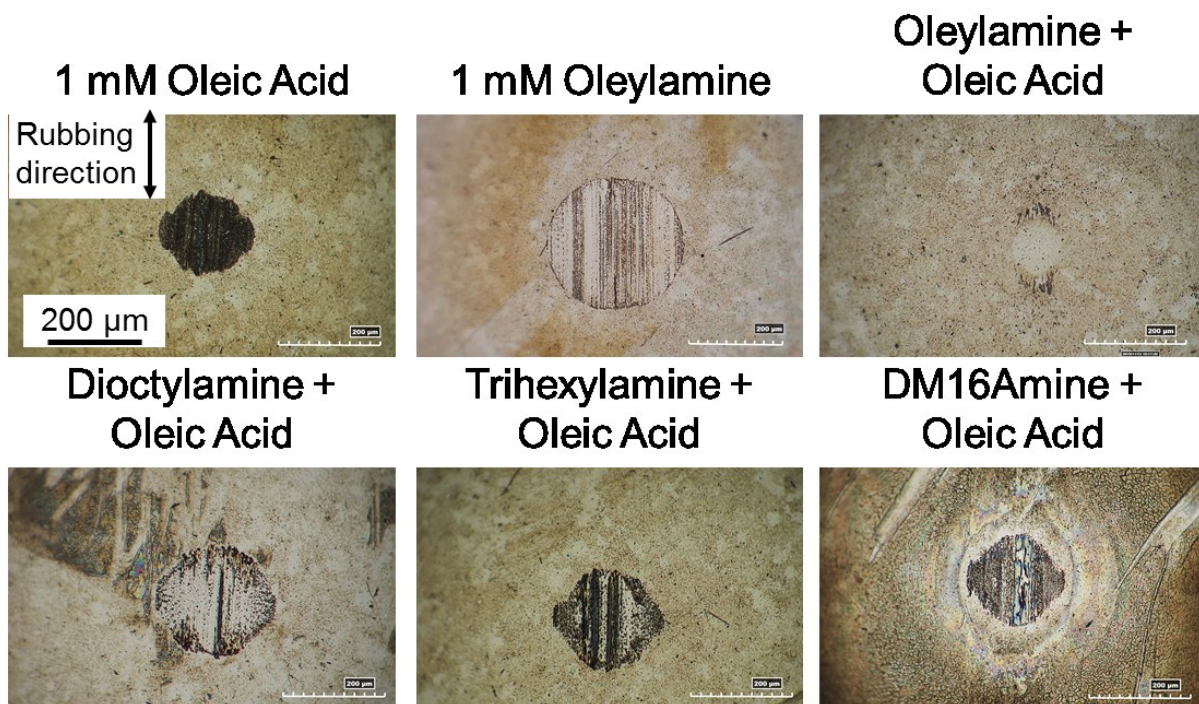


Figure 6-9: Optical micrographs showing representative wear scars on steel balls lubricated by oleic acid mixtures with different amines.

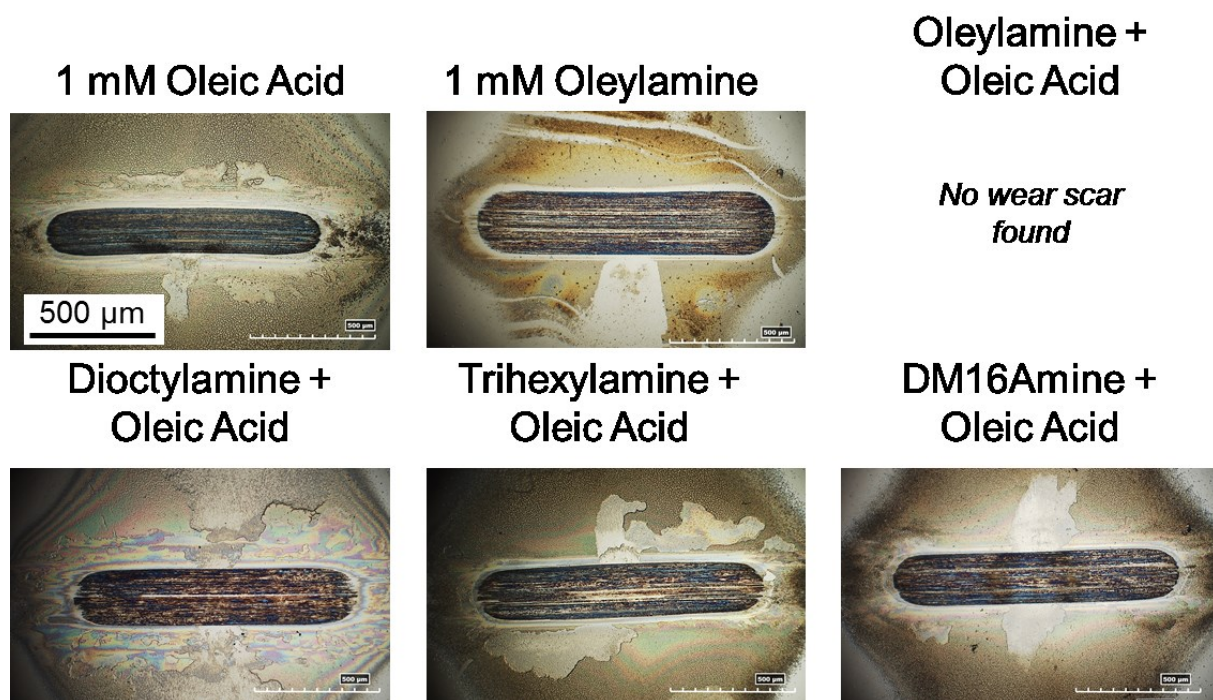


Figure 6-10: Optical micrographs showing representative wear scars on steel disks lubricated by Oleic Acid mixtures with different amines.

6.5.2. Interactions between oleic acid and amines in hexadecane

The origin of the synergy between oleic acid and amines requires further exploration. FTIR spectra of 0.5 mM oleic acid solution and 1 mM oleic acid-amine solutions were obtained (see Figure 6-11). Note that all 2-component solutions contain 0.5 mM oleic acid. Carboxylic acids are known to form dimers through hydrogen bonding in solution.¹⁸ The “free” carboxylic acid molecule (monomer) has a C=O stretch at 1766 cm^{-1} and the dimer has a C=O stretch of 1713 cm^{-1} . The change in intensity of these peaks with concentration is non-linear and is determined by the equilibrium constant of the carboxylic acid.¹⁰²

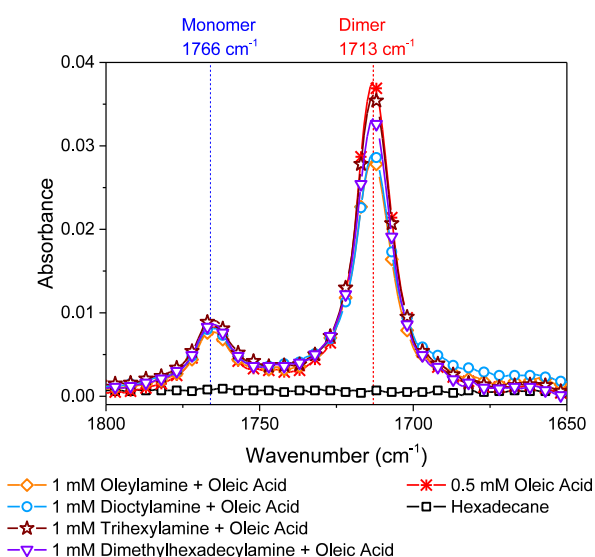


Figure 6-11: IR absorbance of the carboxyl peaks of oleic acid in oleic acid solution and oleic acid-amine solutions.

The concentration of oleic acid monomers and dimers in the solution is correlated to their peak intensities, which can be quantified by estimating the area of each peak. The results are shown in Figure 6-12a. The intensity of the dimer peak is clearly affected by the type of amine used in the oleic acid-amine solutions (triangles) which in an ascending order: oleic acid-OA < oleic acid-DA < oleic acid-DM16 < oleic acid-TA $\approx$ oleic acid. For the intensity of the monomer peak (circles, Figure 6-12a), primary and secondary amine mixtures have lower, while tertiary amine mixtures having greater peak intensity than that of 0.5 mM oleic acid solutions.

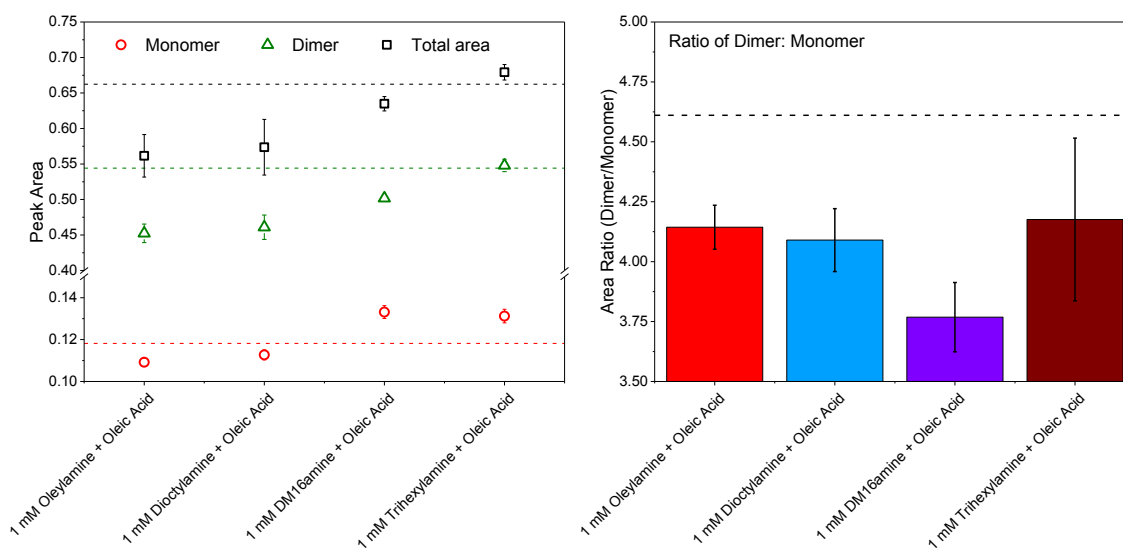


Figure 6-12. The average values measured by FTIR of a) dimer peak intensity, monomer peak intensity, combined monomer and dimer peak intensity; and b) ratio of dimer: monomer peak areas. The dash lines are values for 0.5 mM oleic acid solution.

The combined area of the monomer and dimer peaks of the FTIR spectra (squares, Figure 6-12a) follows a similar trend to that of the dimer peak. This suggests that there is less unreacted acid when oleic acid is mixed with OA, DA and DM16, than oleic acid-TA and single-component oleic acid solutions.

The ratio of the area of the dimer to monomer peaks for oleic acid-amine solutions are shown in Figure 6-12b. The addition of amine reduces the ratio compared to that of 0.5 mM oleic acid (dashed line). For oleic acid-OA and oleic acid-DA solutions, this may be partly due to a reduction in carboxylic acid (see squares, Figure 6-12a) which shifts the equilibrium in favour to the formation of monomers in solution (see Figure 6-13). For the oleic acid-tertiary amine solutions, the tertiary amine may promote the formation of monomer in solution (see also circles in Figure 6-12a). This is in agreement with previous work which showed that a tertiary amine would destabilise a carboxylic acid dimer through the interaction with the lone pair.¹⁷⁶ Hence oleic acid-DM16 solution has the lowest ratio because of its reduced concentration of unreacted oleic acid and the promotion of monomer formation by DM16.

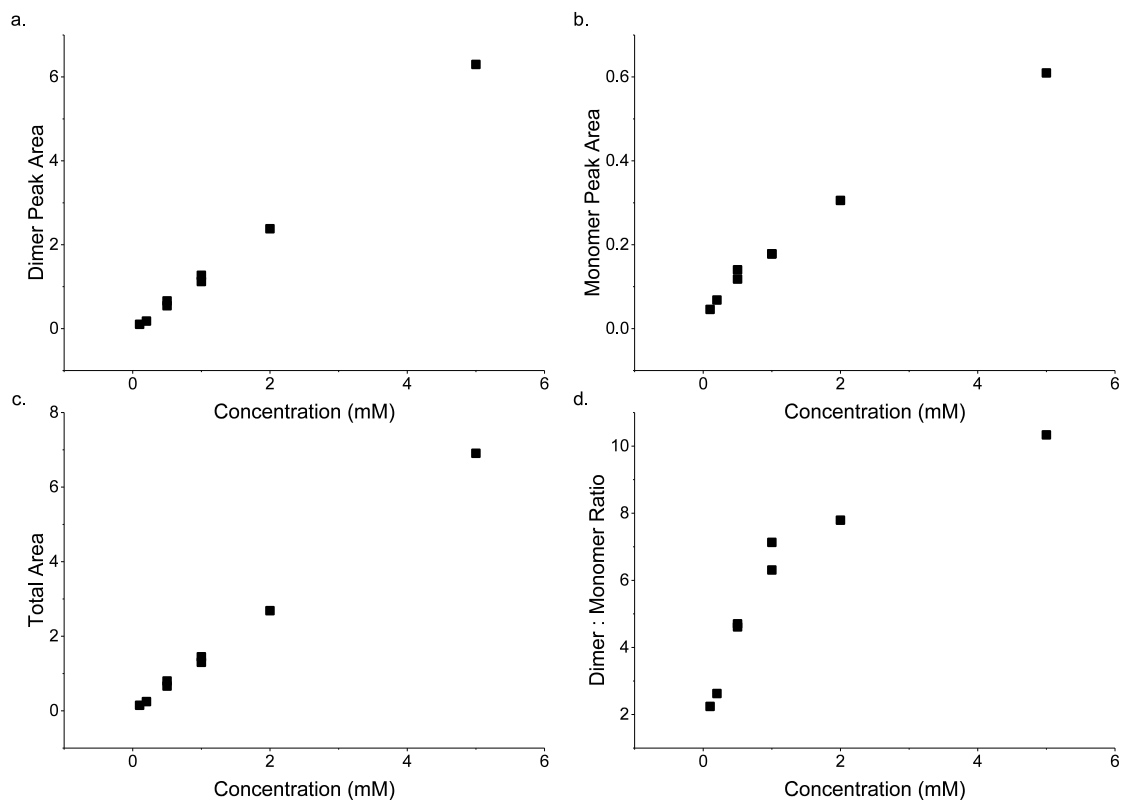


Figure 6-13: The effect of concentration of Oleic Acid on: a. dimer peak b. monomer peak, c. Total area and d. Dimer to monomer ratio.

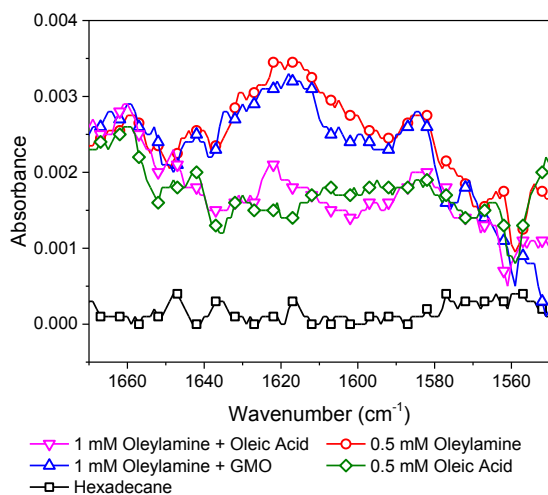


Figure 6-14 IR absorbance of the primary amine peak of 0.5 mM oleic acid, 0.5 mM oleylamine, 1 mM GMO-oleylamine and 1 mM oleic acid-oleylamine solutions.

The primary amine peak (1620 cm⁻¹) was compared among different oleylamine solutions, Figure 6-14. Compared to 0.5 mM oleylamine (red circles), there is a suppression of this peak when oleylamine is mixed with oleic acid (pink inverted triangles), whereas it is unchanged when mixed with GMO (blue

triangles). This suggests that in oleic acid-oleylamine solution, the amine molecule is no longer a primary amine but potentially an ammonium salt. No change in the chemical structure of amine molecule is suggested in GMO-oleylamine solution.

6.5.3. Boundary films formed in oleic acid-amine solutions

Wear tracks on steel disks were analysed using XPS, as shown in Figure 6-15 and Figure 6-16. The wear tracks formed in all oleic acid-amine solutions have lower nitrogen peak signals than those from their respective single-component amine solutions. This is partly due to the lower concentration of amine in the mixtures. The nitrogen peaks, as shown in Figure 6-15a, show that there is a higher nitrogen concentration within the wear scar formed in oleic acid-OA solution (orange) than those in other oleic acid-amine solutions. Some signals from nitrogen peaks can also be observed with oleic acid-DA solution (cyan). Very low signals are measured on wear tracks formed in the two oleic acid-tertiary amine solutions, suggesting these tracks have very small amount of, if any, amine.

Note that the amount of nitrogen in the wear track formed in oleic acid-OA (orange, Figure 6-15a) is less than that formed in GMO-OA (dark yellow, Figure 6-15b). This is also the case with the TA mixtures but the peaks are much smaller. The strong interaction between oleic acid and oleylamine in hexadecane is reflected in the nature of the boundary film formed by oleic acid-OA solution.

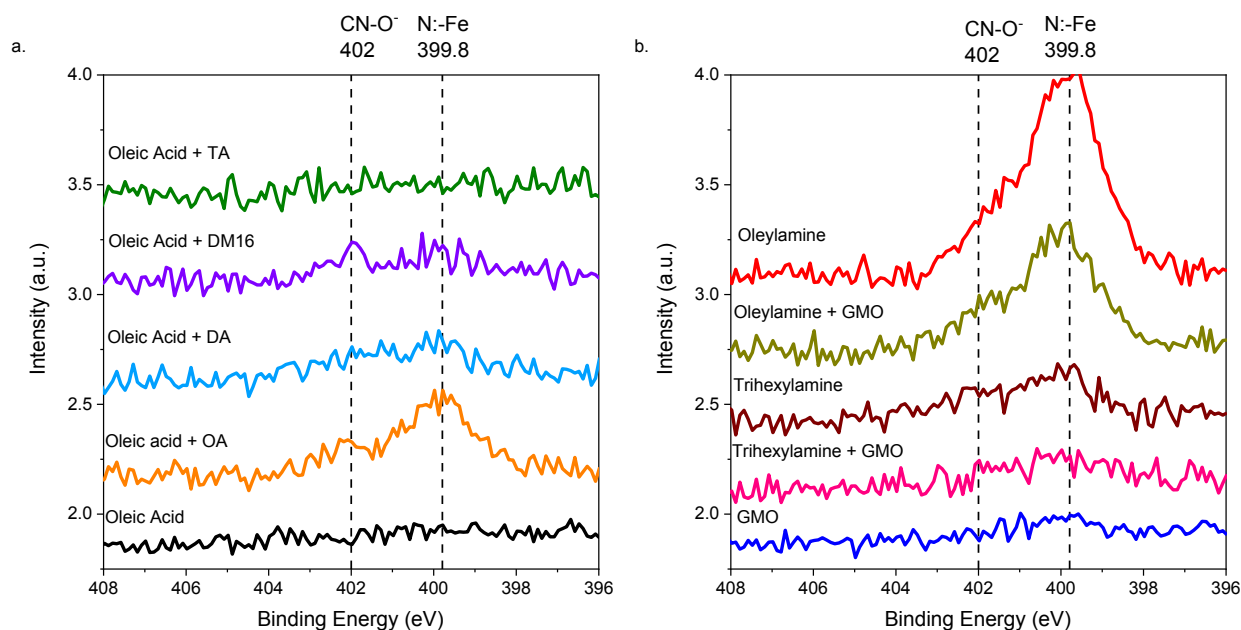


Figure 6-15. The N1s XPS spectra from within wear tracks on steel discs after HFRR tests in (a) oleic acid-amine solutions, and (b) GMO-amine solutions. Curves are offset for clarity.

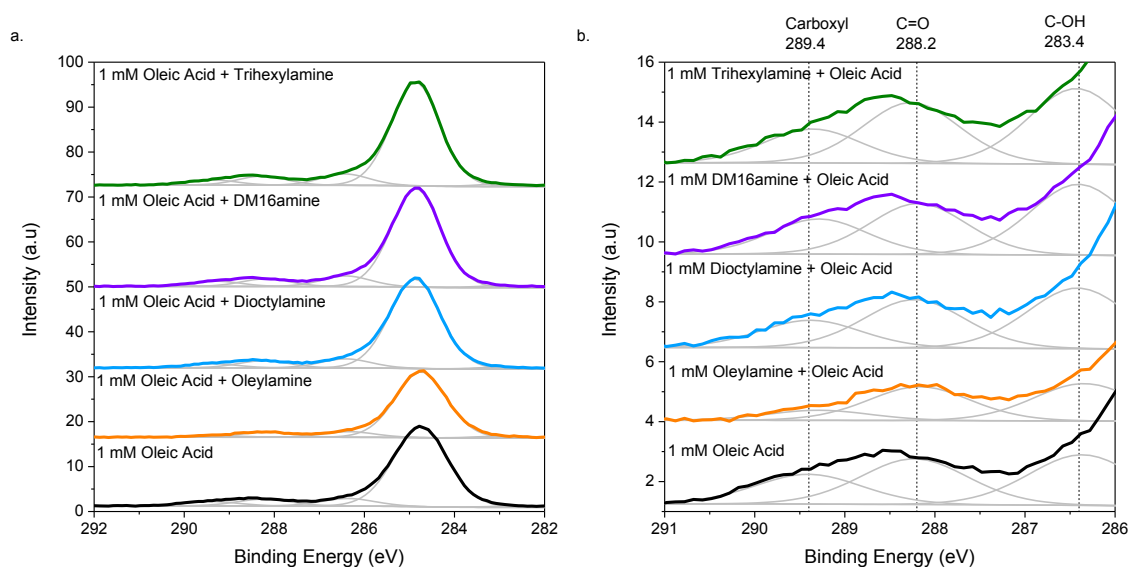


Figure 6-16. The C1s XPS spectra from within wear tracks on steel discs after HFRR tests for oleic acid and oleic acid-amine solutions: (a) spectra for Binding energy 292 -282 eV; (b) an expansion of (a) focusing on binding energy from 291 to 286 eV. Curves are offset for clarity.

Figure 6-16 shows the C1s spectra of wear tracks of oleic acid-amine mixtures. The carboxyl peak (at 289.4 eV) on the wear tracks formed in oleic acid solution (black) and oleic acid-tertiary amine solution (purple and green) have similar intensity, indicating they have similar surface carboxyl concentration

despite that only 0.5 mM acid is in oleic acid-amine solutions. The oleic acid-DA mixture (cyan) has a smaller carboxyl peak, and the oleic acid-OA mixture (orange) having the smallest peak.

6.6. Discussion

6.6.1. Oleic Acid mixtures with Amines

In hexadecane, oleic acid interacts with amine, as shown by FTIR analysis in Figure 6-12. The addition of amine reduces the intensities of the carboxyl peaks within the solution. This effect is especially visible with oleylamine, a primary amine. The effect is less significant with dioctylamine, a secondary amine and diminishes further with tertiary amines.

The reduction of the carboxyl peaks shows a reduction in the amount of free acid in the solution which can be attributed to the formation of a protic ionic liquid, as suggested in the literature.⁷⁸ The carboxyl group reacts to form a carboxylate should show a FTIR peak shift from 1766 cm^{-1} to 1550 cm^{-1} for the asymmetric COO^- stretch,¹⁷⁷ although this peak is not visible due to the hexadecane peaks. Note that results in Figure 6-14 indicate that there is a depletion of the primary N-H stretch in the oleylamine-oleic acid solution. Taken together, our results support that oleylamine and oleic acid react to form a partial ionic liquid additive in hexadecane, which lessens with the saturation of the amine. This agrees with previous work which shows that primary amines form a higher degree of proton transfer than tertiary amines.¹⁷²

The nature of the surface layers formed by oleic acid-amine solutions impact the friction and wear results. For oleic acid-amine solutions that contain secondary or tertiary amines which only interact weakly with oleic acid, oleic acid preferentially adsorbs. This is supported by the XPS spectra taken in wear tracks formed in these solutions having similar peak intensity from the carboxyl groups (Figure 6-16) to that formed in 1 mM oleic acid solution. This explains why these solutions give rise to comparable friction and wear to that of 1 mM oleic acid solution. Note that friction coefficient fluctuates more with 0.5 mM oleic acid solution than with 1mM oleic acid solution and oleic acid-

tertiary amine solutions. Since our results suggest minimal amine on the rubbed surface (see Figure 6-15), the beneficial effect of the addition of tertiary amine in this case may be caused by the tertiary amines destabilising the oleic acid dimer, as shown in Figure 6-12. This could have an impact on the adsorption of the acid to the surface, with the heat of adsorption being greater for the un-hydrogen bonded monomer than the dimer.¹⁷⁸ This could then have an impact on the friction coefficient as the kinetics of surface adsorption has been linked to the steady state friction reduction for OFM solutions.⁵⁹ This effect could help in the stabilisation of the friction coefficient.

For oleic acid-OA solutions, whose components form an ionic liquid additive, both components of the additive are evident on the wear track. They form a boundary layer which has the lowest friction and minimal wear compared to one component 1 mM oleic acid and 1 mM oleylamine solution. This is followed by oleic acid-dioctylamine solution, whose friction coefficient is consistently lower than that of oleic acid by 0.01. Note that XPS results of the wear track formed in oleic acid-DA solution also shows evidence of the existence of amine. This suggests that the more ionic bonded oleic acid-amine solution provides the lowest friction and minimal wear.

Overall, the addition of amines to an oleic acid solution shows benefits to the friction and wear reducing properties with a primary amine showing the greatest benefit. Note that the synergetic effect is unlikely to be achieved if oleic acid and oleylamine barely co-adsorbed on the surface. Hence our results offer strong support that strong specific interaction occurs between oleic acid and oleylamine, as in this case by the formation of an ionic liquid additive.

6.6.2. GMO mixtures with Amines

When GMO is mixed with a primary or a secondary amine, friction coefficients of these mixtures are between those of the two individual solutions, implying that the amine and GMO are both on the surface. For GMO-tertiary amine mixtures however, their friction and wear performance was similar to those of GMO solution, suggesting that in this case, the surfaces are mainly occupied by GMO. This

is supported by XPS results (Figure 6-15b) which show that there is much less amine within the wear track formed in GMO-trihexylamine solution than in GMO-oleylamine solution.

It is likely that the amine additives and GMO are all acting independently. Compositions of surface layers are thus a mere result of competitive surface adsorption, with the propensity to adsorb on steel surfaces decreases with the degree of saturation of amine. Note that hydrogen bonding may occur between GMO and amines in the hexadecane solution. The presence of an N-H in primary and secondary amines, which can be a hydrogen bond donor, is not available to a tertiary amine. Possible strong hydrogen bonding between GMO and primary and secondary amine, may promote co-adsorption of GMO and these two amine additives. The weak interaction between tertiary amine and GMO allows the more polar GMO molecule to preferentially adsorb on surfaces, dominating the friction reduction.

It has long been hypothesized that GMO goes through hydrolysis and forms a carboxylic acid and glycerol in the contact.¹⁷⁵ The results that GMO and amine do not show that same synergy observed between oleic acid and amine in terms of friction reduction is thus perhaps surprising. This may suggest that the hydrolysis process of GMO, if exists, may be altered by the addition of amine, or that GMO does not form a carboxylic acid molecule at all.

6.7. Conclusion

This research shows how interactions among OFM additives can be explored to achieve improved friction and wear properties. Mixing oleic acid and oleylamine in hexadecane has a synergistic effect resulting in a large reduction in friction and wear. This is because the two additives form a partial ionic liquid in the solution, changing the mechanism of friction reduction from that of OFMs (monolayer films) to that of ionic liquids (where the exact mechanism of friction reduction is still unknown). As the saturation of the amine increases, this effect decreases, with tertiary amines having minimal interactions with the oleic acid in hexadecane and as a result no improved friction reduction. For the

primary amine, both the acid and amine were observed in the wear track whereas for the tertiary amine, no amine was observed as oleic acid was preferentially adsorbed.

Since it is suggested that GMO may hydrolyse to form oleic acid, the effect of mixing GMO and amine was also investigated. Unlike what is observed with oleic acid-amine mixtures, no synergetic effect in friction is observed when mixing amines with GMO in hexadecane. This means that it is unlikely that GMO has hydrolysed to a carboxylic acid when mixed with amine in hexadecane. The composition of the boundary layer in a GMO-amine mixture is likely governed by competitive adsorption between additives. When mixing GMO with primary or secondary amines, both GMO and amine molecules are evident on the wear track, leading to a friction coefficient between that of the individual additives. GMO-tertiary amine mixtures provide friction reduction equivalent to an individual GMO solution, with minimal nitrogen observed in wear track, hence GMO preferentially adsorbs in these mixtures.

The existence of N-H bonds is the likely cause of the interaction between amines and other OFM additives in hexadecane. In this particular study, we show that the greater the amount of hydrogen bond donors on the amine, the greater the interaction with oleic acid. Such interaction between amine and oleic acid gives rise to a synergetic effect potentially through the formation of an ionic liquid additive in hexadecane.

Chapter 7. The Friction Reduction of Glyceride Esters

7.1. Abstract

Glyceride esters, more specifically glycerol monooleate (GMO), has long been used as organic friction modifier additive (OFMs) but the mechanism of the friction reduction of GMO is still unclear. The friction, adsorption and surface analysis data of GMO, glycerol dioleate (GDO), glycerol trioleate (GTO) and oleic acid were investigated to understand their friction reduction mechanism. Friction coefficients evolve with time in all cases. How the friction coefficient changes from its initial to its steady state friction coefficients (the transition period) differs among these OFMs. This is likely governed by the adsorption behaviour of an OFM and tribochemical reactions it experienced. For GMO, its tribochemical reaction is thought to involve the formation of a carboxylate on the surface of the wear track. Oleic acid was found to go through a different transition from a weak adsorption of the acid to a tribochemical formation of a carboxylate on the surface providing low friction. GTO weakly adsorbs to the surface, which results in higher friction at the 100th rotation. At temperatures ≤ 50 °C, GDO is thought to go through a similar mechanism to GMO. Above 50 °C, its results are similar to those of GTO.

7.2. Introduction

Carboxylic acids were originally used as organic friction modifiers (OFMs) but were found to be corrosive, so alternative molecules, mainly amines, esters and amides,¹¹ are used instead. A commonly used ester is glycerol monooleate (GMO) which has been shown to be an effective OFM.^{87,109,179} During the esterification of GMO, glycerol dioleate (GDO) and glycerol trioleate (GTO), can also be formed. These more saturated glyceride esters are commonly found as impurities within GMO.

The effectiveness of esters for friction reduction have previously been studied. The friction tests on steel of OFM solutions in a paraffinic mineral oil found that the friction of methyl oleate solution was significantly greater than that of oleic acid or glycerol monooleate. This is attributed to the lack of an OH group within the methyl oleate molecule.⁶¹ Thermocleavable esters, which break down into carboxylic acids under increased temperatures, have previously been synthesised and shown to provide greater friction reduction than the carboxylic acids in a PAO solution within a steel-steel contact. This is thought to be caused by the controlled delivery of the carboxylic acid throughout the test due to the increased temperatures within the contact.⁶³

Simulations have been used to explore the bonding and friction reduction of glyceride esters. Density Functional theory (DFT) has been used to calculate the adsorption energies of OFM molecules on a haematite surface. The results showed that glyceride esters had a higher adsorption energy than carboxylic acids onto iron oxide, and it was thermodynamically favourable for the OH bond of the glyceride to deprotonate on the surface after adsorbing.⁵⁵ Molecular dynamic simulations showed that glycerol monooleate and glycerol monostearate which formed close packed monolayer on a Fe₂O₃ surface are more effective at reducing friction than the corresponding carboxylic acid molecules which formed a similar layer.¹³³

On ta-C diamond-like carbon (DLC) surface, a solution of GMO in PAO gave superlubricity ($\mu < 0.01$). This was caused by the decomposition of GMO molecule within the rubbing contact to form OH terminated groups on the carbon surface.¹⁸⁰ The same mechanism of friction reduction applied to glycerol and other unsaturated OFM molecules on ta-C DLC surfaces.¹⁶¹

Friction experiments in a unspecified commercial base oil show that GMO has a lower friction than GDO < GTO within a steel-steel contact, which modelling data suggests that is caused by GMO having greater hydrogen bonding with the surface and greater surface packing density.¹⁸¹ It has been hypothesised that GMO goes through hydrolysis within the contact to form a carboxylic acid.¹⁷⁵ If this hypothesis is true, then this raises a couple of questions: Would GDO and GTO go through a similar

hydrolysis as a GMO molecule, and how does this relate to the friction results reported above? Does adsorption play a part in this process as suggested in the literature?

The aim of this research is to understand the mechanism of friction reduction of oleyl glyceride esters within tribological contacts. Friction experiments were conducted to investigate the effectiveness of GMO, GDO and GTO in friction reduction as compared to oleic acid. Chemical characterisation of wear tracks were carried out through XPS. These results were linked to adsorption experiments carried out through spectroscopic ellipsometry to understand the impact of surface adsorption on this process.

7.3. Methods and Materials

For this study, 3 different oleyl glycerol esters and oleic acid were used. The performance of glycerol monooleate (GMO), glycerol dioleate (GDO), glycerol trioleate (GTO) and oleic acid, as shown in Figure 7-1, were compared. All additives were 99% purity and bought from Sigma Aldrich. Additives were tested at 1 mM concentration in extra pure hexadecane (Fisher chemical, used as received) (0.046 %, 0.080 %, 0.115 % and 0.037 % respectively). Solutions were stirred on a hotplate at 60 °C for 1 hour before testing.

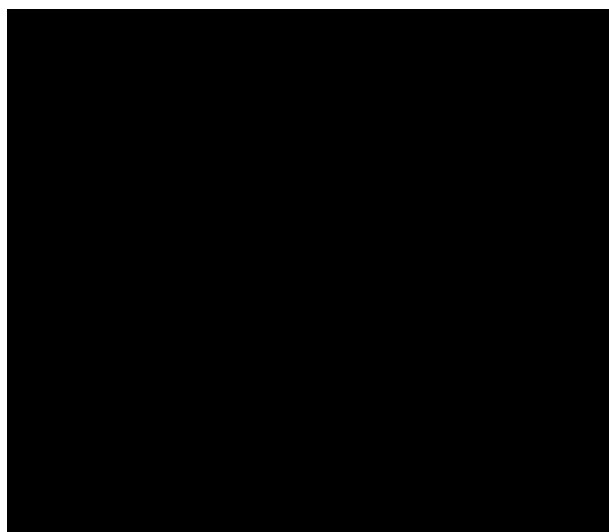


Figure 7-1: The molecules tested, Oleic acid, Glycerol monooleate (GMO), Glycerol dioleate (GDO) and Glycerol trioleate (GTO).

Friction experiments were run using an UMT-2 tribometer from Bruker instruments, which used a ball-on-disk geometry, as described in Chapter 2 Section 2.1. The substrates used were a 15 mm AISI52100 steel disk hardened to 800 Hv and 6 mm AISI52100 steel ball, with an applied load of 5N. Both the ball and the disk were immersed in toluene and sonicated for 30 minutes before cleaning with Oxygen plasma for 1 minute to remove the surface contamination (see Chapter 4 for details). The temperature was controlled throughout the test, with tests conducted at 25, 50, 75 and 100°C. Note that all results at 100 °C and results from GTO at 75 °C are preliminary and further repeats are required to assess their reproducibility. No result from GTO at 100 °C are available.

Adsorption of OFMs on iron oxide was examined with spectroscopic ellipsometry using an EP3 imaging ellipsometer from Accurion. A flow cell attachment was used with the baseplate heated through a heated water pump. The adsorption substrate was a single crystal α Fe₂O₃ and was cleaned prior to testing by being sonicated in toluene and then cleaned with a UV-Ozone cleaner for 30 minutes. The angle of incidence was set at 60 ° with a rotating polariser and analyser used to determine Ψ and Δ values. Two different tests were run, a 2-hour kinetic run with a constant flow of 1 ml/min, and a spectroscopic measurement measuring the growth of the OFM layer on the surface without flow, as previously described in Chapter 2 and Chapter 3.

Chemical analysis of the disks after the tribological tests was conducted using X-ray photoelectron spectroscopy (XPS). A Thermo Fisher K-Alpha system with an X-ray beam energy of 1486 eV was used, measuring the C_{1s} spectra on the surface inside and outside the wear track. A spot size of 200 μ m was used for the measurement and the energy was normalised against the C-C peak at 284.8 eV.

7.4. Results

7.4.1. The effect of Temperature on Friction Reduction.

The effectiveness of GMO, GDO and GTO to reduce friction at 25 °C is shown in Figure 7-2. Two friction coefficients are of particular interest; μ_1 is defined as the friction coefficient during the 1st rotation;

and μ_{100} , the friction coefficient of the 100th rotation, which is used as a surrogate of the friction coefficient at the steady state μ_{ss} . GMO (red circles) provides the lowest μ_1 and μ_{ss} . GDO (blue triangles) has a greater friction than GMO throughout the test. Out of the 3 oleyl glycerol esters, GTO (Green squares) has the highest friction coefficient. It has a slightly greater μ_1 , and a 30% higher μ_{ss} than those of GDO. Oleic acid (black crosses) has a higher μ_1 than all 3 oleyl glycerol esters but its μ_{ss} is similar to that of GDO.

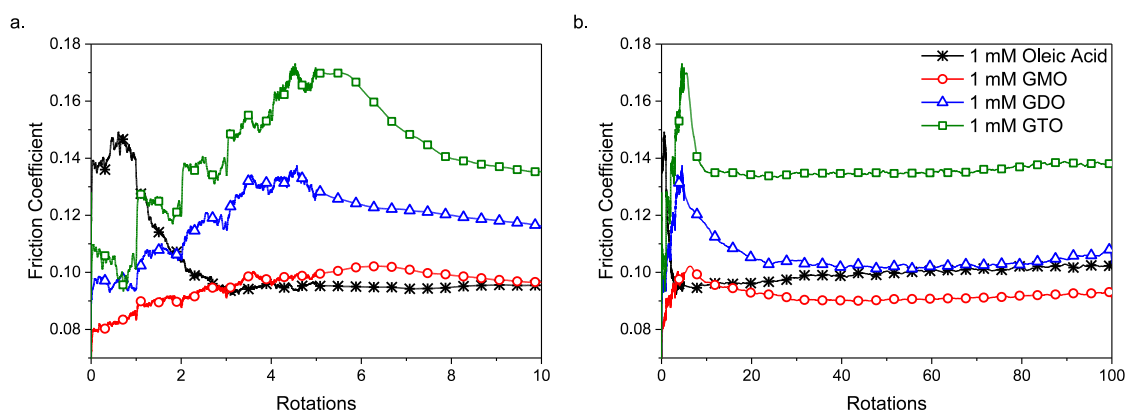


Figure 7-2: The friction reduction of different glyceride esters at 25 °C showing a. the initial friction, and b. the longer term friction.

For the glyceride esters, their friction coefficients rise after the first rotation (see Figure 7-2a). They increase for approximately 5 rotations after which they decrease gradually to their steady state value (see Figure 7-2b). This creates a ‘bump’ in their friction curves. The duration of the transition from the initial friction μ_1 to the steady state friction μ_{ss} varies among the esters. It takes 30 rotations for GMO, 20 rotations for GDO and 10 rotations for GTO (see Figure 7-2b). This bump is not observed with oleic acid; its friction decreases after the first rotation and achieves steady state value after 3 rotations.

At 50 °C (Figure 7-3a and Figure 7-3b), GMO (red circles) has the lowest friction of the 3 esters, followed by GDO (blue triangles), and GTO (green squares) has the highest friction coefficient. Oleic acid (black crosses) has a μ_1 slightly below that of GTO (Figure 7-3a). Its μ_{ss} drops to a value similar to that of GMO (Figure 7-3b).

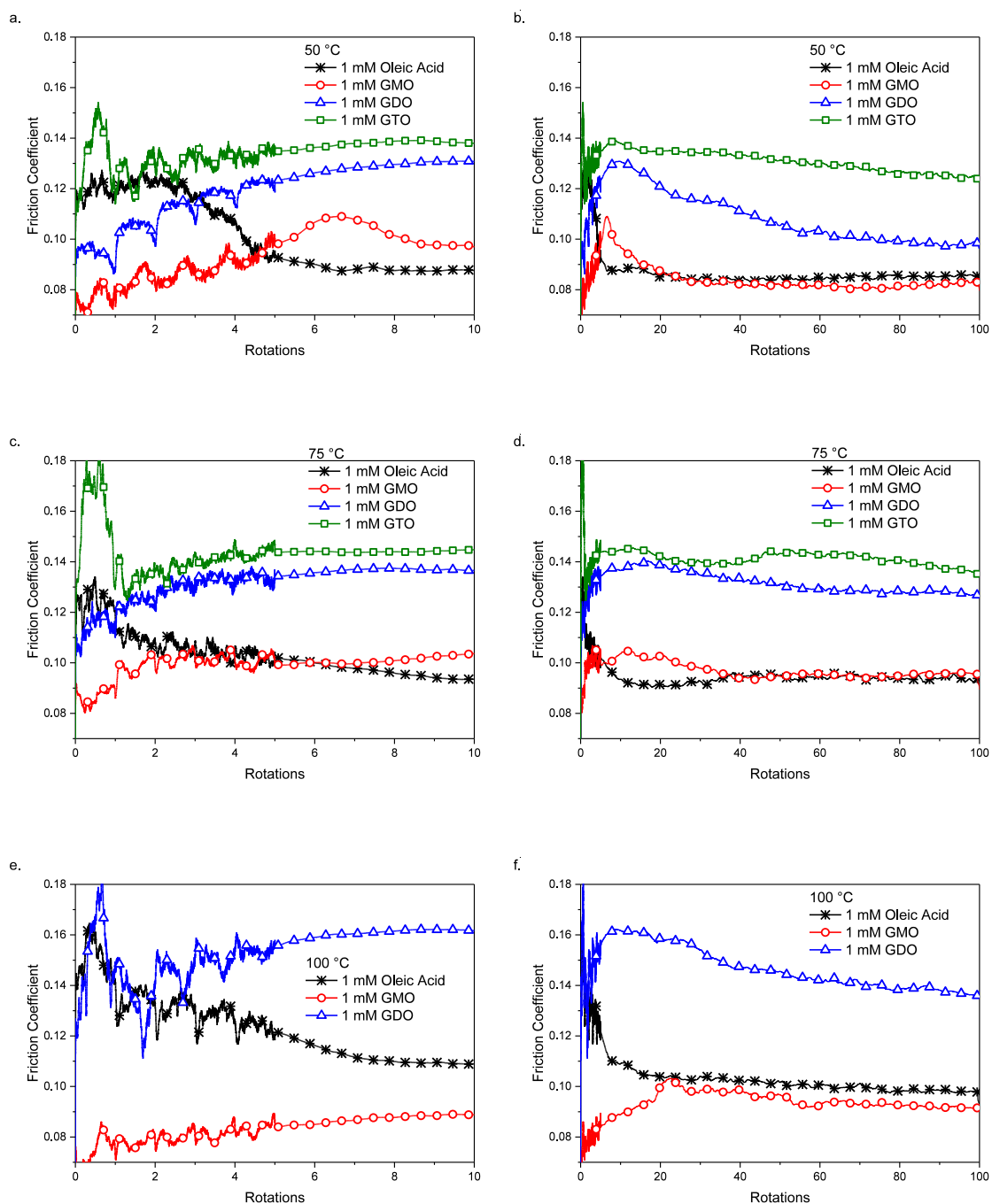


Figure 7-3: The friction reduction of different glyceride esters at (a) and (b). 50 °C; (c) and (d) 75 °C; and (e) and (f) 100 °C.

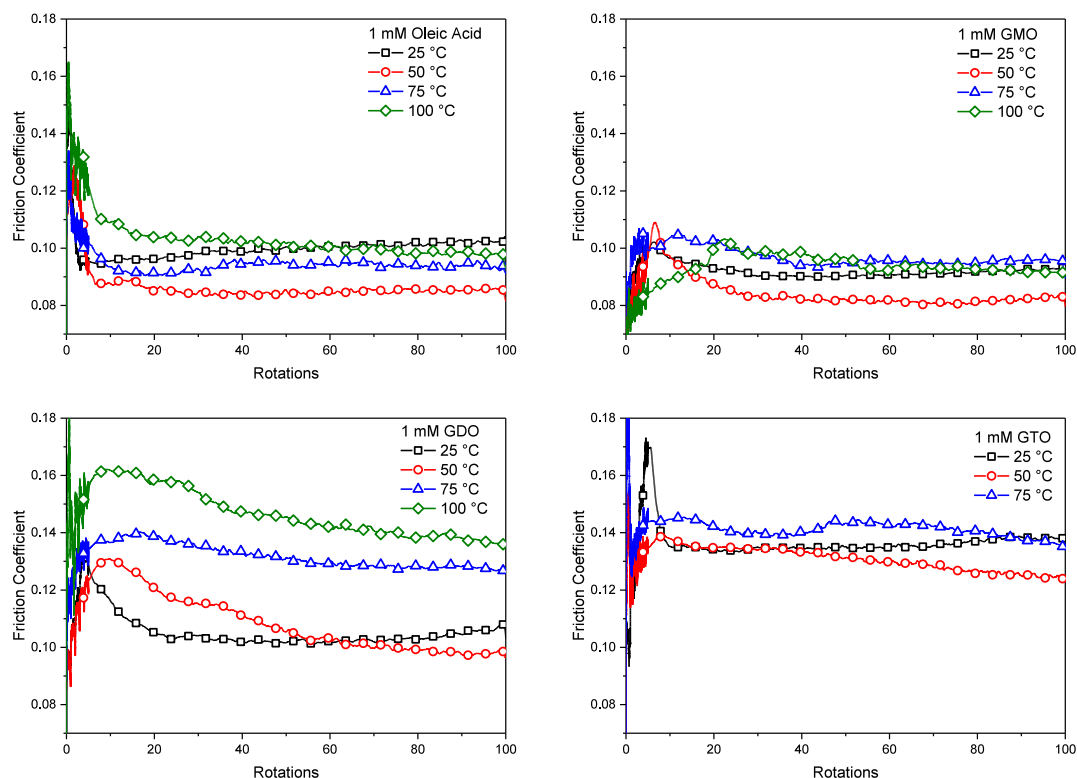


Figure 7-4 Effect of temperature on friction properties of different OFM additives, a) Oleic Acid, b) GMO, c) GDO, d) GTO

Friction traces of all glyceride esters obtained at 50, 75 and 100°C exhibit a bump during the transition from μ_1 to μ_{ss} (Figure 7-3 and Figure 7-4). For 50°C, their maximum friction coefficients occur around the 10th rotation, which is 5 rotations later than what are observed at 25 °C. The maximum friction coefficient of GMO has risen to around 0.11. The transition period at 50 °C is considerably longer than that observed at 25°C, with GMO (Figure 7-4b) and GDO (Figure 7-4c) taking around 30 and 60 rotations respectively. For GTO (Figure 7-4d), the transition period is longer than the duration of the friction test; the sharp bump observed at 25°C has now been broadened significantly.

Observations at 75 °C are similar with those at 50°C. The transition period observed in the friction curves of all three glyceride esters have lengthened (Figure 7-3d and Figure 7-4). For GDO and GTO friction coefficients, steady state is not reached in 100 rotations. Note also that μ_1 of GTO has increased significantly to 0.165 while μ_1 of other OFM only experience a slight increase (Figure 7-3c).

Preliminary results suggest that observations at 100°C is qualitatively similar to those observed at lower temperatures, with a further lengthening of the transition period (see Figure 7-3e and Figure 7-3f).

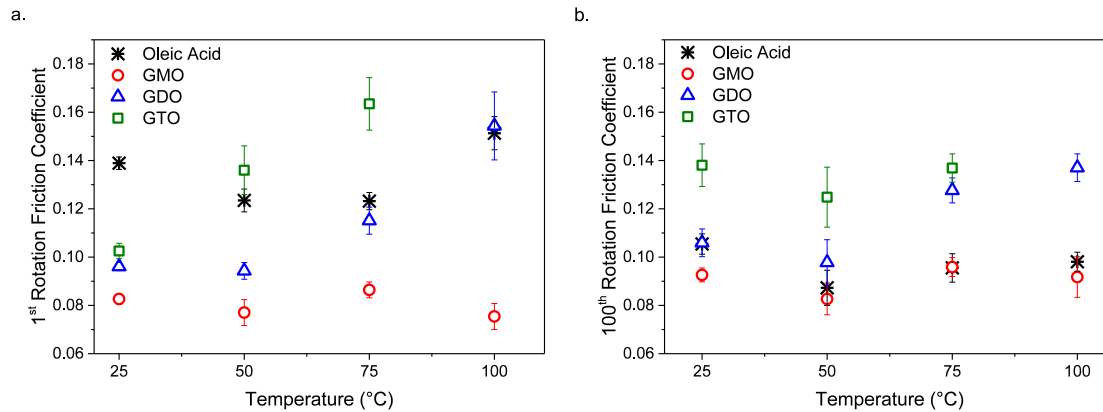


Figure 7-5: A summary of the friction coefficients for different OFMs tested at (a) the first rotation; and (b) the 100th rotation.

A summary of the friction at the first and the 100th rotation is given in Figure 7-5. μ_1 of GMO (red circles, Figure 7-5a) has little variation over the temperatures tested. GDO has similar μ_1 (blue triangles, Figure 7-5a) at 25 °C and 50 °C but then μ_1 rises as the temperature increases above 50 °C. For GTO (green squares, Figure 7-5a), μ_1 increases linear with temperature. For oleic acid (black crosses, Figure 7-5a), μ_1 is reduced slightly as the temperature is increased from 25 °C to 50 °C, but increases when the temperature is at 100 °C.

μ_{100} of GMO and GTO (red circles and green squares respectively, Figure 7-5b) are relatively insensitive to test temperatures and are about 0.09 and 0.13 respectively. Note that μ_{100} of GTO at 100°C is not available. μ_{100} of GDO at 25 and 50 °C are similar and slightly higher than those of GMO at the same temperatures; while at 75 and 100°C, they are comparable to that of GTO at 75 °C. μ_{100} of oleic acid are close to those of GMO at 50-100 °C but is a slightly higher at 25 °C and similar to that of GDO. It is important to point out that at 75 and 100°C, the friction traces of GDO have not reached steady state. Hence, its steady state friction coefficients at these temperatures will be lower than μ_{100} stated here and may approach those values of GMO.

7.4.2. The Effect of Temperature on Adsorption.

The adsorption of the different OFM additives on Fe_2O_3 surface was monitored by ellipsometry. Results from the kinetic measurements at 25 °C are shown in Figure 7-6a. They show that after replacing neat hexadecane with an OFM solution at time = 0, delta decreases. This suggests an increase in adsorption film thickness. GMO (red circles, Figure 7-6a) shows the largest initial drop of delta, which then continues to decrease over time at a slower rate. GDO (blue triangles, Figure 7-6a) has a lesser initial drop in delta than that of GMO but a quicker rate of the decrease in delta after the first few minutes of adsorption, showing a larger decrease in delta after 2 hours. Oleic acid (black crosses, Figure 7-6a) shows a small decrease in delta and adsorbs the least amount on Fe_2O_3 surface. Spectroscopic measurements show 1 mM GMO and 1 mM GDO give adsorbed film of similar thickness after 2 hours of adsorption (Figure 7-7), despite the difference in the decrease of the delta value in the kinetic run. Further repeats are required to understand this discrepancy.

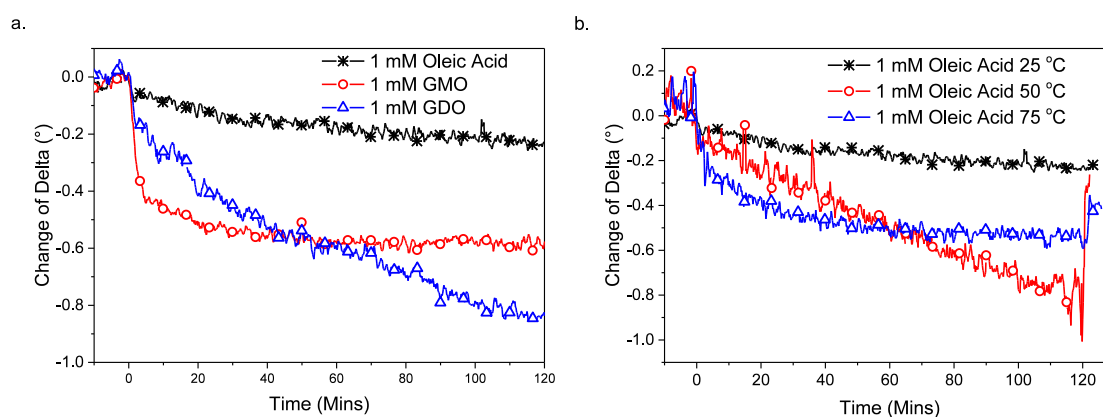


Figure 7-6: The change in delta value with adsorption time for (a) different OFM additives at 25 °C, (b) 1 mM Oleic acid at different temperatures, Note the increase in delta after 120 minutes is caused by the stop of the flow which is only seen at elevated temperatures.

The effect of temperature on adsorption of Oleic acid is shown in Figure 7-6b. At 50 and 75 °C, oleic acid shows a greater drop in delta value compared to 25 °C. These kinetic results at increased temperatures are considered unreliable because of the greater noise within the base line. At time = 120 minutes the flow is stopped, an increase in the measured delta value is observed, showing the unreliability of the kinetic measurements at increased temperatures. The enhanced noise is caused

by the change in refractive index of the injected solution, as described in Chapter 2 Figure 5. To fix these issues an attachment to the liquid cell would need to be made which would control the temperature of the tubing containing the injected fluid. Due to the issues discussed, the rest of the discussion is based on results from the spectroscopic measurements, Figure 7-7, which is run with no flow.

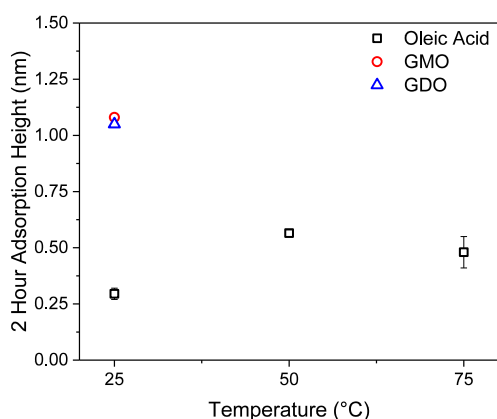


Figure 7-7: A Summary of the adsorption of different OFM additives after a 2-hour adsorption time.

Thickness of the adsorbed films formed in OFM solutions after 2 hours can be modelled based on data obtained with spectroscopic measurements (details in chapter 2). The results are summarised in Figure 7-7. Oleic acid forms a thicker film at 50 and 75 °C than 25 °C. The increased temperature promotes chemisorption over physisorption of the acid molecule onto the surface, enabling a thicker layer to be formed.⁷⁶ Despite different growth kinetics as shown in Figure 7-6, adsorbed films of GDO and GMO have similar thickness after 2 hours of adsorption at 25 °C.

7.4.3. Chemical Analysis of the wear track

Initial results of C_{1s} XPS analysis conducted inside and outside of the wear tracks formed on steel discs in GMO and oleic acid solutions at 25 °C are shown in Figure 7-8. The carbon spectra, which have been normalised to the carbon-carbon peak at 484.8 eV, show 5 peaks, (Figure 7-8a). The peak of interest is the carboxyl peak, as shown in Figure 7-8b. The adsorbed oleic acid detected outside of the wear track (black) shows a peak binding energy at 289.55 eV, which shifts to 289.15 eV when measured in

the wear track (red). This decrease in binding energy has been previously related to a chemical change of stearic acid on iron oxide from the free acid to a reacted carboxyl on the surface.¹⁰⁶

For GMO the intensity of the carboxyl peak is a very low when measured outside the wear track. It is however significantly higher when measured in the wear track, suggesting greater levels of carboxyl within the wear track. This could be caused by shear induced adsorption of GMO onto the wear track or by the formation of a carboxyl on the surface, similar to that of oleic acid.

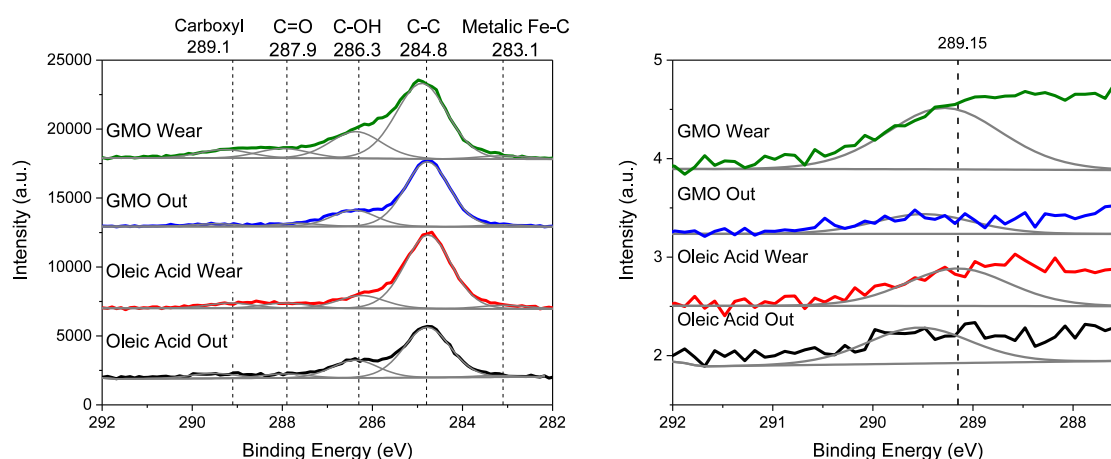


Figure 7-8: XPS results of C1s peaks inside and outside the wear track for GMO and oleic acid test after 100 rotations at 25 °C, b. focus on the carboxyl peak.

7.5. Discussion

The friction results suggest that there are 3 stages to the friction test, the first rotation friction (μ_1), the steady state friction (μ_{ss}), and the transitional stage between μ_1 and μ_{ss} . The characteristics of this transitional stage depends on OFM chemistry.

7.5.1. First Rotation Friction

As discussed in the Chapter 5 the friction of the first rotation is linked to the thickness of the OFM adsorbed layer on a Silicon wafer. The link between the friction of the first rotation in steel-steel contacts to the height of the adsorbed OFM layer on Fe_2O_3 is shown in Figure 7-9a. It shows that the friction of the first rotation increases linearly with decreasing adsorbed layer thickness obtained after 2 hours of adsorption time. For measurements at 25 °C the adsorption height at 10 minutes adsorption

time can be measured during the kinetic run, Figure 7-9b. This also shows a similar decrease of friction with increasing adsorption height.

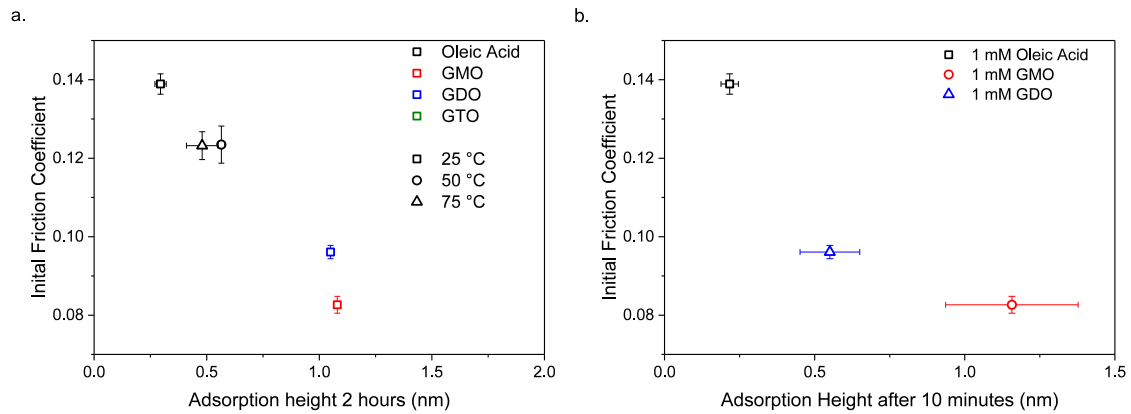


Figure 7-9: The correlation between the friction of the first rotation and the fit thickness of the adsorbed layer at a) 2 hours and b) 10 minutes. Note 10 minute graph only contains data for tests at 25 °C.

While a very thin adsorbed layer on Si wafer also leads to high μ_1 in Si-glass contacts, a critical adsorption height of 0.6 nm after 10 minutes (and 1.0 nm after 2 hours adsorption) is identified beyond which μ_1 remains low (see Figure 5-15). On a steel surface there is no evidence of a critical thickness at the adsorption heights measured in Figure 7-9. Further tests are required with additive solutions which adsorb to form a thicker layer on the surface to determine if a critical adsorption height forms on a steel/ Fe_2O_3 surface.

Note that the steel-steel contact experiences a greater estimated maximum Hertzian contact pressure (1.16 GPa) than the glass-Si contact (1.07 GPa). Hence a more densely packed/thicker layer is required to sustain the load in steel-steel contacts. Steel substrates is also rougher than the Si substrates, although for both systems the λ ratio $\ll 1$.

The effect of temperature on the friction of the first rotation of the different additives provides information about the adsorption of these additives at these temperatures (Figure 7-5a). The adsorption of GMO is not impacted by temperature as seen by μ_1 remaining constant with temperature. GDO shows an increase in initial friction after 50 °C, which suggests that GDO adsorbs

less at 75 °C and 100 °C. The first rotation friction of GTO increase with temperature, from 25 °C. This shows that as the saturation of the glyceride increases, the temperature stability of the adsorbed layer decreases. This is because the more saturated GTO does not have any OH bonds, and GMO has been modelled to adsorb to an Fe₂O₃ surface through its OH groups, as seen by DFT calculations in the literature.⁵⁵

7.5.2. Steady State Friction

The steady state friction appears to have 2 different regimes for the glyceride esters. Lower friction regime (with a friction coefficient of 0.08 – 0.10) which is achieved by GMO, oleic acid and GDO below 50 °C and a higher friction regime (friction coefficients of 0.12-0.14) for GTO and GDO at higher temperatures.

The steady state friction coefficient for each solution was plotted against the first rotation friction in Figure 7-10. For 1 mM GMO (red) at all test temperatures and 1 mM GDO (blue) up to 50 °C, μ_{ss} and μ_1 are positively linked, with $\mu_1 \leq 0.1$ and $\mu_{ss} \leq 0.11$. When $\mu_1 > 0.1$ for the glyceride esters (i.e. GDO at 75 and 100 C and GTO at all test temperatures), a higher μ_1 , independent of μ_{ss} , is obtained. This suggests that there is a critical adsorption height (which relates to adsorbed layer density) to produce a low μ_{ss} . If this is the case then there is potentially a different mechanism for the friction reduction of the solutions which provide a $\mu_1 > 0.1$, resulting in a higher μ_{ss} . Comparative chemical analysis of wear tracks between the solutions giving lower μ_{ss} and higher μ_{ss} may provide an explanation of what is causing the difference in friction coefficients.

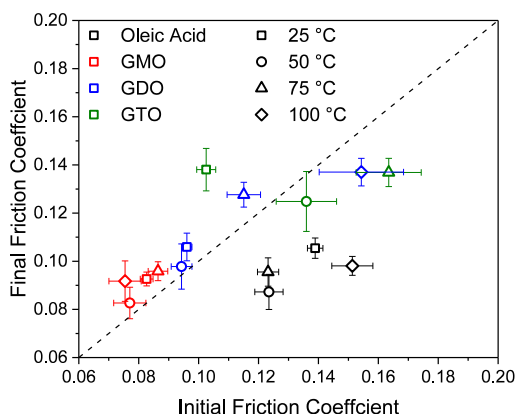


Figure 7-10: A plot showing the correlation between the initial friction and final rotation friction

For oleic acid (black symbols), there appears to be little correlation between first rotation friction and steady state friction, with the first rotation friction coefficient being greater than the steady state friction coefficient. Note that the XPS spectra for oleic acid in Figure 7-8 suggests oleic acid changes from the acid on the surface to the carboxyl. Together from friction results in Figure 7-10, our results support that oleic acid goes through a shear induced adsorption/reaction with the metal surface to form a carboxylate. These results suggest that the same surface oleates are responsible for the steady state friction of oleic acid and GMO.

7.5.3. The transition friction

The glyceride esters tested show a local maximum between the initial friction coefficient and the steady state friction coefficient. Such local maximum is not observed with oleic acid (see Figure 7-2). The initial XPS data potentially shows the formation of a carboxylate within the wear track formed in GMO, Figure 7-8. From this we hypothesise that the increase in friction is caused by the mechanochemical hydrolysis of GMO into a carboxylate on the steel surface. The formation of a carboxylate anion has previously been observed with ToF-SIMS in wear tracks formed in solutions of GMO and methyl oleate.⁶¹ We hypothesise the adsorbed GMO molecule provides low friction, as shown by the first rotation and degrades to a potential unknown intermediate product which provides an inferior friction reduction, before forming the carboxylate. The friction coefficient in this transition

period shows the progression of the reaction. Initially friction increases, showing the formation of the intermediate product. Friction then decreases as carboxylate forms on the surface. As the OFM on the surface is thought to be partially removed by the contact,¹⁸² the steady state friction is an equilibrium of the adsorption of GMO, the formation of the carboxylate and the removal of surface species by the contact.

By increasing the temperature of the friction test, the transition period is lengthened, as shown in Figure 7-4. In some cases, the peak of the bump in the friction data is also delayed. These observations suggest that by increasing the temperature, the reaction from the intermediate product to the carboxylate is being slowed. This could be because of the increased temperature might increase the removal of the intermediate from the surface by the contact, slowing the formation of the carboxylate.

Exploratory tests in Figure 7-11 show that the rate of decrease from the friction peak can be increased by increasing the load at which the friction test is run at, with the higher the load the quicker the decrease in friction. Increasing the load provided a substantial increase in contact pressure but a minimal increase in the predicted contact temperature (T_{rise}), as calculated by the Archard temperature equation.¹⁸³ This suggests that the reaction is indeed shear induced although further work is still required to confirm this.

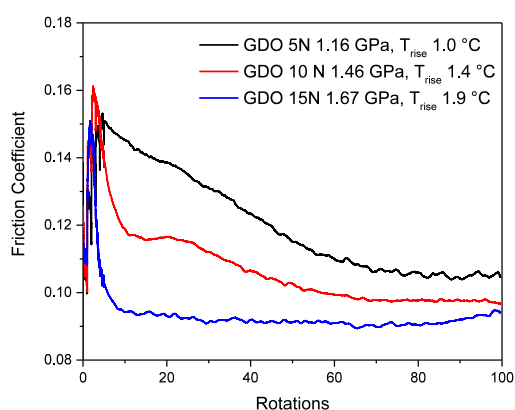


Figure 7-11: An exploratory test examining the impact of applied load on the friction trace of 1 mM GDO at 25 °C

Further work is needed to confirm these hypotheses. Repetition and completion of the tests mentioned within this chapter is required to confirm the validity of the initial results mentioned here. Surface analysis on the chemical composition of the tribofilm formed within the wear track could be used to distinguish the difference between the wear track of GDO at 50 °C and 75 °C. Simulations, such as reactive molecular dynamics or DFT could be used to predict the reaction pathway of the hydrolysis of GMO on a Fe_2O_3 surface to show the structure of the hypothesised intermediate surface species.

7.6. Conclusion

The friction reduction of different oleyl glyceride esters was tested with friction and adsorption measurements compared to oleic acid. The glyceride esters showed 3 stages of friction reduction, initial friction, transition friction and final friction.

Preliminary ellipsometry data suggests that the adsorption height of OFM additives on Fe_2O_3 is linked to the first rotation friction within a steel-steel contact. As the OFM layer increases in thickness on the surface, the friction of the first rotation decreases. This finding is similar to that of Chapter 5 on Si although no critical adsorption height was identified on Fe_2O_3 due to limited data points.

GMO showed the lowest first rotation friction, with minimal change in friction with an increase in temperature up to 100 °C. For GDO the initial friction began to increase after 50 °C, with the initial friction of GTO increasing with temperature. The final friction of GMO is low ($\mu_{ss} \leq 0.11$) at all temperatures tested, along with GDO below 75 °C. GTO had a constantly high final friction, similar to that of GDO at or above 75 °C.

All 3 glyceride esters show a bump in their friction curves, with the maxima at 25 °C at around 5 rotations, which broadened as the temperature increases. For the lower friction GMO and GDO < 75 °C, the transition may suggest the formation of an intermediate product before forming a carboxylate on the surface as suggested by the XPS spectra. The higher friction GTO and GDO ≥ 75 °C, are thought to go through a similar intermediate species but the chemistry of the end product is still uncertain.

Oleic acid, conversely to the glyceride esters, has a weak adsorption to the iron oxide surface. The acid goes through a tribochemical reactions to form a low friction layer of carboxylates on the surface, which is impacted minimally by increasing the temperature. The tribofilm within the wear track of oleic acid is similar to that of GMO, suggesting that the friction reduction of these two additives has the same cause, even though the mechanism to achieve this tribofilm is different.

Chapter 8. The Impact of Base Oil Impurities on the Tribological Properties of OFMs.

8.1. Abstract

Base oils such as hexadecane are known to contain impurities but the impact of these impurities on friction reduction performance of low concentration OFM solutions is unknown. UV-Vis spectrophotometry shows that some of these impurities can be removed by filtering the hexadecane through silica gel, activated alumina and 3Å molecular sieves. The as-received hexadecane gives lower friction caused by its impurities adsorbed onto the surface. These impurities affect the friction reduction performance of OFM additives by impacting the adsorption, the transition friction or even the steady state friction coefficient for different additives. Further work needs to be done to understand the cause of these changes. Removing these impurities is essential to understanding the friction reduction properties of organic friction modifier additives.

8.2. Introduction

Impurities within base oils have been known to change the tribological properties of the oil in the boundary lubrication regime. The previously unknown *oiliness* additive which gave enhanced properties to natural oils over mineral oils of the same viscosity was an impurity within the oil.¹¹ We now know that natural oils contain fatty acids which act as additives within the base oil. Since manufacturers want to control what additives are in the lubricant, the purity of base oils has improved.

Hexadecane was chosen as the base oil for this study as it is readily available, commonly used in literature and has a relatively well-controlled chemical composition. Hexadecane with a purity of $\geq 99\%$ is commercially available, with identities of impurities not disclosed by the manufacturers. Some

impurities could be non-polar, such as branched isomers of hexadecane. Other likely impurities come from the oxidation of hexadecane; it has been shown to oxidise at temperatures over 100 °C forming compounds with various functional groups such as hydroperoxides, ketones, carboxylic acids, alcohols and esters.^{184–187} Hydrocarbons can also be photo-oxidised to form compounds of similar functional groups.¹⁸⁸

Despite knowing impurities being present in commercially available hexadecane, some studies have chosen to presume its cleanliness.^{20,59} Others purify hexadecane. The methods of purification are; recrystallization, filtration, and reduced pressure fractional distillation but absolute purity is still difficult to achieve.¹⁸⁹ Filtration with silica gel and activated alumina is the most common method of removing the impurities.^{56,126,190} Silica gel has an amorphous SiO₂ structure with a high surface area. It is commonly used as a desiccant for the adsorption of water and other polar species.^{56,126} Activated alumina is gamma phase Al₂O₃ which has a high surface area and its pores trap small polar molecules.^{56,126,190} 3 Å molecular sieves, which are ceramic beads with a less well defined composition that have pores of 3 Å, have also been used to absorb water from organic solvents.¹⁹¹

The cleanliness of the hexadecane can be checked through observing the surface tension of the solution through direct measurement,⁵⁶ or by observing the spreadability of a drop of the hexadecane placed on water with a pH of 10.¹²⁶ When heated close to its boiling point, pure hexadecane would not discolour whereas if impurities are present, the solution turns yellow upon heating.¹⁹² Water contamination of the hexadecane can be tested through a Karl Fischer titration.

Since this thesis studies the properties of OFM additives, of which only small quantities (0.03 wt%) are required to have large tribological benefits, impurities in hexadecane could have a significant effect on the lubricating properties of the oil and mask the effect of the OFM. Interactions between the OFM and the contaminants may cause synergistic or antagonistic effects changing the friction reducing properties of the OFM. The aim of this research is to determine the effect the impurities within hexadecane has on the friction reduction of the base oil itself and OFM solutions. The impurities

will be identified through UV-Vis spectroscopy with the adsorption and frictional properties of the as received and cleaned solution tested with ellipsometry and the UMT-2. The effect of the cleanliness of the hexadecane of OFM additives is discussed by using examples from previous chapters.

8.3. Methods and Materials

Two commercial available hexadecane (99% Reagentplus from Sigma Aldrich and 99% from Alpha Aesar), both stated with a purity of 99 %, were used in this study. Brockman 1, neutral activated alumina (purchased from Sigma Aldrich); silica gel (high-purity grade, pore size 60 Å, 200-425 mesh particle size, purchased from Sigma Aldrich) and 3Å molecular sieves were used to clean the hexadecane. The OFMs used, stearic acid, octadecylamine, glycerol monooleate, oleic acid and oleylamine were all purchased from sigma Aldrich with a purity $\geq 99\%$. 1 mM OFM solutions in both as-received and cleaned hexadecane were prepared.

UV-Vis spectrophotometry with a 1 cm quartz cuvette was used to obtain the UV-Vis spectra of all solutions. Spectra were normalised against the spectrum of an empty cuvette and were taken as an average over 3 measurements. Adsorption measurements were run with an Accurion EP3 imaging ellipsometer (see details on method in Chapter 2, Section 3.1). Single crystal Fe_2O_3 was used as the substrate. After a stable baseline of cleaned hexadecane was achieved, as-received hexadecane solution was added for an adsorption time of 2 hours. The growth of the surface layer was measured through both a kinetic measurement and a spectroscopic measurement.

Friction tests were run using the CETR ball on disk tribometer (for details, see Chapter 2, section 2.1). Tests were run at room temperature using 6 mm balls and 15 mm disks made of AISI52100 steel with the latter hardened to 800 Hv. The ball was loaded onto the disk with a force of 5N, creating a maximum Hertzian contact pressure of 1.16 GPa. The disk rotated with a rotation diameter of 1 mm at a speed of 1 mm/s for 100 rotations. Substrates were sonicated in toluene before further cleaning with oxygen plasma for 1 minute.

HFRR (high frequency reciprocating rig) friction tests were done using a 6 mm diameter ball and a 8 mm diameter disk with the disk hardened to 800Hv. A load of 500g was used, providing the same contact pressure to those with the CETR test. The stroke length was 1 mm with a frequency of 50 Hz, at a temperature of 50 °C. Substrates were sonicated in toluene before further cleaning with oxygen plasma for 1 minute, as shown in Chapter 4 to remove surface contaminants.

8.4. Results

8.4.1. Base oil only systems

To clean hexadecane, it was passed through a filter column approximately 30cm long consisting of activated alumina, 3 Å molecular sieves and silica gel, as shown in Figure 8-1. This caused little change to the visible appearance of the solution but removed a nutty aroma from the solution, which indicated the removal of volatile aromatic compounds which were responsible for the smell.

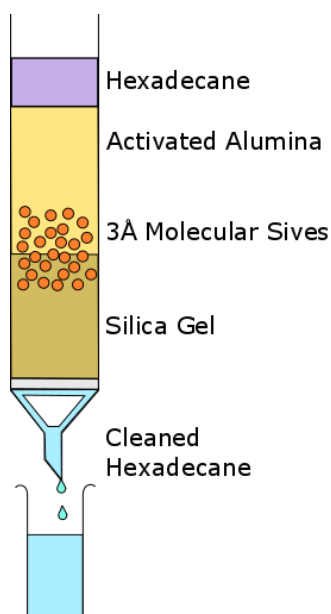


Figure 8-1: A diagram showing the filtration of hexadecane.

To identify the impurities within the hexadecane, UV-Vis spectrophotometry was used. Of the two different brands tested, hexadecane purchased from Alpha Aesar and hexadecane purchased from

Sigma Aldrich prior to April 2019 are grouped as hexadecane 1 and hexadecane purchased from Sigma Aldrich after April 2019 named as hexadecane 2 (the quality of the chemical changed during this study). Figure 8-2 shows the absorption spectra for different hexadecane solutions tested. As received hexadecane 1 (red, Figure 8-2a) shows a main peak at 205 nm with a broad secondary peak at 270 nm. When cleaned the main peak at 205 nm is reduced in intensity, while the secondary peak has been completely removed. A peak at 270 nm may indicate compounds with an oxygen group are present in the solution, showing the filter column removes polar species. The expected peak for the π - π^* transition in a C-C bond is between 180-260 nm. Note that the lower the $sp_2:sp_3$ ratio, the lower the peak wavelength.¹⁹³

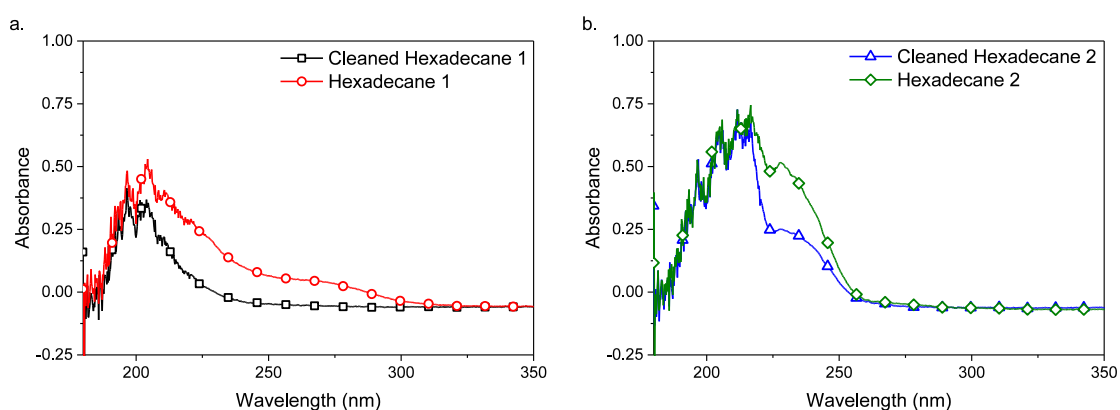


Figure 8-2: The UV Vis spectra of different hexadecane solutions.

Hexadecane 2 (Figure 8-2b) shows saturation of the absorbance of wavelengths up to 220 nm with a secondary peak around 230 nm, which are likely caused by aromatic carbon with high sp_2 content. When filtered, the hexadecane still shows saturation of the absorbance peaks with wavelengths below 220 nm but a 50 % reduction in the absorbance of the 230 nm peak.

Comparing spectra of as-received hexadecane 1 and hexadecane 2 shows that they contain different impurities. In addition, the filter column is better at removing impurities from hexadecane 1 than hexadecane 2. Cleaned hexadecane 1 was chosen as the base oil for the tests mentioned in this thesis, with the hexadecane used for each chapter stated in Table 8-1. Similar UV-Vis spectra was measured for the base oil used in Chapters 5, 6 and 9. The base oil was tested regularly while running

experiments to test the cleanliness and to confirm the removal of the impurities. For Chapter 7, extra pure hexadecane was purchased from Sigma Aldrich, which provided a similar spectra to that of cleaned Hexadecane 1. Chapter 4 uses as received hexadecane.

Table 8-1: The use of different hexadecane solutions within this thesis.

Chapter Number	Chapter Title	Hexadecane Used	UV-Vis peaks ~270 nm
4	Effect of Cleaning	99% as received	Yes
5	Adsorption of OFM	99% Filtered	No
6	Mixed OFM	99% Filtered	No
7	Glyceride esters	Extra Pure	No
9	Glycerate Esters	99% Filtered	No

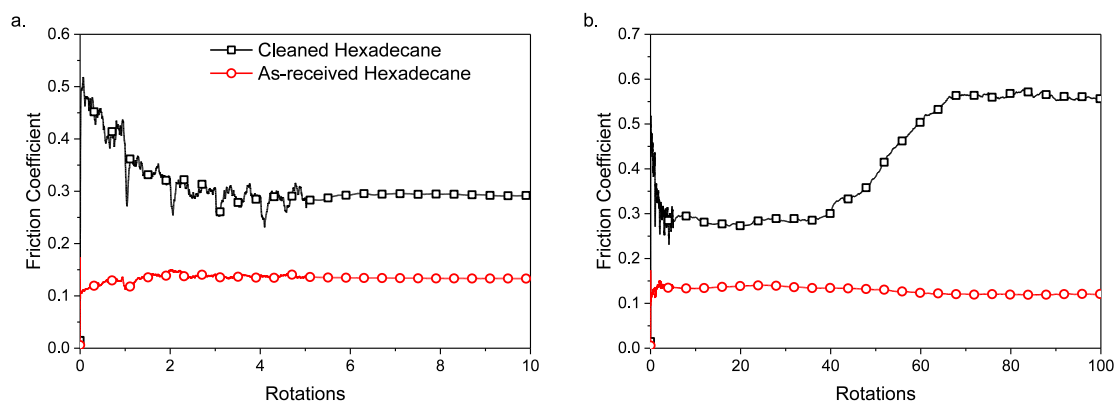


Figure 8-3: The friction of as-received and filtered hexadecane 1, (a) the initial friction and (b) over the full 100 rotations tested..

Impurities in hexadecane impact the friction coefficient in the boundary lubrication regime, as shown in Figure 8-3. As received hexadecane (red circles) shows a stable low friction coefficient throughout the test, with a friction coefficient of 0.13. This is likely due to its impurities adsorbed on surfaces. This friction remains constant throughout the test for the full 100 rotations as shown in Figure 8-3b.

Cleaned hexadecane (black squares) has a high friction coefficient during the first rotation. The friction coefficient is then reduced over the next 2-3 rotations to 0.3, most likely caused by the smoothing of the surfaces caused by the contact. After the 40th rotation, friction begins to increase. The friction coefficient stabilises again after the 60th rotation where the friction is high and similar to that of a dry steel on steel contact.¹⁹⁴ This shows that filtered hexadecane provides no benefits to the lubrication of steel-steel contact at our test conditions.

The adsorption of the impurities onto Fe₂O₃ as measured by ellipsometry are shown in Figure 8-4. Results from the kinetic measurements show that the impurities adsorb on Fe₂O₃ crystal at a constant rate over the entire 2 hour period (see change in delta keeps dropping, red) while filtered hexadecane shows no noticeable adsorption (see relatively constant delta, black). The spectroscopic ellipsometry measurements shows the thickness of the impurities adsorbed layer after 2 hours is about 0.8 ± 0.1 nm. This shows that the impurities in as-received hexadecane, which are removed from the solution by the filter, are surface active. This causes the difference in tribological properties between as-received and cleaned hexadecane.

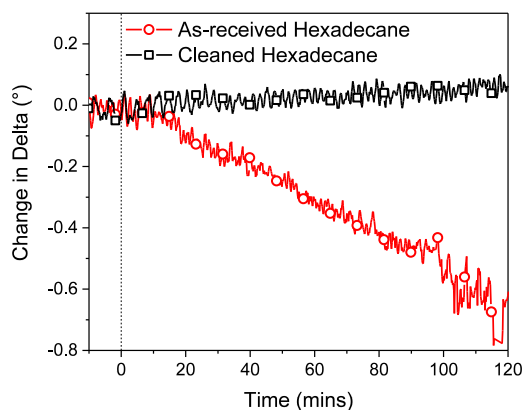


Figure 8-4: The adsorption of as-received hexadecane by ellipsometry

8.4.2. OFM Friction Reduction

The impact of impurities in the hexadecane on the effectiveness of an additive depends on the additive used. It ranges from little or no effect, to some effect on the initial adsorption, the transition friction and also the steady state friction performance of OFM additive.

Chapter 4 reports beading of the test solution on the disk after the test for both 1 mM octadecylamine (ODA) and 1 mM stearic acid (STA) solutions made with as received hexadecane when the surface is cleaned with oxygen plasma. It was hypothesised that oleophobic layers are formed on steel surfaces when the surface is cleaned properly as measured by Zisman *et al.* previously.¹²⁶ When the tests were repeated with cleaned hexadecane, only octadecylamine had an oleophobic layer on the surface. The cleanliness of hexadecane on friction of 1 mM ODA and 1 mM STA is shown in Figure 8-5, where 1 mM ODA (Figure 8-5a) sees no change in friction reduction. Stearic acid, on the other hand, has a greater first rotation friction with the cleaned hexadecane (see Figure 8-5b). The decrease in the friction of the first rotation has been linked with the increasing of adsorption height, as found in Chapter 5 and Chapter 7. Our results here imply that the contaminant causes the stearic acid to have a greater adsorption onto the surface reducing the friction of the first rotation and forming the oleophobic layer. Note the 1 mM STA solution made of as-received hexadecane (Figure 4-4) is constant over 100 rotations while neat as-received hexadecane results in higher friction (see Figure 8-3b). 1 mM ODA shows initial low friction regardless which hexadecane is used. This suggests ODA has a stronger initial adsorption onto the steel surface than STA. It is unclear if the contaminants have an impact on the adsorption of ODA.

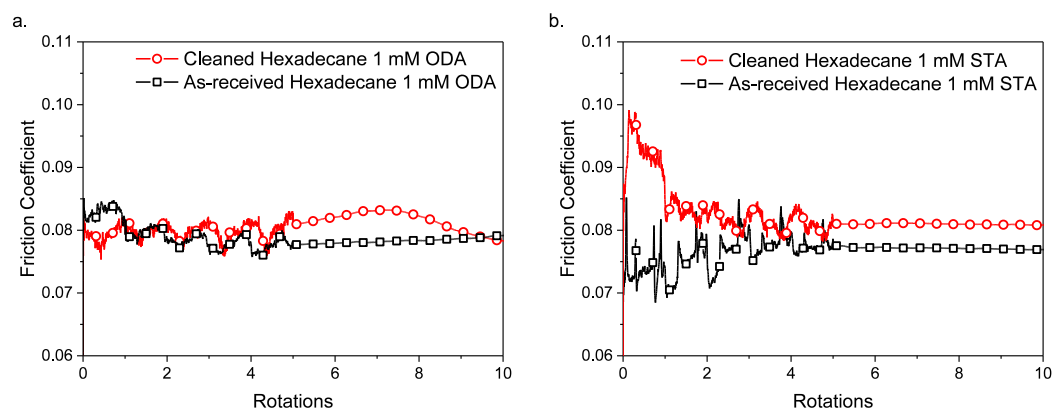


Figure 8-5: The effect of cleaning of hexadecane on a) 1 mM octadecylamine solution and b) 1 mM stearic acid solution as measured with UMT-2.

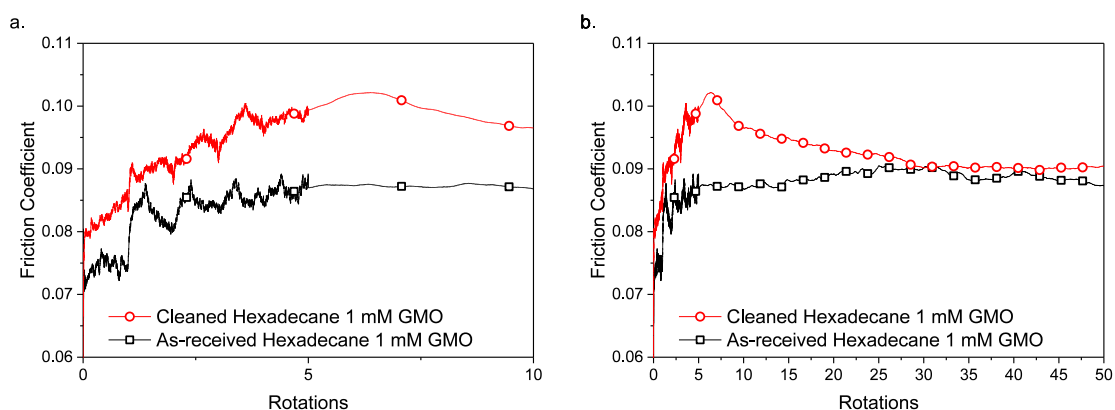


Figure 8-6: The effect of cleaning of hexadecane on the friction reduction of a 1 mM GMO Solution as measured with UMT-2.

For 1 mM glycerol monooleate (GMO), as shown in Figure 8-6, friction coefficients until about the 30th rotation are different obtained with as-received (black) and cleaned (red) hexadecane are different. With as-received hexadecane, the initial friction is lower and the friction is relatively stable after a few rotations. With the cleaned hexadecane, the initial friction is 0.01 higher and there appears to be 'a bump' in the friction. This bump is thought to show the formation of an intermediate compound during the hydrolysis of GMO to a carboxylate on the steel surface. Details on this anomalous friction trace are in Chapter 7.

Impurities in hexadecane can also affect the value of steady state friction coefficient in some cases. This is best illustrated by using the mixture of 0.5 mM oleic acid and 0.5 mM oleylamine in hexadecane. Mixing oleic acid and oleylamine results in the formation of a partial ionic liquid which provides superior friction reducing properties in cleaned hexadecane as tested with HFRR (see red, Figure 8-7, details in Chapter 6). When the mixture is prepared in uncleaned hexadecane (black squares) friction is much higher, suggesting that the impurities interfere with the interaction between these molecules.

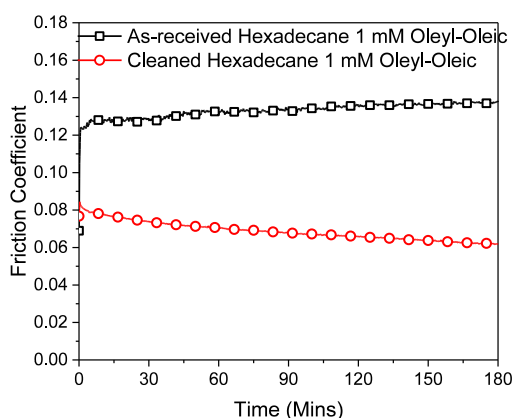


Figure 8-7: The change in friction of the mixture of oleic acid and oleylamine with cleaned and as-received hexadecane as measured with HFRR.

8.5. Discussion

These results show the potential impact of impurities in base oils on effectiveness of OFM additives. In the case of as-received hexadecane studied, UV-Vis spectroscopy showed the removal of chemicals with a high sp_2 content and oxygen containing species. The likely oxygen containing impurities could be the oxidation products of hexadecane which include alcohols and carboxylic acids. These impurities adsorb onto the surface and reduce friction in the boundary lubrication regime. They also interact with the OFMs to alter their friction reducing properties. They affect the adsorption of carboxylic acids onto the surface but not amines, as shown in Figure 8-5. These impurities also affect interactions between additives. The synergistic effect between oleic acid and oleylamine observed in cleaned hexadecane is not observed in as-received hexadecane, Figure 8-7. This suggests that the impurities

interact with the carboxylic acid within the solution, increasing its adsorption but also preventing the formation of the ionic interaction between the acid and the amine.

Impurities in base oil may impact of the tribofilm formation process. In cleaned hexadecane, GMO shows a 'bump' in its friction which trace is thought to show the presence of an intermediate species during the hydrolysis of the ester to the surface carboxylate. This bump is not observed when the solution is made with as-received hexadecane. This suggests that the impurities may catalyse the reaction, speeding up the formation of the carboxylate and thus removed the friction transition. Ester hydrolysis can be catalysed through either acids or bases.¹⁹⁵ Acid catalysed hydrolysis is most likely with carboxylic acids as a potential contaminant.

The presence of carboxylic acids of variable chain lengths within the solution could form a mixed monolayer on the surface. Stearic acid (C18) would co-adsorb with the carboxylic acid impurity ($\leq$ C16) forming a mixed monolayer on the surface. Mixed monolayers with different chain lengths has been tested by AFM previously with Trichlorosilane monolayers, showing that two additive monolayers with mixed tail lengths produce lower friction than the individual additive monolayers.¹⁰⁷ This could explain the lower friction observed by stearic acid in Figure 8-5b. Although this would not explain why the ionic interaction was not observed when oleic acid was mixed with oleylamine.

Further work on the impact of the impurities of hexadecane is needed to get a better understanding of all these phenomena. Chemical characterisation of the impurities within each hexadecane solution could be acquired using liquid cell FTIR, although a longer path length than 1 mm may be required due to the low concentration of these impurities. XPS of the wear tracks obtained in the different hexadecane solutions tested could also be used to identify some of the functional groups on the surface both inside and outside the wear track. Liquid chromatography could be used to separate out the impurities from the solution and then characterised through mass spectrometry.

The impact that these impurities have on OFM solutions could shed light on the variability of the results provided within the literature. Carboxylic acids tested with cleaned hexadecane showed no

signs of multilayer formation within a contact,¹⁹ whereas when tested with as-received hexadecane shows the formation of a multilayer when under pressure.¹⁵⁶ The difference of these two results could be caused by the interactions of the OFMs with the impurities within the hexadecane.

8.6. Conclusion

This research has looked at the effect of impurities in hexadecane base oil on performance of OFMs. Hexadecane was characterised using UV-Vis spectroscopy which shows the removal of some contaminants by a filter of silica gel, 3Å molecular sieves and activated alumina. Impurities in as-received hexadecane adsorb to the surface and provides a friction coefficient of 0.13. Cleaned hexadecane, however, has a greater friction coefficient and no measurable adsorption. This shows that impurities in as-received hexadecane are surface active and are removed from the solution by the filter.

When mixed with OFMs, the impurities have varying effects. For some additives such as octadecylamine, no difference was measured between the solutions made with cleaned and as-received hexadecane. Acid head groups appear to show an interaction with the impurity which enhances adsorption to the surface but is detrimental for the ionic interaction oleic acid has with oleylamine. Glycerol monooleate shows a transitional bump in the friction when made with cleaned hexadecane, but is removed when using as received hexadecane.

Further research is required to fully understand the interaction these impurities have with OFM additives. However they are best to be removed for the aim of understanding the friction reducing mechanism of organic friction modifier additives.

Chapter 9. The Friction Reduction of Glycerate Esters

9.1. Abstract

Esters are thought to hydrolyse within a tribological contact, forming its constituent carboxylate and alcohol. To test this assertion, the friction reducing properties of glycerol monooleate (GMO) and oleyl glycerate were compared. Results show that they have similar initial and intermediate friction, implying that they have similar adsorption and transition mechanisms. Oleyl glycerate however provides significantly lower steady state friction than GMO. A similar observation about the steady state friction is made with stearyl glycerate compared to glycerol monostearate (GMS). The OFM layer within the wear track was measured through spectroscopic imaging ellipsometry showing the glycerate formed a thicker film within the wear track than the glyceride. An initial hypothesis is proposed that a glycerate oligomer brush is formed within the wear track although further work is required to test this hypothesis.

9.2. Introduction

Esters are thought to potentially break down within a contact to form the corresponding acid and alcohol.¹⁷⁵ Spikes¹¹ hypothesised that ethyl stearate and stearyl acetate should produce different friction since they should produce different long chained fatty acid and fatty alcohol when hydrolysed.¹¹ However he found that ethyl stearate and stearyl acetate produced similar friction coefficients, as seen in Figure 9-1. It is suggested that rubbing alone is not enough to hydrolyse esters within a contact and that other factors, such as the presence of water or a strong acid, may also be required.¹⁹⁶ In Chapter 7, we found that a strong initial OFM adsorption was required to produce low friction at the steady state, as in the case of GMO (Figure 7-4). Hence surface adsorption strength may influence the hydrolysis of an ester within the contact. Ethyl stearate and stearyl acetate, unlike

glycerol monooleate, have no additional OH groups. Thus they would presumably have a weaker adsorption onto the surface than GMO.

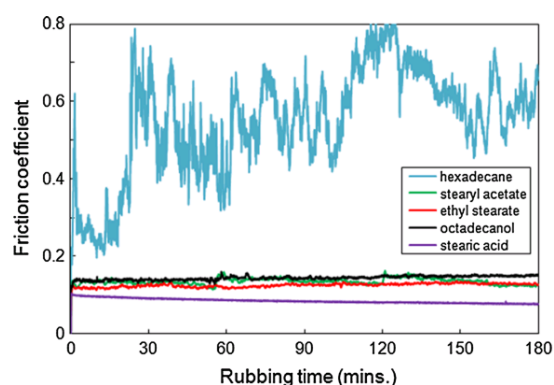


Figure 9-1: The friction reduction of different esters at 100 °C, as measured with HFRR. Figure copied from ref 2 with permission.

To test the hypothesis that esters hydrolyse within a contact and thus result in similar friction of their constituent long tailed groups, two glycerate esters are tested and compared to the equivalent glyceride esters. A glycerate ester is formed from the esterification of glyceric acid and a fatty alcohol. Structures of these glycerate molecules are very similar to those of glyceride esters; both sets of molecules have two OH groups which enhance their adsorption to the surface, and the same tail group (for structures see Figure 9-2). Once hydrolysed within the contact these two molecules would form different alcohols and carboxylates. Thus they are expected to have different steady state friction coefficients. The aim of this study is to understanding of the mechanism of lubrication of esters by comparing the friction reduction performance of glycerate and glyceride molecules.

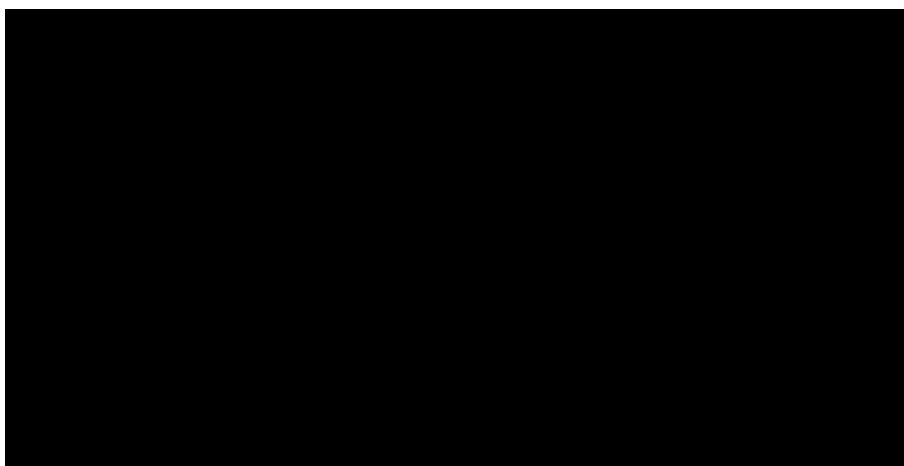
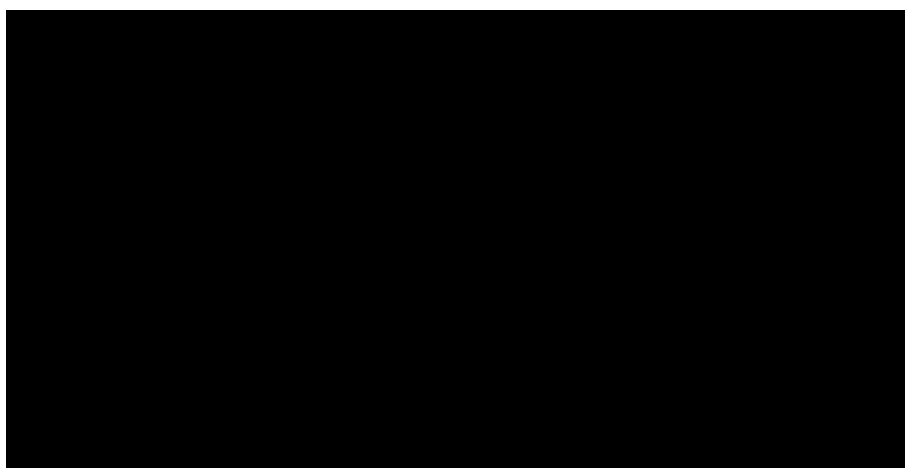


Figure 9-2 The structure of the different glycerates and glycerides tested.

9.3. Methods and Materials

Stearyl and oleyl glycerate esters (SG and OG respectively) were synthesised in collaboration with the University of Manchester according to the procedure set out in literature¹⁹⁷ with the final structures



shown in

Figure 9-2. They were received as powders and their molecular structures were confirmed using NMR spectroscopy by Dr Sophie Campen. Glycerol monooleate (GMO) and glycerol monostearate (GMS) was purchased from Sigma Aldrich (purity $\geq 99\%$). The solvent used was n-hexadecane (99%, Sigma Aldrich) which has been filtered through activated alumina, 3Å molecular sieves and silica gel. Solutions were made at 1 mM concentrations (0.036 wt% for stearic acid and oleic acid, 0.046 wt% for GMO, GMS, SG and OG). The solutions were mixed by stirring and heating at 60 °C for 1 hour.

Friction tests were carried out on the CETR UMT-2 ball on disk tribometer. A 15 mm diameter steel disk hardened to 800 Hv with a 6mm diameter steel ball, both made from AISI 52100 steel, were used as substrates. The contact was fully flooded with 2 ml of solutions, and was left for 2 minutes before rubbing began to allow OFM adsorption onto the surfaces. During the test, the ball was static while the disk rotated, forming a rubbing track with a radius of 1 mm. The sliding speed at the contact was 1 mm/s and each test consisted of 100 rotations and a load of 5 N was used. Tests for oleyl tailed molecules (OG and GMO) were run at room temperature (25 °C) and tests for stearyl tailed molecules (SG and GMS) were run at 50 °C due to their lack of solubility at room temperature. After the test, the disks were rinsed with hexane and stored for further analysis. Note hexadecane used in this Chapter is different to that used in Chapter 7, so friction results for 1 mM GMO here may differ from those previously reported. For effects of impurities on hexadecane in performance of OFM, see Chapter 8.

Thicknesses of OFM layers on wear tracks were measured in air using spectroscopic imaging ellipsometry. Psi and delta values were taken of the surface inside (3 locations) and outside (2 locations) of a wear track using 44 wavelengths from 371-1000 nm with an angle of incidence of 60 °. The values obtained were then modelled using the EP4 modelling software, using the steel surface optical model as shown in Figure 9-3 (for details, see Chapter 3). The thickness of the effective medium layer is presumed to be the same as the roughness as found with AFM, with the roughness of outside the wear track at 2.43 nm and inside the wear track at 3.03 nm. Each value is an average of measurements from 3 different disks.

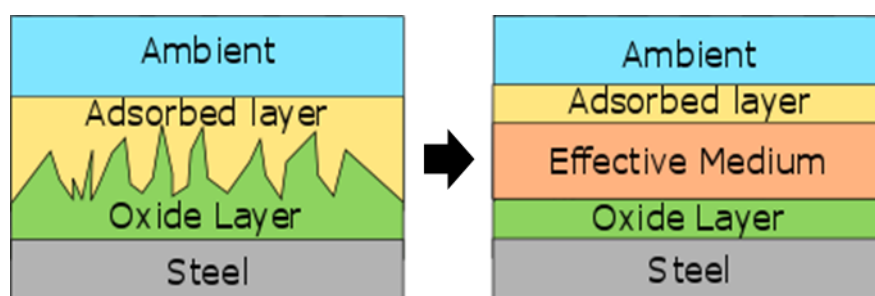


Figure 9-3: The optical model used to measure the thickness of the OFM layer on a steel surface.

9.4. Results

The friction reduction of oleyl glycerate compared to GMO is shown on Figure 9-4. Their friction coefficients follow each other closely for the first 10 rotations, as shown in Figure 9-4a. Their comparable initial friction coefficients suggest that their adsorbed films on steel have similar properties. After the 1st rotations, their friction coefficients increase, reached a maximum at about the 4th rotation, then decrease. After the 10th rotation, their friction coefficients show different trends. The friction of GMO (black squares) has stabilised whereas the friction of the oleyl glycerate (blue triangles) continues to decrease reaching a friction coefficient of 0.065 (Figure 9-4b).

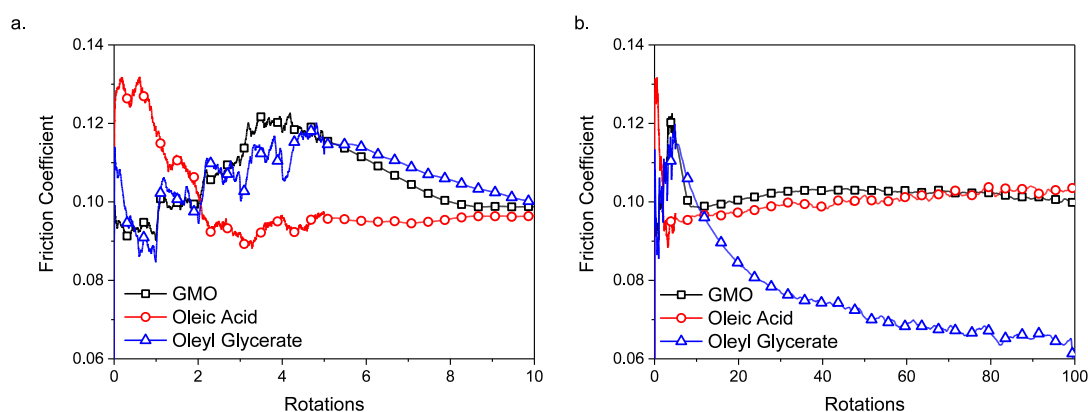


Figure 9-4: The friction performance of 1 mM oleic acid, GMO and oleyl glycerate solutions at 25 °C

Stearyl glycerate (blue triangles) gives a higher friction coefficient than GMS (black squares) during the first rotation at 50 °C, see Figure 9-5a. This may suggest SG has a thinner adsorbed layer on steel, as the friction of the first rotation is linked to the adsorption height (see Chapter 5 and Chapter 7). The friction trace of stearyl glycerate does not show a bump as observed in the case of GMS, GMO and oleyl glycerate. Instead it drops gradually and reaches a steady state friction of 0.07 (see blue triangles, Figure 9-5b), which is lower than that of GMS. The lack of a bump in the friction trace from SG solution is unclear. It may be due to varying level of contaminants in different solutions. As discussed in Chapter 8, these contaminants are thought to remove the ‘bump’ in friction, potentially

by catalysing the reaction but does not alter the steady state friction. Further tests are necessary to confirm this result.

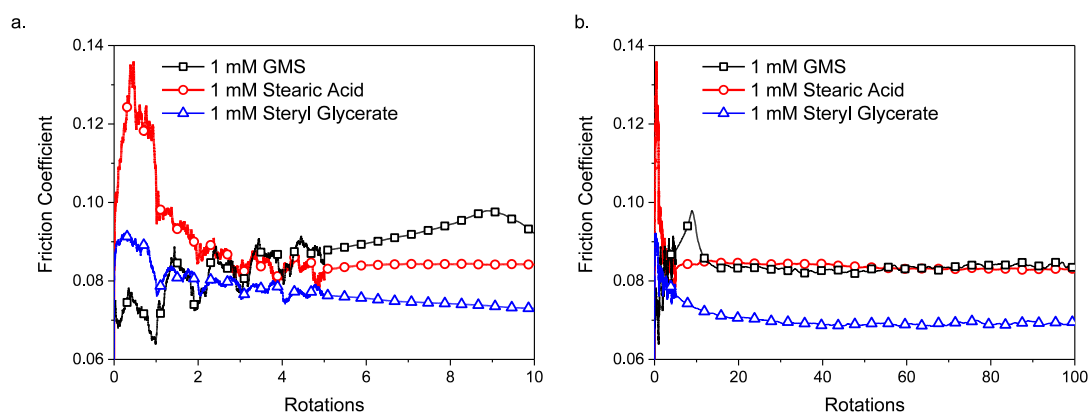


Figure 9-5: The friction performance of 1 mM stearyl glycerate, GMS and stearic acid solutions at 50 °C

After the test, the surface of the disk was examined using spectroscopic ellipsometry. Thicknesses of the surface layers formed by GMO and oleyl glycerate were compared, see Figure 9-6. Their surface layers formed outside of the wear track were both around 2 nm (blue bars). The surface layers inside wear tracks (red bars) are thicker than those outside, with an increased thickness of 0.5 and 3.5 nm for GMO and oleyl glycerate respectively (green bars). Note the length of a GMO and oleyl glycerate molecule is around 2.4 nm.

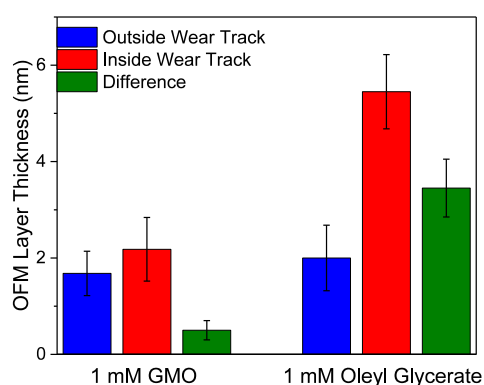


Figure 9-6: The change in OFM layer thickness between inside and outside the wear track for GMO and oleyl glycerate.

9.5. Discussion

With similar chemical structures, one may expect the equivalent glycerate and glyceride forming similar surface layers on steel (schematics in Figure 9-7a), providing similar friction reduction. Our results support this is indeed the case for oleyl glycerate and GMO. Their adsorbed layers are of comparable thicknesses on steel, as confirmed by ellipsometry measurement obtained outside the wear tracks. They also give similar initial friction coefficients during the first rotation.

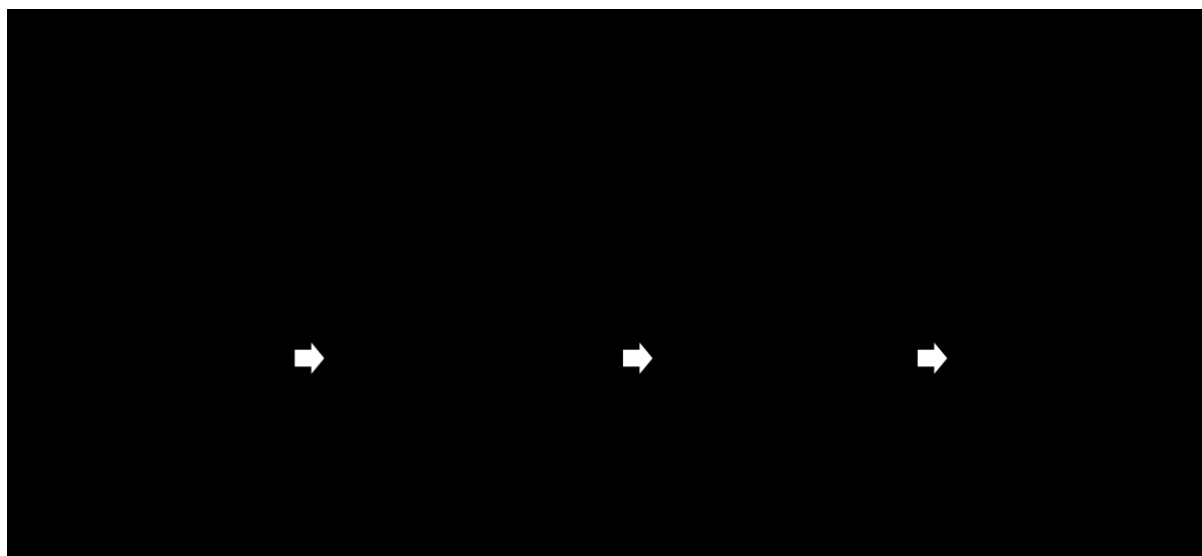


Figure 9-7: The hypothesised mechanism of the friction reduction of oleyl glycerate ester. a. initial adsorption, b. mechanochemical hydrolysis, c. Layered adsorption, d. polymerisation and hydrogen bonding cross linking.

This is not the case for stearyl glycerate and GMS. Their behaviour could indicate that adsorption strength of equivalent glycerate and glyceride may differ at higher temperatures. This may also be due to contamination within the hexadecane of the SG solution. Further tests are needed to confirm this result.

After the first rotation, friction coefficient increases and then subsequently decreases when GMO is used. This observation is linked to the mechanochemical hydrolysis of the ester, as discussed in Chapter 7. The close resemblance of the friction traces of GMO and oleyl glycerate during the first 10 rotations suggest that oleyl glycerate goes through a similar mechanochemical process initially during rubbing, potentially forming a similar intermediate product. GMO was hypothesised to hydrolyse into

glycerol and an oleate molecule on the surface whereas oleyl glycerate would hydrolyse into oleyl alcohol and a glycerate on the surface from glyceric acid.

The hydrolysed products of these ester OFMs would govern the steady state frictional response. This is the case for GMO, with its steady state friction coefficient similar to that of oleic acid (Figure 9-4b). Following the same argument, one may then expect that that steady state friction of oleyl glycerate will resemble that of oleyl alcohol. Indeed It has previously been hypothesised that the mechanochemical hydrolysis of an ester, such as stearyl acetate, would produce the friction of the corresponding alcohol, although this was not observed in the results presented.¹¹ If oleyl glycerate hydrolyses to become oleyl alcohol, it is likely to have a higher steady state friction coefficient than GMO since fatty alcohols provide a higher friction than the corresponding fatty acid, as seen in Chapter 4. Our results contradict this hypothesis, with oleyl glycerate having lower steady state friction coefficient than GMO (Figure 9-4b). The failure of the hypothesis to explain the behaviour of oleyl glycerate may stem from its neglect of the acidic product of the hydrolysis, a glycerate. Note, as discussed in Chapter 6, a mixture of GMO and oleylamine does not produce the same synergy as oleic acid and oleylamine, suggesting that the product of the hydrolysis of GMO is an oleate not a free acid. Therefore oleyl glycerate would form a glycerate on the surface, not free glyceric acid.

Once hydrolysed, the iron glycerate on the surface may have protruding hydroxyl groups (Figure 9-7b) which could enable further adsorption of oleyl glycerate molecules to the surface (Figure 9-7c). Continuous rubbing may allow the hydrolysis and esterification of these newly adsorbed oleyl glycerate molecules, causing polymerisation of glycerate on the surface, as shown in Figure 9-7d. Note, low concentrations glyceric acid has previously been hypothesised to produce an ester within a rubbing contact to produce enhanced friction and wear reduction compared to a glycerol solution.¹⁹⁸ The polymerisation of the glycerate would result in an oligomer brush layer inside the wear track. Hydrogen bonds between the OH groups on the glycerate oligomer would enhance the stability of this layer, as demonstrated in Figure 9-7d.

The formation of a 'friction polymer' has previously been observed within tribological experiments. For example, a high molecular weight iron containing compound was detected within the test solution after running a 4 ball wear test, with steel specimens in paraffin oil.¹⁹⁹ The nature of these polymers are thought to be controlled by an equilibrium between their formation governed by asperity flash temperatures, and their decomposition due to the shear forces within the contact.²⁰⁰ Stinton *et al.* found that esters can form during rubbing in hexadecanoic acid and hexadecan-1-ol, although no sign of polymerisation was observed when diacids and diols were used.¹⁹² When formed on the surface, these long chain esters would have significantly weaker intermolecular interactions between the adsorbed species than the glycerate oligomer brush layer hypothesised to be formed in this study. The esters formed within the contact could be subjected to re-hydrolysis. This could be the reason why polymerisation was not observed for the long chained diacids and diols. The addition of the inter-chain hydrogen bonding of the glycerate oligomers may increase the stability of the layer slowing the re-hydrolysis of the ester.

Film thickness measurements by ellipsometry (Figure 9-6) support the formation of an oligomer brush through the polymerisation of the hydrolysed oleyl glycerate molecules in the wear track. The results show that the surface layer in the wear track, presumably the oligomer brush, is about 3 nm thicker than that outside the wear track, which likely consists of a monolayer of oleyl glycerate on the surface. The thickness of the layer outside the wear track is measured as 2 nm, suggesting a slightly tilted layer of the 2.4 nm long oleyl glycerate molecule. The 5-6 nm thick oligomer brush layer formed within the wear track will be more effective in preventing metal-metal contact and potentially reduce the friction coefficient, as in the case of polymer brushes.^{192,201,202} In this scenario, the saturation of the fatty alcohol tail groups will play no role in the formation of the surface layer, and hence the friction reduction. The formation of an oligomeric glycerate layer in the wear track suggest that the straight chained stearyl glycerate and oleyl glycerate would have similar steady state friction coefficients. Further friction tests at the same temperatures are required to confirm this.

An alternative hypothesis for the existence of a thicker layer in the wear track formed by an oleyl glycerate solution is the formation of thick layer of iron glycerate soap within the wear track. This has previously been observed with long chained carboxylic acids in the presence of water. The metal carboxylate soap can increase the measured film thickness by an order of 10 nm, as measured with interferometry.^{19,203} There are contradictory findings which suggest that the addition of water does not affect the friction reducing properties of fatty acid OFM solutions,¹⁰¹ so the formation of a thick layer of iron glycerate soap would not explain the enhanced friction reduction the glycerates have compared to the fatty acids.

Further research would be required to test these hypotheses. Different test conditions could be used to determine under what conditions this film forms, and whether the thickness of the OG film can be controlled. Surface analysis such as ToF-SIMS could be used to characterise the tribofilm within the wear track of the glycerate to determine whether an oligomer brush has been formed or if it consists of iron glycerate. AFM could be used to confirm the topological change within the wear track providing more information on the morphology of the tribofilm formed.

9.6. Conclusion

The friction of glycerate esters has been compared to that of glyceride esters. While the initial and intermediate friction is similar at 25 °C between oleyl glycerate and GMO, the steady state friction is different, with the glycerate providing significantly lower friction. This suggests that both ester molecules go through a similar process of hydrolysis but carboxylate products of the reaction differ, with GMO and oleyl glycerate forming an oleate and a glycerate respectively on the surface. Ellipsometry shows that the OFM layer is thicker in the wear scar than the rest of the disc, with the difference being 3 and 0.5 nm for oleyl glycerate and GMO respectively. It is hypothesised the thicker oleyl glycerate tribofilm is a glycerate oligomer brush formed through hydrolysis and subsequent esterification of multilayer glycerate molecules. Further work is required to test this hypothesis.

Chapter 10. Conclusions and Future Work

10.1 Abstract

The aim of this project was to gain better understanding of the friction reducing mechanism of organic friction modifier additives. This enables better application of additives and to enhance the design of future OFM additives. The effects of contamination, adsorption, interactions between OFM additives and the friction reduction of esters were studied. When measured in a clean system, OFM additives adsorb to the surface, reducing friction during the first passing of a contact. This friction reduction is linked to the thickness of the OFM layer on the surface. During rubbing, some OFM additives may undergo tribochemical reactions. Specifically, both carboxylic acids and esters forming carboxylates within the wear track. The chemistry of the resulting carboxylate will determine the steady state friction coefficient achieved by the additive.

In this chapter the main conclusions of this project are discussed with potential applications, and avenues to progress this work further are outlined.

10.2. Conclusions

1. To examine friction reducing properties of organic friction modifier additives in an idealised system, the system needs to be free from surface contaminants and solvent impurities.
 - a. Surface contamination impacts the friction of the first rotation. Cleaning the surface with oxygen or argon plasma removes the contamination and enables the OFM solution to dictate the friction from the first rotation.
 - b. The surface contamination impacts the steady state friction measured for some additives and at some concentrations.

- c. Solvent impurities are thought to interact with the OFMs in solution. This interaction changes the friction reducing properties of some OFMs and can affect the first rotation friction, the transition friction and the steady state friction reduction.
 - d. Some of the impurities within hexadecane can be removed by passing the base oil through a filter containing 3Å molecular sieves, silica gel and activated alumina.
 - e. Within engineering systems contamination is unavoidable. Understanding the impact of contaminants on the friction reduction of OFMs enables the better design of lubricant additives.
2. Ellipsometry can be used to measure the *in situ* adsorption of OFM additive from oil based systems.
- a. The adsorption of various OFM additives has been measured on silicon wafer (SiO₂ surface) and Fe₂O₃ crystal surface. A decrease in the delta value during OFM adsorption was converted to a layer thickness using a surface model.
 - b. Calibration tests were run to determine the refractive index of the adsorbed OFM layer on the surface (1.55). Careful consideration is required to model the refractive index of the adsorbed OFM layer due to how similar the value is to the ambient hexadecane solution (1.43). Inaccurate modelling of the OFM refractive index would lead to large variation of the modelled film thickness.
 - c. Adsorption results obtained through a QCM were converted to layer thickness by the Cuyper's equation, these thickness values matched the adsorption of OFMs onto silicon as measured with ellipsometry
3. The thickness of the adsorbed layer of OFM additives is linked to the first rotation friction (μ_1) of the solutions.
- a. The thicker the OFM layer on the surface, the lower the μ_1 , as found on silicon and as initial work suggests on steel/Fe₂O₃.

- b. On silicon there is a critical adsorption height of 0.6 nm, above which there is less of a reduction in friction with increasing layer height. This layer height could be linked to surface density of 100 Å²/molecule. When developing a lubricant, the critical adsorption height/surface density of an OFM onto a surface could be used as a threshold value to determine suitability of using an OFM.
 - c. A tribometer can be used to compare the adsorption of different OFM additives onto a surface. This is useful when the properties of the solution prevent the measurement through other means, such as the solution having a high extinction coefficient which would prevent the user from using ellipsometry or the solution has a high viscosity which prevents the adsorption from being measured accurately with QCM.
 4. Interactions between OFM additives can produce synergistic friction reduction by forming an ionic liquid within the solution.
 - a. A mixture of oleic acid and oleylamine has been shown to form an ionic liquid within solution which provides synergistic friction reducing properties. The friction reduction was significantly greater than the two individual additives.
 - b. Oleic acid mixed with more saturated secondary and tertiary amines produce a less effective synergistic friction reduction.
 - c. No synergy is observed when oleylamine is mixed with glycerol monooleate (GMO). This shows that when mixed with oleylamine, GMO does not hydrolyse to form an oleic acid molecule under rubbing as previously suggested in the literature.
 5. Strong adsorption to the surface is required for glycerol esters to produce a low steady state friction coefficient, which is linked to the structure of the esters acid group.
 - a. The esters which had an initial friction coefficient < 0.1 provided a low steady state friction.
 - b. These well adsorbed esters are hypothesised to hydrolyse within the rubbing contact to form carboxylates on the surface.

- c. A bump is observed within the friction trace which is prolonged with temperature but shorted with increasing load. This bump is hypothesised to show the formation of an intermediate product during the hydrolysis of the ester to the surface carboxylate.
 - d. Higher loads and lower temperatures are thought to increase the reaction rate of the intermediate to the carboxylate. Therefore Oleyl glycerides are best used in conditions with high loads and low temperatures to promote the formation of a low friction carboxylate layer on the surface.
6. Glycerate esters are hypothesised to form a glycerate oligomer brush tribofilm.
- a. Glycerate esters provide a lower steady state friction than the corresponding fatty acid and glyceride ester and the formed tribofilm is 3 nm thicker than the surrounding adsorbed surface layer.
 - b. Further work is required to test this hypothesis.

10.3. Future Work

1. Amides are a type of OFM additive which was not studied within this thesis. It also has potential to hydrolyse within the contact to form its corresponding acid/carboxylate and ammonia. Using similar techniques as used in this work, the friction reduction mechanism of amides can be studied.
2. To further the work with ellipsometry, a setup could be developed to study in solution thickness of the OFM layer during rubbing. The diagram in Figure 10-1 shows a potential set up of the system, with a ball on disk contact and the ellipsometry laser pointed at a separate part of the wear track to measure the film thickness. This system would be able to determine the formation of a multilayer film on the surface which may be formed in the contact, as observed in literature in OFM solutions in the presence of moisture¹⁹ and with OFMs under pressure¹⁵⁶ as well as the formation of the thick oleyl glycerate layer on the surface. This may

also be used to monitor changes of surface properties of other additives such as ionic liquids, ZDDP and MoDTC.

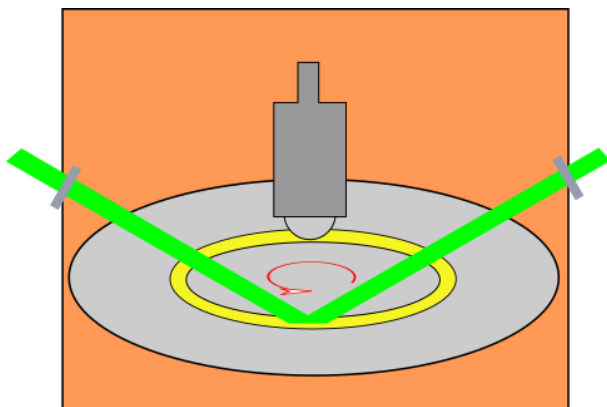


Figure 10-1: A diagram showing a potential set up for in-situ ellipsometry of the wear track

3. Further work is needed into the understanding of what happens after the first rotation for different OFM additives. A method of understanding this could be by seeing the impact the first rotation has on other known effects, such as the odd-even effect. The odd-even effect sees a difference in the surface properties of a monolayer depend on if there is an odd or even number of carbon atoms in the tail of the adsorbed molecule.²⁰⁴ One would expect that this effect would be observed for the first rotation, but it is unknown if this effect continues after the first rotation. If this frictional effect is not observed at the steady state then it implies that the tribofilm is not a well organised monolayer, and that the friction reduction of OFMs is more than just the formation of a SAM within the contact.
4. OFM additives are rarely used in binary solutions as tested here and instead are normally used in combination with other additives within a lubricant. Further understanding of the interactions of OFMs with other lubricant additives are therefore required. Competitive adsorption of different additives may impact tribofilm formation and friction reduction, producing different synergies and antagonisms.

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Appendix

Table 0-1: The refractive index of hexadecane at different temperatures.

Cauchy values	25 °C	50 °C	75 °C
A	1.413	1.406	1.404
B	3.026	2.268	1.186
C	0	0	0

Table 0-2: The refractive index fitting for Fe_2O_3 .

Lorentz	Frequency	2.837
	Strength	4.855
	Dampening	0.668
Tauc Lorentz	A	111.153
	E_0	3.004
	E_g – Band Gap	2.023
	C	1.896
Tauc Lorentz	A	36.966
	E_0	2.297
	E_g – Band Gap	1.974
	C	0.316
Eps fix	ϵ_1	2.889
	ϵ_2	0.171

Table 0-3: The refractive index fitting for the Steel disks.

Lorentz	Frequency	2.639
	Strength	26.804
	Dampening	1.765
Lorentz	Frequency	1.696

	Strength	318.687
	Dampening	7.139
Lorentz	Frequency	0.652
	Strength	19.222
	Dampening	0
Eps fix	ϵ_1	1
	ϵ_2	0

Table 0-4: The refractive index fitting for the steel oxide layer.

Lorentz	Frequency	3.449
	Strength	15.635
	Dampening	1.930
Lorentz	Frequency	1.253
	Strength	0.029
	Dampening	0.075
Lorentz	Frequency	9.040
	Strength	39.515
	Dampening	0.012
Eps fix	ϵ_1	1
	ϵ_2	0

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