NTNU
Norwegian University of
Science and Technology

Formulation of Enhanced Water-Glycol Lubricants for Offshore Components

The Influence of Thickeners in Environmentally Acceptable Lubricants on the Wear of a Steel Piston Cylinder

Jostein Iversen

Subsea Technology
Submission date: June 2016
Supervisor: Nuria Espallargas, IPM
Co-supervisor: Angelika Brink, Sintef
Szymon Bernat, IPM

Norwegian University of Science and Technology
Department of Engineering Design and Materials

Jostein Iversen

Formulation of Enhanced Water-Glycol Lubricants for Offshore Components

The Influence of Thickeners in Environmentally Acceptable Lubricants on the Wear of a Steel Piston Cylinder

Master's thesis in Subsea Technology, Operations & Maintenance

Trondheim, June 2016

Supervisor: Nuria Espallargas

Norwegian University of Science and Technology
Faculty of Natural Sciences Technology
Department of Materials Science and Engineering

NTNU – Trondheim
Norwegian University of
Science and Technology

Abstract

The service life of offshore stainless steel cylinders used for riser tensioner systems is lower than expected. This is due to the complex degradation mechanisms, like corrosion, wear and fatigue that take place under the harsh environmental conditions encountered in the North Sea. After extensive research focused on increasing the service life of the riser tensioner system, a viable solution using uncoated, super-duplex stainless steel has showed promising results. The disadvantage of using this system is that the low hardness, super-duplex stainless steel piston, is found to wear of at the mid-stroke area. This indicates that there are some tribological conditions that are promoting wear. Several lubricants and seals have been tested to improve the wear resistance of the system, however this thesis is focused on improving the water-glycol, fire-resistant lubricants used for offshore hydraulic cylinders.

By testing different commercially available polymer thickeners under both hydrodynamic and boundary lubrication conditions, the lubricating behaviour of the fluids that are used in piston cylinder applications have been evaluated. The studies show clear indications that high-molecular weight, non-Newtonian polymers are performing poor in hydraulic applications. A low molecular weight thickener with Newtonian behaviour is preferable.

The most promising thickener for improving the water-glycol lubricant was found to be Thickener C. This is a low molecular weight polymer that provided near-Newtonian shear stability, low degree of temperature-viscosity dependency, low COF at hydrodynamic lubrication and lower wear in boundary lubrication than the reference lubricant in use today. The formulated lubricants thickened with Thickener C, may improve the service life of the direct riser tensioner system by reducing the wear at boundary lubrication and COF at hydrodynamic lubrication.

Sammendrag

Levetiden til rustfritt stål som brukes for offshore sylindre i stigerør spenningssystem er kortere enn forventet. Dette er fordi komplekse nedbrytningsmekanismer som korrosjon, slitasje og utmatting finner sted under de tøffe betingelsene som møtes i Nordsjøen. Etter omfattende forskning hvor fokuset har vært på å forlenge levetiden til spenningssystemet, har super duplex stål uten coating/belegg gitt gode resultater. Et problem har vært at det er funnet slitasjemerker på midten av vandrestaget, noe som indikerer at slitasjemekanismer er til stede. Flere smøroljer og forskjellige forseglingsmaterialer har vært testet for å undersøke slitasjemotstanden til systemet. Denne oppgaven har undersøkt hvordan de brannresistente, vann-glykol smøreoljene kan forbedres.

Ved å teste ulike typer tykningsmidler ved både hydrodynamisk og grensesjikt smøring, og gjennom reologistudier, har smøreevnen til egen-komponerte oljer blitt utforsket. Studiene viser klare tegn på at polymer baserte tykningsmidler, med høy molekyl vekt, er uegnet for hydrauliske applikasjoner. Polymerer med lav molekyl vekt og ikke-skjærtynnende oppførsel er ønskelig.

En av tykningsmidlene som er studert, tykningsmiddel C, påviste gode resultater hvor den viste svak tegn til skjærtynnende oppførsel, lav påvirkning av tidsavhengig tykning, høy skjærstabilitet, lav friksjonskoeffisient under hydrodynamisk smøring og lavest slitasje ved grensesjikt smøring.

NTNU - NORWEGIAN UNIVERSITY
OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF ENGINEERING DESIGN
AND MATERIALS

MASTER THESIS SPRING 2016
FOR
Jostein Iversen

Formulation of enhanced water-glycol lubricants for offshore components

During the last years, several attempts to overcome wearing of the offshore components have been made. One of the main approaches was to try different materials selections, while the other focused on lubricants and its ability to reduce direct contact between mating surfaces.

The main objective of this project thesis will be to test at lab scale the effect of isolated parameters in the degradation mechanisms occurring in selected offshore components. The work will specially focus on how the lubricant behaves at different working conditions and based on the results proposing new ideas for improving it.

The work will include:

- Relevant literature review to the topic.
- Lubricant formulation.
- Tribological testing.
- Advance surface characterization (3D optical microscopy, SEM, chemical analysis, etc.).
- Correlate the testing parameters and the observed features.

The work will be connected to an industrial project with relevant Offshore industries.

Formal requirements:
Three weeks after start of the thesis work, an A3 sheet illustrating the work is to be handed in. A template for this presentation is available on the IPM's web site under the menu "Masteroppgave" (https://www.ntnu.edu/web/ipm/master-thesis). This sheet should be updated one week before the master's thesis is submitted.

Risk assessment of experimental activities shall always be performed. Experimental work defined in the problem description shall be planed and risk assessed up-front and within 3 weeks after receiving the problem text. Any specific experimental activities which are not properly covered by the general risk assessment shall be particularly assessed before performing the experimental work. Risk assessments should be signed by the supervisor and copies shall be included in the appendix of the thesis.

The thesis should include the signed problem text, and be written as a research report with summary both in English and Norwegian, conclusion, literature references, table of contents, etc. During preparation of the text, the candidate should make efforts to create a well arranged and well written report. To ease the evaluation of the thesis, it is important to cross-reference text, tables and figures. For evaluation of the work a thorough discussion of results is appreciated.

The thesis shall be submitted electronically via DAIM, NTNU's system for Digital Archiving and Submission of Master's theses.

The contact person is Nuria Espallargas

Nuria Espallargas

Torgeir Welo
Head of Division

Nuria Espallargas
Professor/Supervisor

NTNU
Norges teknisk-naturvitenskapelige universitet
Institutt for produktutvikling
og materialer

Preface

This thesis finalizes my Master's degree at Department of Engineering Design and Materials at the Norwegian University of Science and Technology (NTNU). The project has been carried out in collaboration with NTNU and SINTEF.

I would like to thank the following people for their help with my project thesis;
PhD candidate Szymon Bernat for helping me approach my objectives and the important discussions regarding my results, Angelika Brink for giving me feedback and directions and my supervisor professor Nuria Espallargas for providing the project.

Trondheim, 2016

Jostein Iversen

Table of contents

List of figures

List of tables

1 Introduction

In offshore drilling, a riser system is used to ensure safe and reliable drilling operation. The riser is a steel segment that encapsulates, protects and shields the drill string and fluid during drilling. Offshore drilling is performed from rigs and vessels anchored to the seabed, leaving the rig exposed to the forces from the sea and wind. These forces acting on the rig and the riser need to be controlled and the systems designed to control the riser are called riser tensioner systems.

The direct riser tensioner system (DRTS), used by NOV, consist of six rods of 18-meter length that give the rig the possibility for ultra-deep water offshore drilling. This means that DRTS allows drilling at a water depth of 3000 meters. The system in use is a N-line riser tensioner system that supplies a constant tensioning of the riser. A failure of the DRTS may lead to down time, the riser could break and in worst case; blow-out of the well. The revenues losses during down time can easily reach USD 550,000- per day. [1]

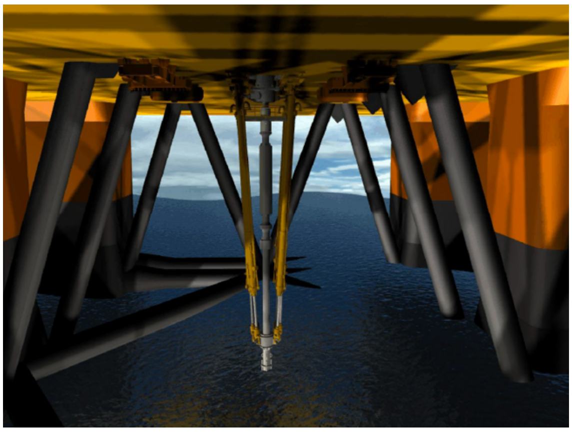


Figure 1 - N-line riser tensioner system (adapted from [1])

The DRTS has experienced several cases with failures due to complex degradation mechanisms. During the last years, several attempts to reduce wear of the riser components have been made [2-6]. One of the approaches was to try different material and coating systems, while other focused on the lubricants and its ability to reduce the contact between the mating surfaces.

1.1 Background

In 2011, C. von der Ohe assessed the complex degradation mechanisms occurring in the riser tensioner system, where he introduced the importance of this topic for the industry and research. [2] C. von der Ohe et. al. [1] has reviewed the piston failures of the riser tensioner system where different types of materials and coating solutions was examined. The review found that using super duplex stainless steel (SDSS) without any coating or surface treatment has been a viable solution, but not optimal due to abrasive wear marks observed in the mid-stroke area [3].

M. Tyrhaug [4] further assessed the complex degradation mechanisms, where he tested different seal materials, lubricants and surface roughness's for NOV. The results summarized pin wear, coefficient of friction and change of viscosity. He came to the conclusion that an increase in lubricant viscosity is the result of metal ions and polymer wear-loss.

On the other hand, P. Skjerstad [5], concluded that an increase of viscosity in hydraulic fluids is due to evaporation of the water in the water-dominant lubricant. It should be mentioned that different materials have been tested when performing the experiment, but the lubricants used are all water-glycol based hydraulic fluids. These results explain the need for further research on the topic.

J. Iversen [6] studied the effect of seal-geometry on the COF, compared different offshore materials and looked on the differences between the lubricant and water in terms of lubrication of the hydraulic cylinder system. The results showed that the test set-up used for cylindrical geometry gave unpredictable results and was time consuming compared to the regular pin on plate set-up. The materials being evaluated showed a similarity in terms of COF and wear when using the reference lubricant. Together with the promising service life of SDSS [1], this lead to the further research of SDSS as the substrate/rod material for the hydraulic cylinder. Further research of the lubrication of the cylinder is necessary to understand the tribological system.

1.2 Problem description

The purpose of this thesis is to investigate the wear mechanisms occurring in the DRTS and to improve the lubricant used in the N-line piston system delivered by NOV. By reducing the wear and friction of the lubricated contact, the service life of the system may be extended. The effect of different types of commercially available thickeners on the tribological performance of the fluid will be investigated. This will involve formulation of tailor made lubricants, testing and evaluation in terms of the wear and shear stability.

The thesis will include the following:

1. Rheology study of the aqueous thickeners commercially available in the market
2. Study the effect of different types of thickeners on wear and friction
    a. under hydrodynamic lubrication conditions
    b. under boundary lubrication conditions

1.3 Research method

The research done in this thesis will consist of the following steps:

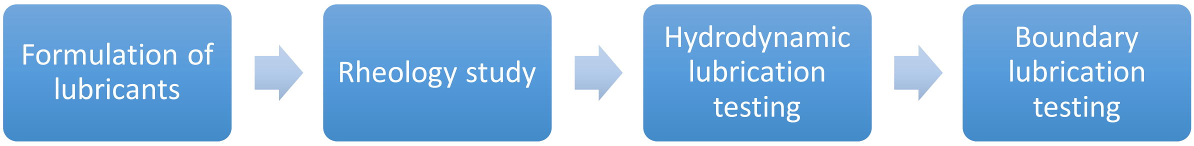


Figure 2 - Scientifically process

The lubricant formulated in this thesis was formulated to achieve similar properties as the hydraulic fluid used in the industry. Currently, NOV wants to use a water-glycol lubricant with a dynamic viscosity of 52 mPas. It will therefore be necessary to formulate lubricants with similar viscosity to compare with the lubricant in use. There would also be interesting to analyse and quantify the wear and friction coefficient while using the same lubricant with both lower and higher viscosity.

A total number of 12 lubricants will be formulated with different thickeners. This will give a good representation of how the lubricant behave under specific tribological conditions while thickened with different types of thickeners. The formulation process was conducted in a similar procedure for all the lubricants. The reason for this was to achieve a similar dispersion quality for all the lubricants. The viscosity provided by the thickener-additives are strongly influenced by the formulation procedure. By using the same lubricant formulation procedure, (room temperature, with the same mechanical stirrer and a similar shear rates) reliable formulations should be provided.

The viscosity of the lubricants was measured in a rheometer at 40˚C. The lubricants that were close to the reference lubricant viscosity of 52 mPas were used in tribometer testing. Together with a lower and higher viscosity formulation (30 and 80 mPas), the influence of thickener concentration and lubricant viscosity was studied. Information about the rheological properties of the lubricants was received through temperature- and shear-stability studies.

Due to the different lubricating contacts present in the riser cylinder, two different tribological experiments were carried out. The hydrodynamic lubrication observed in the polymer seal of the cylinder is simulated in the reciprocating tribometer (TE88) with high speed (100 mm/s) and low pressure (12 MPa) configuration. The boundary lubrication observed in the bearing of the cylinder is simulated by the pin-on-disc tribometer at low speed (7.85 mm/s) and high contact pressure (2461 MPa) configuration. These experiments will give information of the applicability of the lubricants in a hydraulic system.

1.4 Limitations

The thesis will be focused on lubricant formulation and the influence of different types of thickeners on frictional properties of the system. Corrosion aspects of the fluid will not be taken into account. Corrosion of the steel samples will theoretically be protected by the corrosion inhibitor additive used in the formulation. To analyse the influence of the lubricant on the corrosion of the steel surface, further research must be performed. Qualitative studies by use of visual interpretation and microscope may thus be used. If corrosion plays a significant role in the degradation mechanisms, it will most certainly be visible for the human eye. Fracture or fatigue mechanical analyses of the samples will not be performed, even though these forces are interacting in the service of the pistons. Biological degradation of the lubricants will also not be analysed.

1.5 Structure of the thesis

This thesis will consist of a study of the research regarding degradation mechanisms that have influenced the DRTS. The study will take into account earlier progress and research. Relevant theories and descriptions of the problems and system will be described in the theory chapter. The main part will consist of the experiments performed and a thoroughly discussion of the results.

2 Theory

2.1 Tribology

Tribology is the study of surfaces in relative motions and their interaction [7]. It is a multidisciplinary term used when studying the friction, wear and lubrication of a system.

Surface characteristics, material selection and material compatibility, lubricating properties, environmental conditions and physical properties are influencing the interactions between the surfaces in motion, and are therefore of tribological importance.

2.1.1 Friction

Friction is measured as the force acting in the opposite direction of the moving system. In a system that stands still or is moving at a constant acceleration the friction force is equal to the moving forces. This can be illustrated by Figure 3 and Amatons law:

$$F_{Friction} = \mu F_{Normal}$$, where μ is the COF and F is the force.

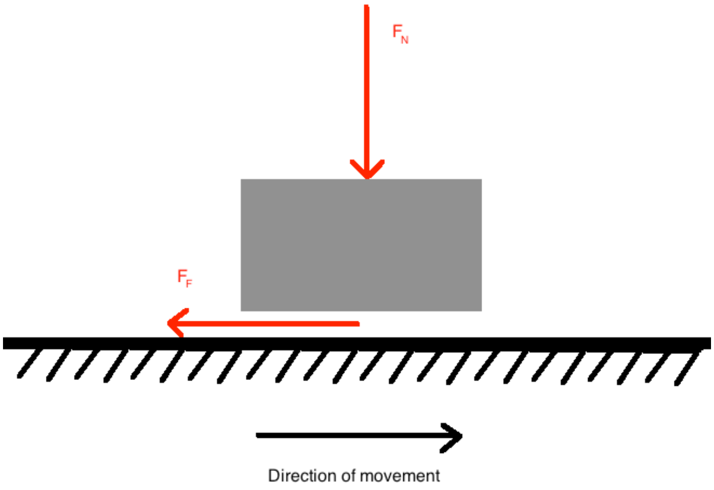


Figure 3 - Dry friction

It is important to mention that this law is only valid for dry friction, and not for a lubricated contact. This law may be used if independency of surface and velocity is assumed. This is not the case for polymers due to their visco-elasticity [8]. Frictional information indicates how the system is operating and if it is in a good or bad condition. In moving machinery like a piston cylinder, friction between surfaces will result in wearing of the components, heat and noise. In other words, friction is an important topic for the engineer to have an understanding of.

2.1.2 Contact mechanics

Types of contacts can be divided into plastic and elastic contact. Pure plastic contact is given by the relationship between load and area:

$P = \frac{F}{A}$, P is the pressure, F is the load and A is the contact area. [7]

Due to the elasticity of the materials, the contact pressure between two mating surfaces is in need of being determined in other means. In 1881, Hertz formulated the equation for pure elastic contact pressure, where he defined how different contact geometries inflicted the pressure-area relationship. By assuming frictionless contact, smooth surfaces and small deformations, the elastic deformation can be calculated. [7]

In the pin-on-disc experiment performed in this thesis, a ball on plate configuration is used. The ball on plate situation is characterized as circular/point contact, as seen in Figure 4:

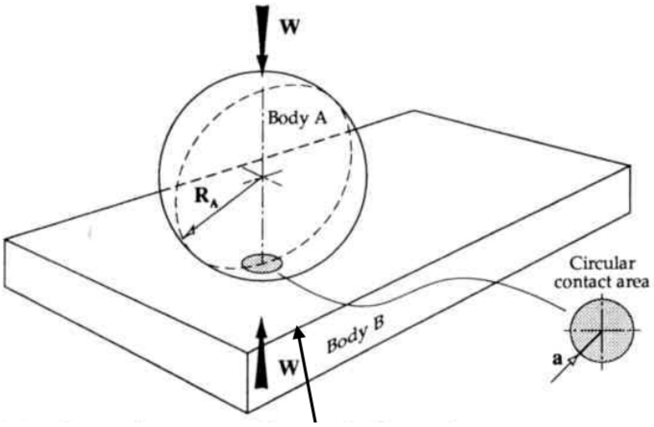


Figure 4 - Circular/point contact (adapted from [7])

The maximum contact pressure can be calculated by Hertz equations for circular/point contact:

$$P_{max} = \frac{3F_N}{\pi a^2}$$, F_N is the normal load and a is the radius of the contact area. [7]

The calculations are shown in the Appendix.

2.1.3 Surface topography

The surface profile is given by the waviness and the roughness of the surface. Different roughness values describe different characteristics of the surface. In the industry the R_a –value is the most used parameter to describe the surface roughness. It is named the centre-line average and represents the average roughness value over the recorded profile of the surface. The R_a-value is given by the formula:

$$R_a = \frac{1}{L}\int_0^L |z|dx$$, where L is the recorded length and z is the height of the profile.

One of the disadvantages of this roughness parameter is that surfaces with different profiles, may have the same R_a–value due to the average value of peaks and valleys. [7] This means that the R_a-value does not fully describe the surface characteristics.

2.1.4 Lubricated contacts

In lubricated contacts, the Stribeck curve shows the relation between the COF and the Hersey number:

$$S = \frac{\eta * V}{F_N}$$, where η is the dynamic viscosity of the lubricant, V is the speed of the system and F_N is the normal force. [9]

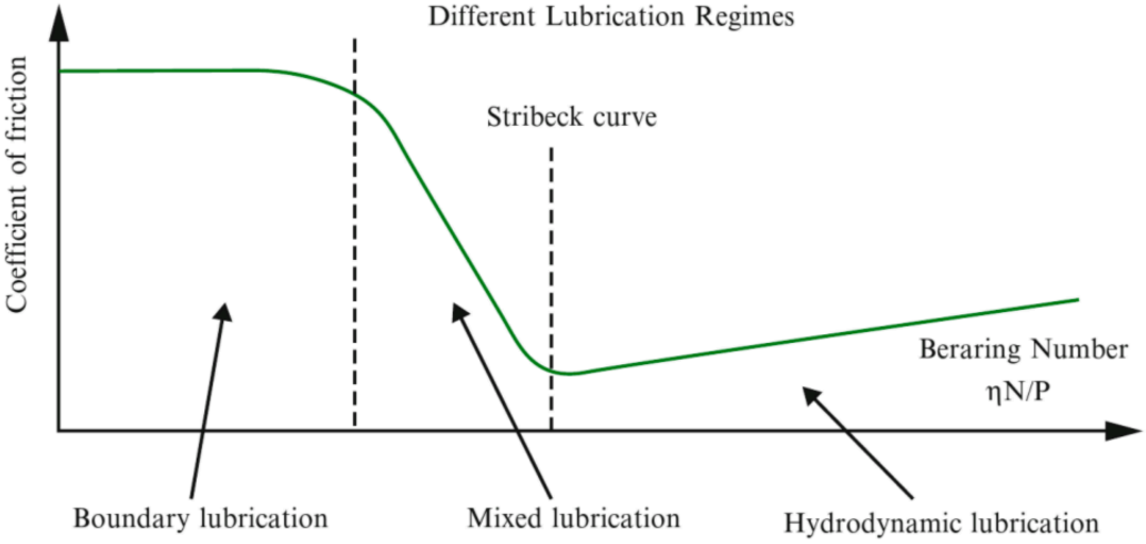


Figure 5 - Stribeck curve

The Stribeck curve is divided into different regimes which describe the different conditions of the lubricated contact. The different regimes are boundary-, mixed-film- and hydrodynamic lubrication. Boundary lubrication is characterized by a low lubricant film thickness, high COF and high wear. This means that the surface asperities from both working elements will come in contact and wear will deteriorate the materials. Mixed lubrication is the transition regime between boundary and hydrodynamic lubrication. This is typical for start-stop conditions i.e. pistons used in engines and hydraulic cylinders. In this regime the surface asperities will come in contact during the start- and stop-conditions. This is due to the low speed, which will reduce the film thickness of the lubricant. When the piston is accelerating it will develop a film-thickness required to separate the surfaces and move into the hydrodynamic lubrication regime. In the hydrodynamic lubrication regime, the tribosystem is characterized by full film thickness where two mating surfaces are fully separated with lubricant semi-solid film. Hydrodynamic lubrication is achieved by using a convergent geometry, high speed, high viscosity and low load. This results in a system where the lubricant is fully separating the surfaces and is characterized by low friction and wear [9].

2.2 Materials

This chapter introduces the materials in focus, their use in the hydraulic cylinder application and their properties.

2.2.1 Seal materials

A system containing hydraulic fluid needs a sealing mechanism that prohibits the fluids to escape the system. In a hydraulic cylinder piston system there are seal barriers to encapsulate the fluids, and to protect the fluid reservoir from debris and contamination from the outside environment [10].

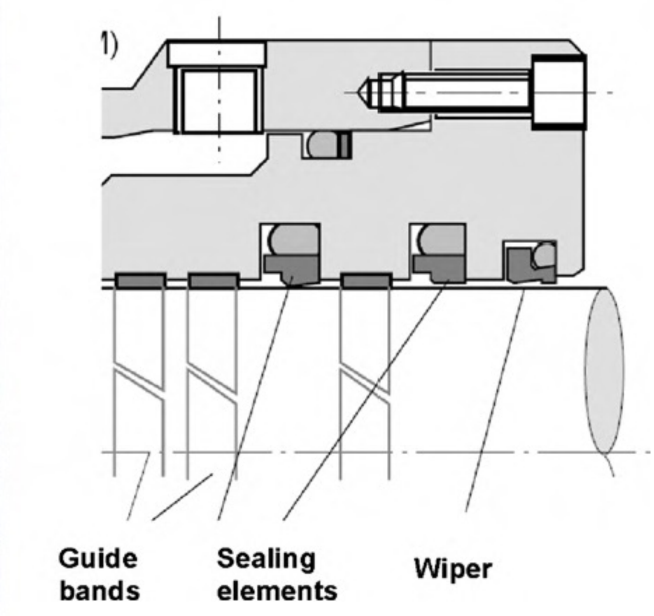


Figure 6 - Packing box showing the piston cylinder and seal (adapted from [1])

In reality, there is always a partial leakage of lubricant to the environment, and the sea-water will to some extent contaminate the hydraulic fluid. The main function of the seal is to reduce the leakage and contamination to a minimum [10]. The seal can be made of many different materials like metals, ceramics and polymers. This thesis will not take into account different seal geometries or surface structures that are available.

2.2.1.1 Polymer seals

Polymers used as seal materials are usually softer than the opposite material, i.e. steel. This exposes the polymer to wear and material loss in a tribological contact. The benefits of using a polymer as a bearing material is the polymers ability to react on pressure differences. It changes geometry due to its ductility and therefore seals well and uniformly [10].

2.2.1.2 Polyethylene

Polyethylene (PE) is a thermoplast that is widely used in many different products and industries. The ethylene is obtained from a refinery and is polymerized into polyethylene $(-CH_2-CH_2-)_n$. The length of the polymer chain is possible to tailor into preferable lengths and is also a measure of the molecular weight. A change in the molecular weight changes the different properties of the polymer. There are different types of commercially polyethylene available: low density, medium density, high density and ultra-high molecular weight (UHMWPE) [11].

2.2.1.3 Ultra-high molecular weight polyethylene

UHMWPE is a commercially product of PE that is characterized by high impact strength, high toughness, high wear resistance and low coefficient of friction. The main tribological feature of this polymer is its high wear resistance in lubricants with water content, good abrasion resistance and a relatively low temperature limit [8]. The seal material used for the experiments in this thesis is the UHMWPE polymer.

2.2.1.4 Transfer film of polymeric seal to the steel

A consequence of using polymers is the formation of a transfer film layer on the opposing surface. The transfer film is transported from the polymer towards the counter material inducing a changed material composition in the contact and leading to a decrease in COF. The transfer film development is highly effected by the load, speed, temperature, opposing material surface roughness and the hardness of the polymer [12]. A transfer film for UHMWPE vs SDSS was found in both Skjerstad [5] and Tyrhaug's [4] research, but the polymer transfer was found to be dependent on the lubricant in use and surface roughness. On the other hand, Iversen's [6] results from 2015 showed no sign of film transfer for the reference lubricant together with UHMWPE and SDSS.

2.2.2 Offshore steel

Steel used for offshore applications are often high alloy steel with special alloying elements. These elements ensure corrosion resistance and high strength properties of the alloy. Due to the harsh environment experienced offshore, these properties are necessary to maintain safe operation. The steel used in the TE88 tests is the SAF2507 SDSS delivered by Sandvik Materials Technology. SDSS is an austenitic-ferritic stainless steel that consists of 25% chromium and is used for extreme harsh weather conditions due to its high mechanical strength and excellent corrosion resistance [13].

2.2.3 Alumina

Pure alumina (99,5%) is used as the counter-material for the ball-on-disk tribometer study. Alumina (Al_2O_3) is a very hard material that is commonly used as an abrasive material. The properties are found in the datasheet and Table 3 [14].

2.2.4 Lubricants

Lubricants are used to reduce friction, wear and act as a coolant, disposing the heat in moving machinery. In the industry, lubricants are often divided into three different groups; mineral, synthetic and water-based lubricants. The lubricants used in this thesis will only be water-based lubricants. Water-based lubricants are used for applications when fire and environmental restrictions need to be followed. Due to the fire restrictions at the offshore platform, the DRTS requires a water-based hydraulic fluid.

After the second world-war, the Naval Research Laboratory investigated the use of water-glycol based hydraulic fluids. Due to several cases of fires related to petroleum based oils, the need of a fire-resistant lubricants was developed. In 1950, Brophy and Fitzsimmons [15] studied the aqueous non-flammable hydraulic fluids as a substitute for mineral oils. The study found that high-boiling alcohols, like glycols, could be used together with water and polymers to achieve an inflammable, lubricating fluid for hydraulic applications. To receive a satisfying fire-resistance, a water-volume of 40% was needed for the base. Another benefit with using glycols is their well-known properties as a liquid coolant.

The fluid delivered by NOV is a water-glycol lubricant consisting of an additive package and up to 50% water. It contains corrosion inhibitors and thickeners that give the kinematic viscosity of 52 mPas at 40˚C. The name of the lubricant is not revealed due to confidentiality. The most used glycol is di-ethylene glycol. Due to the water content, corrosion inhibitors and viscosity-index improvers are needed. The disadvantages of using a water-glycol lubricant is poor film thickness and low viscosity index [16].

According to the standard DIN 51502, which assess fire-resistant hydraulic media, a water-based polymer solution containing maximum 60% glycol is termed as a Hydraulic Fluid C (HFC) [17].

The composition of HFC, according to ISO VG 46 is:

- 25% mono- and oligoglycols
- 15% polyglycol
- 10% additives
- 50% water

Its requirements are as follows:

- Suitable viscosity
- Shear stable
- Relatively low- viscosity-temperature dependence
- Good lubricating action
- Good resistance to wear

2.2.5 Rheology modifiers

To achieve the viscosities required for different flow systems, different additives are added to the lubricants. These additives are called rheology modifiers or thickeners. The thickeners modify the rheological properties in the lubricants where they alter properties like viscosity, sagging, settling etc. The two main classes of thickeners are organic and inorganic, as shown in Figure 7.

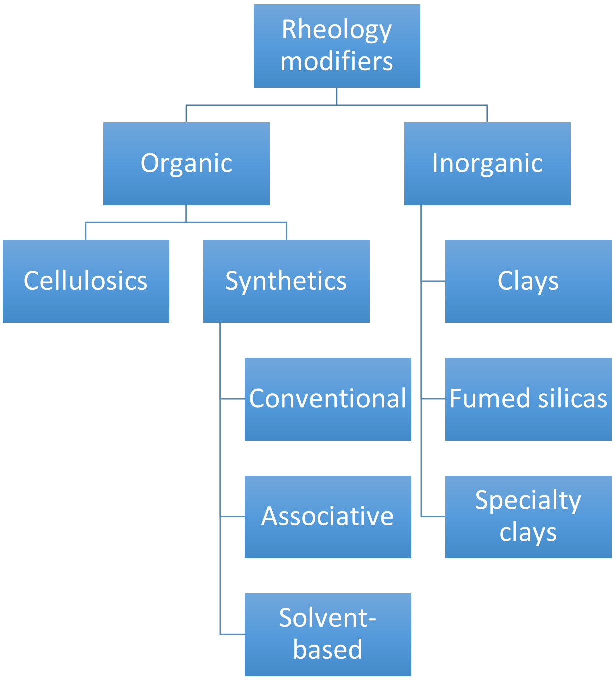


Figure 7 – Different types of rheology modifiers (adapted from [18])

2.2.6 Corrosion inhibitors

The presence of water in the water-glycol lubricants introduces the problems related to corrosion of the steel components. By the use of corrosion inhibitors, the water is hindered contact with the steel by a protective film formed on the surface.

2.3 Rheology

Rheology is the study of flow of matter. The behaviour and properties of a lubricant are important to understand and can be determined through viscometer studies.

In Figure 8, a simple shear model is depicted. The model of Newtonian shear shows two separated surfaces moving relative to each other with a fluid trapped in-between. In this model the distance between the two surfaces is so small that the viscosity is assumed to be constant over the whole distance.

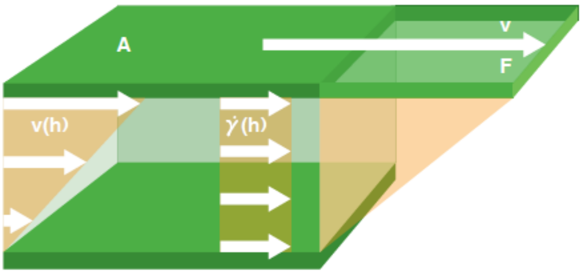


Figure 8 - Simple Newtonian shear model (adapted from [17])

The relationship between the shear force τ and the shear rate $\gamma^{\cdot}$ gives us the dynamic viscosity, as shown in the formula below:

$$\eta = \frac{\tau}{\gamma^{\cdot}} \; [Pas]$$

Kinematic viscosity is the relationship between the fluids dynamic viscosity and density.

$$\nu = \frac{\eta}{\rho} \left[\frac{mm^2}{s}\right]$$

Different rheological properties of lubricants are required in different tribological systems. The most important characteristics of fluids are mentioned below and illustrated in Figure 9.

Newtonian fluids are characterized by constant viscosity at different shear rates. This means that the viscosity of the lubricant is not influenced by the operating rate of the machinery. This is typical behaviour of mineral and synthetic oils under normal operating conditions.

Non-Newtonian fluids are characterized by a shear rate dependency of the viscosity. Some of the different types of non-Newtonian fluids are pseudoplastic, dilatant and Bingham plastics.

Pseudoplastic fluids exhibit shear thinning behaviour at increasing shear rates. This is a typical characteristic for polymer-based thickeners, which are common in water-based lubricants. Due to this, these lubricants show great storage stability, where settling is reduced due to the high viscosity experienced at low shear rates. Polymers are often used as viscosity-index (VI) improvers, where the random polymer coils are stretching when the temperature increases. VI – improvers are used when a lubricant with a lower temperature-viscosity dependence is desired.

Dilatant fluids exhibit shear thickening behaviour. This means that the viscosity will increase at increasing shear rates.

Thixotropy is an important property for polymer-thickened lubricants. Thixotropy is related to the degree of gradually loss of viscosity during shear conditions, and show a time dependent viscosity build up when relieved. The degree of thixotropy is generally represented by the hysteresis area observed during a viscosity measurement, as seen in Figure 9 [18].

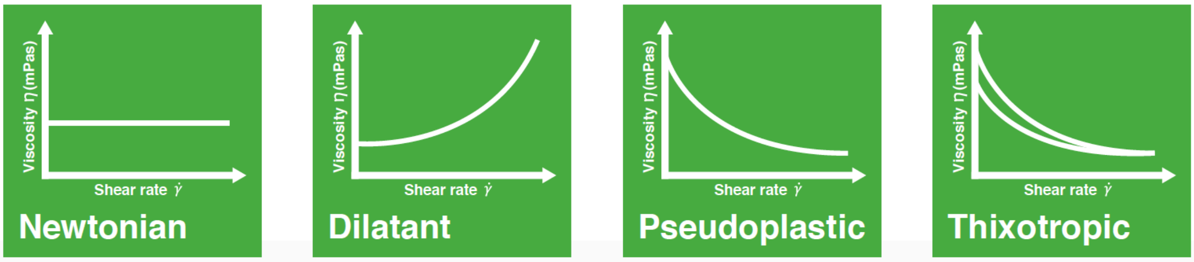


Figure 9 - Rheology profiles (adapted from [18])

2.3.1 Viscosity

Viscosity describes a fluid's ability to shear when opposed with a force. The higher the viscosity, the higher the resistance of the fluid to flow. Viscosity increases as the pressure increases, and decreases as the temperature increases. This makes many lubricants unusable under certain conditions, and additives like VI - improvers are added to maintain the viscosity throughout its useful temperature range. Under shear conditions, the viscosity influences the film thickness of the lubricant and is an important parameter to control in moving machinery i.e. a hydraulic piston cylinder [7]. A higher viscosity will in most cases provide a higher film thickness, and as mentioned in chapter 2.1.4, this will reduce the COF.

2.3.2 Thickening mechanisms of polymers

The rheology modifiers studied in this thesis is the organic polymer thickeners. Both cellulosic and synthetics. Water-soluble thickeners are often called conventional or volume-exclusion thickeners. These thickeners absorbs and retain the water molecules, causing a swelling reaction [19]. In this case the thickener is occupying a large volume in the lubricant matrix, thus increasing the viscosity. Another kind of volume exclusion thickener is the alkali swellable emulsions (ASE). This is typical for some modified cellulosic thickeners and methacrylates. The ASE thickeners are characterized by high molecular weight and pseudoplastic behaviour of formulated lubricants. The thickening mechanism is triggered by an increase in pH [19].

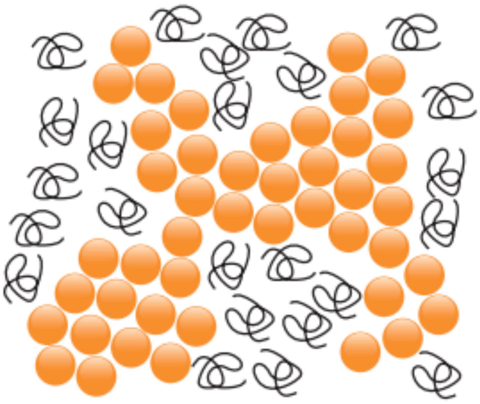


Figure 10 - Volume exclusion thickener (adapted from [19])

Associative thickening mechanism is another important thickening mechanism for the synthetic polymers. In this situation, hydrophobic, low molecular weight polymers are creating a physical network instead of absorbing the water molecules. The lubricant viscosity is dependent on the properties of the physical network.

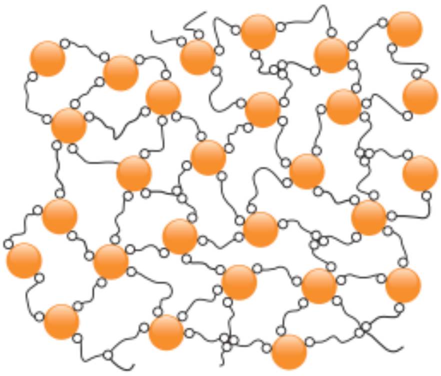


Figure 11 - Associative thickener (adapted from [19])

2.3.3 Polymer shear stability

Polymer-based thickeners are suffering from excessive mechanical shear forces. Studies show that high molecular weight polymers are prone to both temporary and permanent viscosity loss due to mechanical shearing [16] [20-23]. This lead to the importance of assessing the lubricants shear stability. When polymer-thickened fluids are opposed to severe shear, the random coil of the polymer is severely distorted and may break. This is especially important for the high molecular weight polymers that are commonly used as VI - improvers. In Brophy and Fitzsimmons [15], they mention that this occur for polymers with molecular weight above 15,000. All polymer thickeners used in this thesis is above this molecular weight, thus it is safe to assume that shear breakdown will occur. Polymer degradation in terms of mechanical breakdown is studied in [23], where they found that the resistance of polymer degradation is related to the geometry and flexibility of the structure, and to the inherent strength of the polymer backbone.

The shear breakdown results in permanent viscosity loss, and must be separated from the temporary viscosity loss experienced due to the pseudoplastic behaviour of the polymers. Minimizing the level of non-Newtonian behaviour is beneficial for the hydraulic application in terms of adequate system lubrication. A Newtonian fluid behaviour will ensure good start- and stop conditions, where lower forces are required to shear the hydraulic fluid, and sufficient film thickness at all shear rates.

The temporary viscosity drop observed for the polymer thickened fluids is due to the polymer's spherical coils are aligning to the flow, reducing its hydrodynamic volume, which then again reduces the viscosity of the fluid. This can be seen in Figure 12. This reduction in viscosity is, with increasing shear, reaching a limit of maximum distortion of the coil. When the speed of the system is reduced, the coils branches out and the viscosity is recovered. This non-Newtonian behaviour is observed for all polymers at some degree.

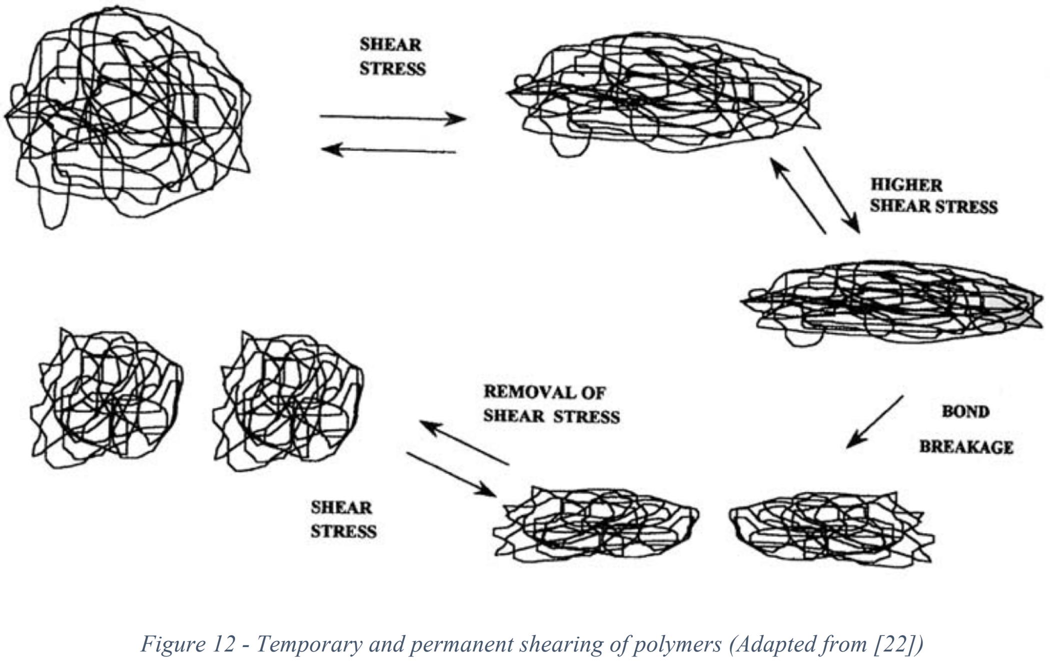


Figure 12 - Temporary and permanent shearing of polymers (Adapted from [22])

The permanent viscosity drop is related to the severing and distortion of the polymer bonds. When the shear rate is high, the mechanical forces shearing the lubricant may reduce the viscosity of the hydraulic fluid permanently. Mechano-degradation, is the term used for this molecular degradation and may be detected through fuel injection shear stability testing as described in the ASTM D 3945 standard [24].

For the water-glycol hydraulic fluid to perform well in the hydraulic application, it is important that the fluid ensures good pumpability at low temperatures and sufficient film strength at higher temperatures. This means that the viscosity-temperature relationship of the hydraulic fluid is in need of being controlled. A sufficient viscosity at low temperatures will ensure that the piston will move without any substantial increase in power, thus ensure low wear a situation where low wear is expected. When the temperature increases it is important that the viscosity is maintained so that the materials in contact is supplied with a sufficient film thickness. These properties are difficult to obtain due to the temperature-dependent viscosity of the fluid.

2.4 Wear mechanisms

The wear mechanisms that are present in hydraulic cylinders used under offshore conditions are dependent on the materials in contact. Both contacts of interest are with the SDSS as the rod material. For the N-line cylinder there are two tribological contacts in focus:

1. The bearing application
2. The sealing application

The counter-material chosen in the pin-on-disc test is pure alumina (Al_2O_3) [14]. This situation is simulating a bearing application where the alumina is facing the SDSS. For the sealing application, the SDSS cylindrical rod is in contact with a UHMWPE, polymer seal. Both of the situations are assumed to be lubricated at all times. Wear between hard materials like steel and alumina is often described by adhesive wear, abrasive wear, fatigue wear, or a combination of these. Corrosion is especially important to have in mind due to synergistic wear mechanisms that are occurring in parallel to the tribological wear [2].

After two years of operation, it was found [1] that the SDSS pistons were suffering from mechanical wear. The piston surface showed signs of longitudinal wear-marks indicating that a wear mechanism is reducing the integrity of the cylinder. The two most common mechanical wear types are abrasive and adhesive wear.

Abrasive wear is occurring when the harder material is plastically deforming and gradually reducing the material of lower hardness in the contact [7]. Abrasive wear is divided into two body- and three body abrasion wear. Two body wear mechanism is characterized by the deformation of softer material by harder material through ploughing or scraping action of the surfaces. Three body wear mechanism is a different type of abrasive wear, where the wear debris particles are cut-loose and are rolling in-between two surfaces. The particles may also be introduced from the environment, where the particles are contaminating the hydraulic system, and may get imbedded in the materials. A typical example of this is sand particles that are trapped in between the seal and rod.

Adhesive wear is characterized by local-welding of the softer to the harder material in a surface to surface contact [7]. This is typical for unlubricated, hard surfaces where the contact forces between two materials exceeds the shear forces, leading to a shearing of the subsurface of the softer material.

The wear may be quantified by volume loss of the material and by use of Archard's formula:

$V = \frac{KF_NS}{H}$, where V is volume, K is the wear constant, F_N is the normal load, S is the sliding speed and H is the hardness of the soft material [7].

Wear of polymer materials cannot be described by the wear mechanisms mentioned earlier. In tribological contacts, polymers behave differently as compared to metals and other factors influence friction, lubrication and microstructural features. Those factors are in need of being elaborated to fully understand this type of wear.

The contact between SDSS and UHMWPE is dependent on many different factors. The counter surface in this case will be the SDSS, and thus the hardness, roughness and surface energy is important. The hardness of the SDSS is several times larger than the polymer, meaning that the abrasive wear-resistance of the steel should be higher than that of the polymer. Studies show that the surface topography is highly influencing the rate of wear, where rough and very smooth surfaces are both prone to intense wear processes [8].

It is also known that the degree of chemical activity of the counter surface influences the thickness of the transfer film. An active surface is able to maintain a thicker transfer film than a less active surface. This means that noble materials are less qualified as being used in combination with polymer seals due to lack of the beneficial wear effects of transfer film layers [8]. Another disadvantage of polymers is that they may melt at elevated temperatures. This mechanism is termed melted wear, and is usually not observed for lubricated contacts [8]. Polymers used in excessive service are also prone to fatigue wear. It has been proven that UHMWPE is experiencing an increase in wear after a long sliding distance. This is because the bonds between the crystalline parts are being gradually weakened by the vibrational and cyclical stresses, ultimately leading to breaking of polymer wear-debris [8].

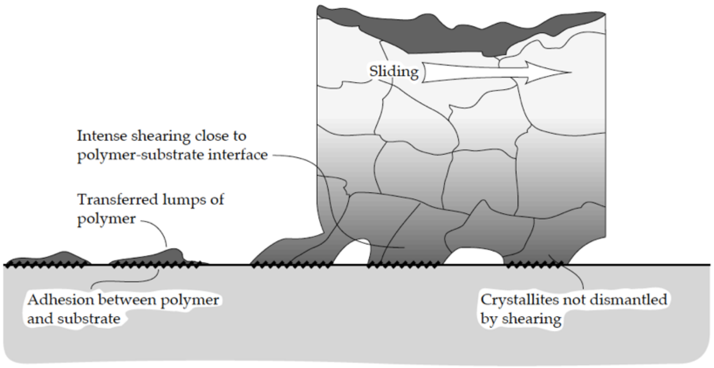


Figure 13 –Film transfer of most polymers (adapted from [8])

The wear mechanisms between the polymer and steel are also greatly influenced by the lubricating fluid and its additives. The introduction of water into the tribosystem causes an increase in wear of the polymer. It is also noted that corrosive agents influence the wear of polymers, but the research regarding this is not fully understood [8] [25].

3 Experimental

3.1 Sample preparation

It was discovered [4-6] that surface roughness of mating materials had a major influence on the coefficient of friction between the SDSS plate sample and the UHWMPE polymer pin. This is also in conjunction to research [8]. Preparing of the SDSS plates used in the tribological experiments was done by diamond polishing with a grinding and polishing machine. By diamond polishing, a surface of high homogeneity is achieved, thus reducing the influence of human error observed when grinding to $R_a = 0{,}3\ \mu m$.

The grinding and polishing procedure required to ensure diamond polished surface is presented in Table 1.

Table 1 - Grinding and polishing procedure

STEP	SIC – PAPER VALUE
1	80
2	220
3	500
4	1000
5	2000
6	3 micron spray
7	1 micron spray

3.2 Rheological study

The rheological properties of the lubricants were studied by using a rheometer. The rheometer used was a HAAKE MARS rotational rheometer. The dynamic viscosity of the formulated lubricants was measured at a shear rate of 500 s^{-1}, with built-in Peltier element at 40˚C in humid air. A lubricant volume of 2 ml was added to the cup and bob cylinder, where the force required to shear the fluid is measured. This force is related to the viscosity of the fluid. Two types of studies were performed; a viscosity measurement and a full rheological study, where several temperatures were tested under variable shear. These studies consisted of a several steps, which can be found in the Appendix.

3.2.1 Time dependency

Due to the thixotropic properties experienced in polymer based rheology modifiers, the viscosity of the formulated lubricants varied over time. This led to the necessity of looking into the time dependency on thickening. By performing several rheology measurements over time, the influence of thickener concentration on time dependency was studied.

3.3 Lubricant formulation

According to the supplier of the reference lubricant, the ingredients used to formulate the lubricant are water, glycols, thickeners and additives. The content of the base lubricant used in this thesis is confidential.

A number of eleven commercially available thickeners was first tested and tried in terms of lubricant thickening. The chosen thickeners were different types of polymers and cellulosic type that are widely used in the industry for aqueous formulations. The selection criteria were based on availability, solubility with the base and the degree of thickening. The thickeners that showed promising results were then further studied. Only four of the thickeners showed promising properties and were chosen to be used in this thesis. The four types that were chosen are termed as Thickener A, B, C and D, and due to confidentiality, the chemical names of the thickeners are not revealed.

3.3.1 Thickener A

Thickener A is a modified cellulose that can easily dissolve in water and form a stable thin film on the surface of a metal. This is because the thickener has an abundance of functional groups, which allows it to easily be absorbed on the metal surface [26]. It is chemically derived from natural cellulose and is an abundant, cheap resource. Due to its non-toxicity, biodegradability and biocompatibility, it is widely used as a thickener in aqueous formulations. Thickener A is characterized by long polymeric chains that provide an anti-wear flexibility, nano-structure that can penetrate into rubbing surfaces and rigid hexatomic rings that supports and isolates two surfaces in relative motion [26].

3.3.2 Thickener B

Thickener B is a high molecular weight polymer (M_W = 1250000) with the ability to absorb water and retain the molecules, allowing a swelling effect of the lubricant. This polymer is known to be rather chemically stable and do not undergo any chemical reactions under moderate to slight severe conditions. The backbone of the polymer is configured in a random coil shape. The size of the coil is more or less proportional to the polymer molecular weight and the degree of thickening depends on the coil size. Thickener B is an ASE-polymer and the thickening mechanism is known as volume-exclusion thickening. Thickener B also exhibit a uniformly increase in intrinsic viscosity with increasing temperature [22].

3.3.3 Thickener C

Thickener C is a low molecular weight polymer, M_W = 360 000, that is widely used as a rheology modifier [27-29]. The polymer is hydrophilic, non-toxic and bio-degradable.

3.3.4 Thickener D

Thickener D is the same polymer as Thickener C, but has a higher molecular weight. M_W = 1300000. The higher molecular weight ensures a broader distribution of the polymer which is a property given by the intense branching occurring in solutions [27].

In solutions, Thickener C and D is probably dispersed as random coils [27]. They are also able to solve in water as well as other organic solvents, which is an unusual property. This is probably achieved by having both hydrophobic and hydrophilic functional groups [27]. Thickener C and D have shown good adhesion to steel surfaces and is therefore attractive rheology modifiers for aqueous-lubricants [28].

3.3.5 Formulation procedure

The lubricants formulated was mixed and blended by a mechanical stirrer at a shear rate of 500 s^{-1} over 10 minutes until a homogenous, transparent fluid was visually confirmed. If there were signs of particles or the thickener had formed clusters, the stirring time was increased until the lubricant homogeneity was achieved. During the formulation procedure, several factors influencing the fluid homogeneity were noticed. A list of the most important ways to control the thickening of the lubricant and assure homogeneity is given below:

- The speed of the mechanical stirrer
- Total time of stirring
- Pouring of the thickener during mixing
- Stabilization time of the lubricant
- Handling of the lubricant prior to the rheology experiment
- Degree of thickening homogeneity

Due to the mechanical breakdown of the high molecular weight polymers, the speed of the mechanical stirrer was decided to be similar for all formulations. By using the same speed, the shear breakdown will be similar for all repetitions. After 10 minutes of stirring, the formulations showed no sign of heterogeneity and the fluids were transparent. Pouring of the thickener will be influenced by the air surrounding the stirrer, creating an airflow that will force the thickener out in the edges. Some of the thickener-powder will inevitably be lost, and this depends on the speed of the stirrer.

It was later discovered that the thickening of the formulations was highly dependent on time. The viscosity measured one day had either increased or decreased at a later point of time. This meant that the viscosity of the formulations where in need of stabilizing over time as seen in Figure 21.

Due to the thixotropic properties of polymer based lubricants, the handling of the lubricants effected the viscosity measured in the rheometer. This meant that the viscosity measured of the same formulation, differed between the carefully handled sample and the well-shook sample. This was confirmed by viscosity measurements. To reduce this error, a choice was made of performing a light shaking of all the samples prior to the rheology measurements.

A degree of thickening inhomogeneity was found in the lubricants. This can be described as an inhomogeneity in the bulk of the lubricant, where different domains in the fluid was characterized by various viscosities. A fluid consisting of domains with different mechanical/rheological properties will provide difficulties in measuring a correct viscosity of the entire lubricant and needs to be re-mixed.

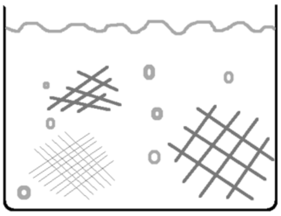


Figure 14 - Beaker with lubricant showing different parts with different thicknesses

3.3.6 Formulation of lubricants

The procedure used to determine the thickener concentrations for the 12 lubricant formulations is presented below in Figure 15, 16 and 17. The figures presents the viscosity increase with thickener concentration and show how the formulated viscosities; 30, 52 and 80 mPas were chosen.

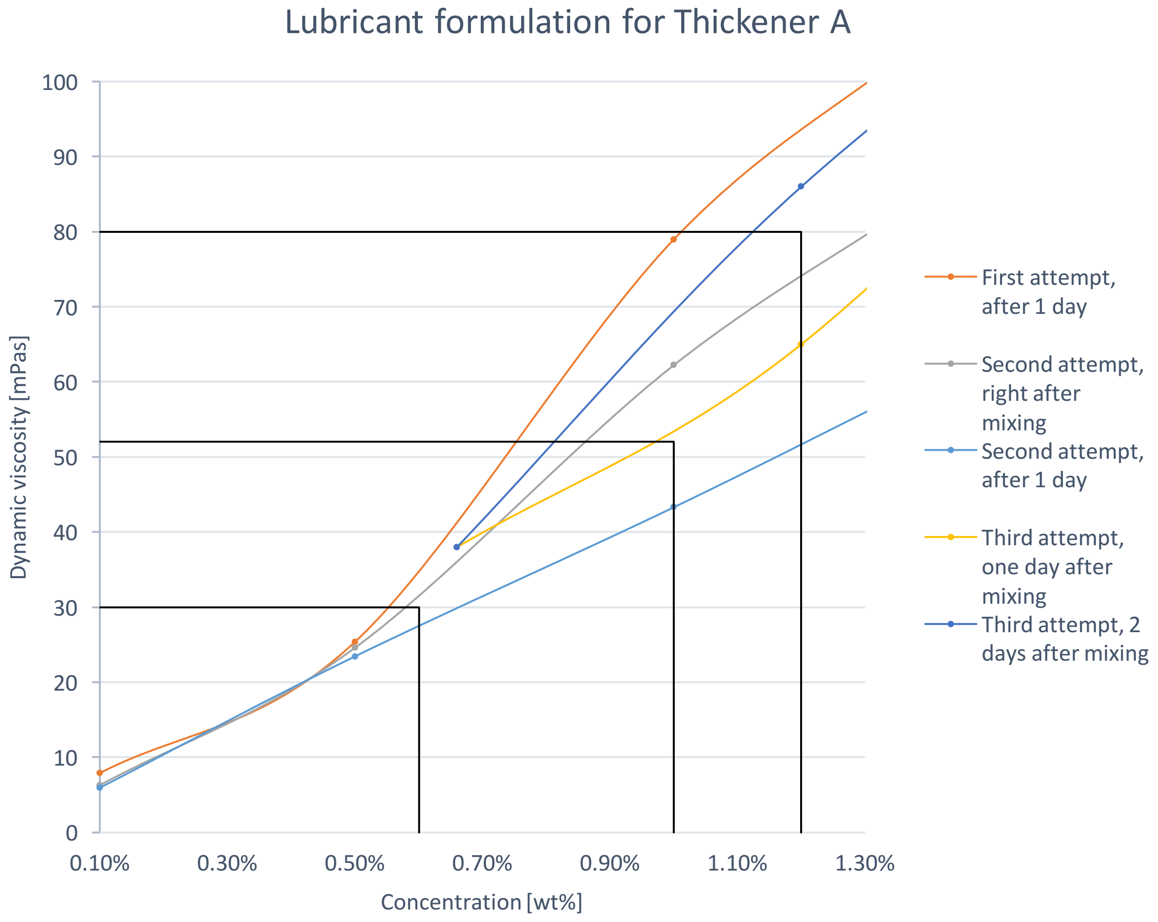


Figure 15 - Lubricant formulation for thickener A

In Figure 15, the formulation of Thickener A is presented. It is clear that the degree of time dependency for the lubricant is increasing with concentration. There is no difference in viscosity over time for concentration between 0.10% to 0.5%. During the second attempt, the viscosity is decreasing after time. On the other hand, the third attempt showed an increase of viscosity after time.

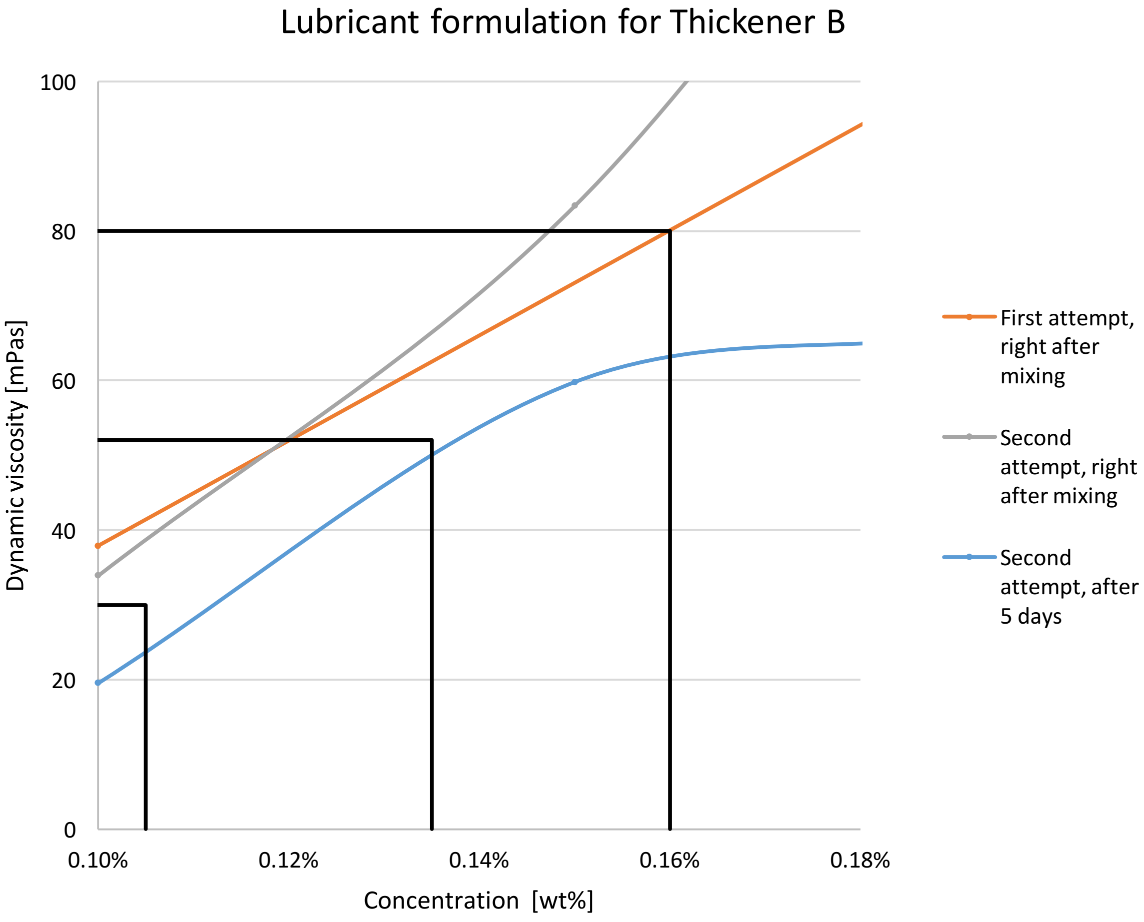


Figure 16 - Lubricant formulation for Thickener B

In Figure 16, the formulation of Thickener B is presented. From second attempt, it is seen that the time dependency is decreasing the viscosity of the lubricant after five days. The viscosity decrease is nearly 30% when compared to the viscosity of the originally formulated lubricant. The increase of viscosity is showing a linear trend when the concentration is in between 0.10% and 0.15%.

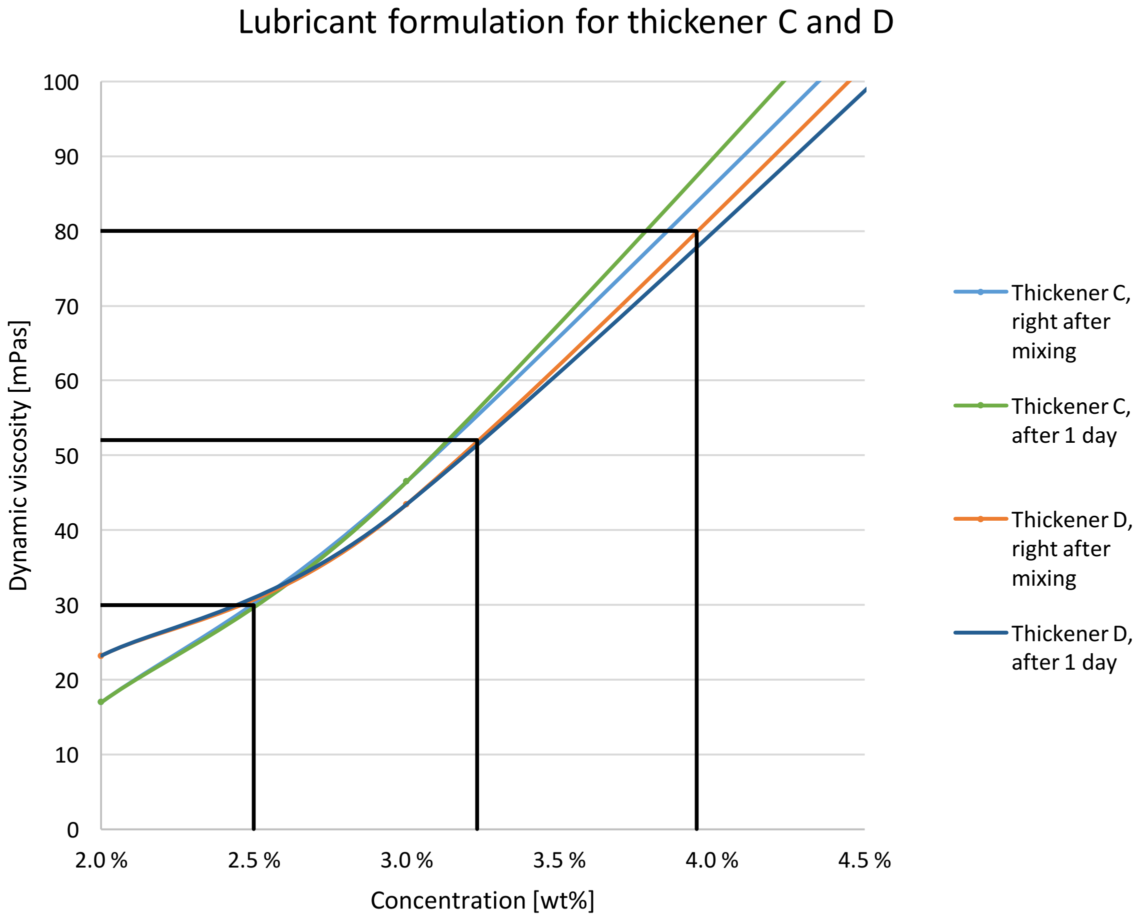


Figure 17 - Lubricant formulation for Thickener C and D

In Figure 17, the formulation of Thickener C and D is presented. Thickener C is experiencing a time dependent increase in viscosity, while Thickener D is experiencing a slight decrease over time. The time dependency is thus very low for these thickeners.

An overview over the 12 formulated lubricants is found in Table 4.

3.4 Tribometer testing

3.4.1 Hydrodynamic lubrication study

The hydrodynamic lubrication study was performed by using the TE88 Multi-Station friction and wear test machine in reciprocating configuration (Phoenix Tribology Ltd., Newbury, UK).

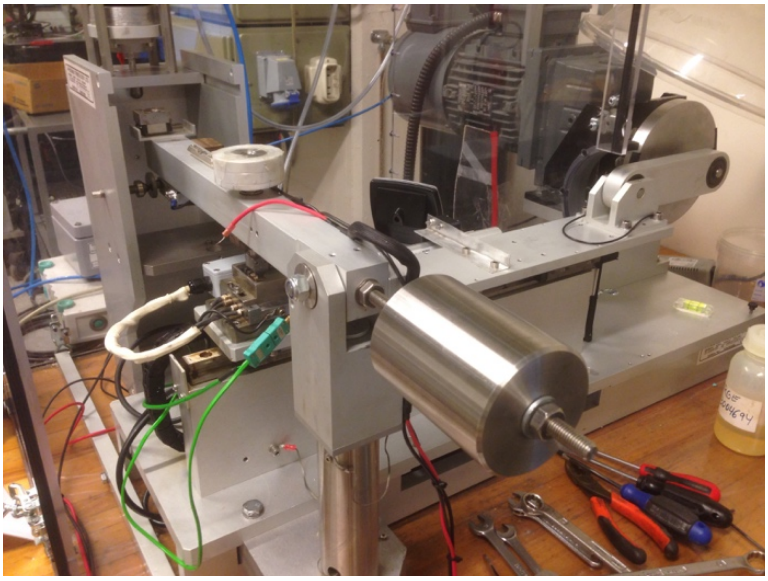


Figure 18 - Reciprocating tribometer TE88

The test set-up consists of a cylindrical pin with circular contact area and a plate counter surface. The materials and parameters used are listed in Table 2. The pin is pushed against the plate sample and the plate is connected to a reciprocating arm, providing lateral forces, as seen in Figure 19. By use of friction sensors, the friction force is measured thus providing the COF.

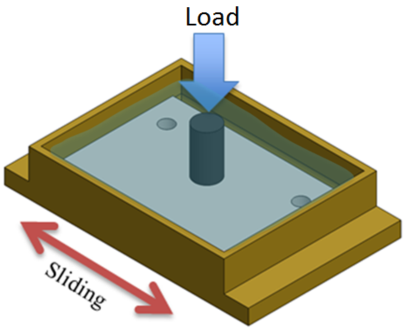


Figure 19 - TE88 configuration with a fluid reservoir

By using high-speed and low contact pressure, we achieve hydrodynamic lubrication condition. This condition is simulating the situation observed between the polymer seal and steel rod used in the N-line riser tensioner.

Table 2 - TE88 test conditions

PARAMETER	VALUE	UNIT
STROKE LENGTH	30	mm
MID-STROKE VELOCITY	100	mm/s
LUBRICANT TEMPERATURE	40	˙C
TEST DURATION	3	Hours
CONTACT PRESSURE	12	MPa
ACQUISITION RATE	25	Hz
PIN DIAMETER	8	mm
PIN MATERIAL	UHMWPE (Z80)	
PLATE MATERIAL	SDSS	
PLATE ROUGHNESS	Diamond polished	

Due to the water evaporation of the water-glycol based lubricants in use, a water-drip system is used to reduce this effect. The water drip is adjusted by a needle valve, where water is added over time to compensate for the water loss through evaporation.

3.4.2 Boundary lubrication testing

A pin-on-disc tribometer was used to simulate the bearing application from the N-line riser tensioner. The pin-on-disc tribometer is delivered by Phoenix tribology.

In this set-up, a ball and plate configuration was used, where the alumina ball with a radius of 3 mm was pushed against the plate with a free-weight load. The ball was loaded with a specific weight to achieve a pre-calculated surface pressure by using Hertz elastic contact equations. These calculations are found in the Appendix. The plate is connected to a rotating disc that supplies the lateral forces required. By use of friction sensors, the friction forces can be measured.

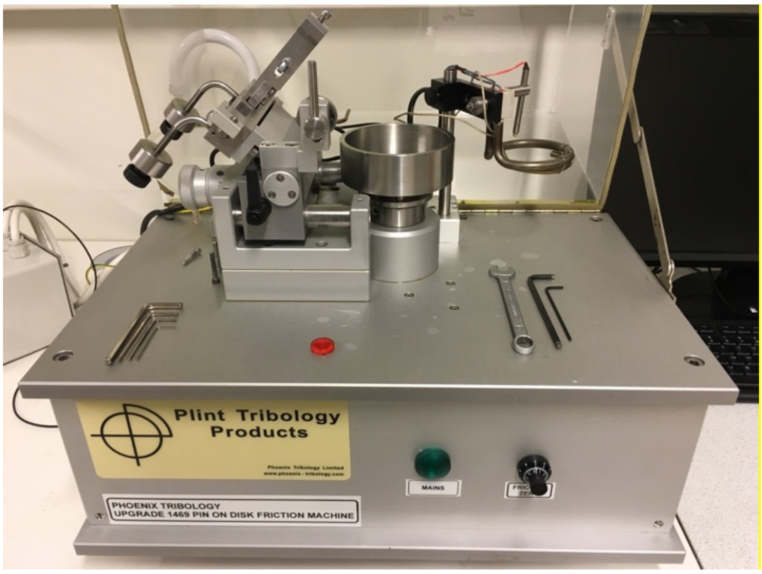


Figure 20 - Pin on disc tribometer

By using low-speed and high contact pressure, boundary lubrication condition is achieved in the contact between the SDSS plate and alumina ball.

Table 3 – Pin-on-disc test conditions

PARAMETER	VALUE	UNIT
WEAR TRACK DIAMETER	10	mm
SPEED	7.85	mm/s
LUBRICANT TEMPERATURE	Room temperature	˙C
TEST DURATION	15-30	Minutes
MAX. CONTACT PRESSURE	2461	MPa
ACQUISITION RATE	10	Hz
BALL DIAMETER	6	mm
BALL MATERIAL	Alumina (Al_2O_3)	
PLATE MATERIAL	SDSS	
PLATE ROUGHNESS	Diamond polished	

4 Results and discussion

4.1 Lubricant formulation

The thickeners that showed promising viscosity, stability and solubility in the water-glycol base, was further used in the thesis. These thickeners are presented in the formulated lubricants Table 4. It is important to specify that the weight concentration of the formulations is not for the total lubricant volume, but the concentrations related to the total base of the lubricant.

Table 4 – Formulated lubricants table

	Concentration [wt%]	**Dynamic viscosity at 40˚C and 500s^{-1} [mPas]**	**Type**
Thickener A	0.660	37	Cellulose thickener
	1.010	54	
	1.200	80	
Thickener B	0.088	26	High M_w alkali swellable polymer thickener
	0.110	44	
	0.213	84	
Thickener C	2.460	35	Low M_w polymer thickener
	3.050	48	
	4.350	72	
Thickener D	2.500	38	High M_w polymer thickener
	3.230	53	
	3.950	80	

Due to problems encountered when formulating the lubricants, several steps of the formulation procedure could have been improved. A study of thickener C and D [28], performed 60 minutes stirring at an elevated temperature of 60˚C and a lower shear rate (200rpm). This study did not mention any difficulties in regards to viscosity variations. This indicates that, especially for the high-molecular weight polymer thickeners, the shear rate should have been reduced and the stirring time should have been increased.

The introduction of lubricant heating during formulation would probably reduce the time dependent viscosity of the polymers and the variations of viscosity found in the lubricants. Heating of the base before adding the thickener may improve the stability, reducing the swelling effect by reducing the strength of the molecular bonds. This may give the solutions better time to adjust to the viscosity change, thus resulting in a higher homogeneity in the formulation.

4.2 Rheology studies

The results from the rheology studies are presented below. The rheology studies performed are time dependency, shear- and temperature - stability studies.

4.2.1 Time dependency

In Figure 21, the dynamic viscosity of the different thickeners at different concentrations have been measured. The figure is showing for Thickener A and B that the viscosity is varying with time, providing no clear answer for anticipating the viscosity. The only clear trend is that the longer time it gets to stabilise; the reliability of the viscosity is higher.

In Figure 15, the viscosity of Thickener A, measured for the second formulation attempt, is decreasing with time and the viscosity measured for the third formulation is increasing with time. The reason for this inconsistency is probably because the inhomogeneity of Thickener A in the base solution was very high. This means that the lubricant was still changing viscosities over time, and the measurements did not give any clear trend on this development. The viscosity of Thickener A probably varied over the volume, resulting in a different viscosity from each measurement.

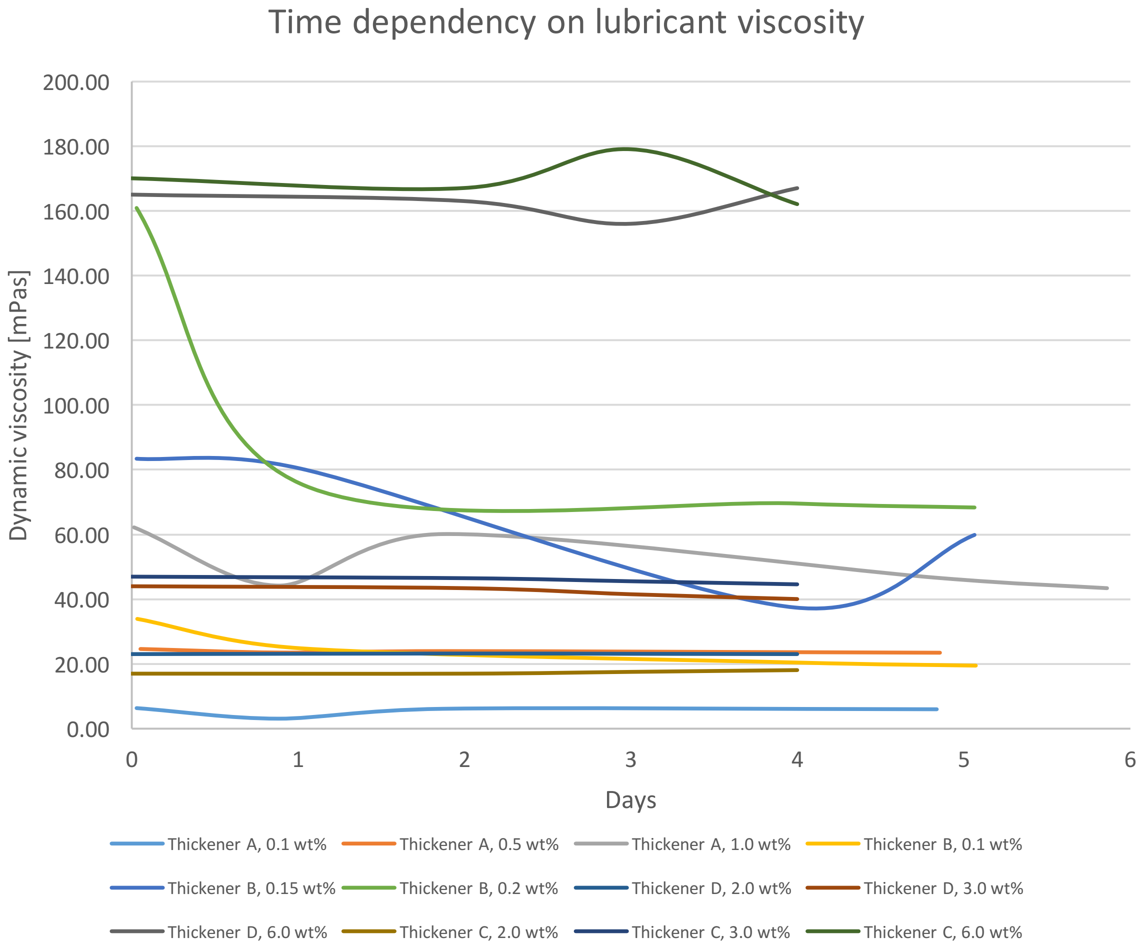


Figure 21 - Time dependency of the different thickeners

On the other hand, the three different concentrations measured are behaving in a rather similar manner over time, increasing and decreasing in viscosity at the same time. This may be because the chemical swelling occurring in the lubricant was still active. The lubricant had not found a state of equilibrium and this influenced the viscosity over time and gave different values between the two formulation attempts. The behaviour mentioned for Thickener A is also observed for Thickener B, as seen in Figure 16. This is in compliance with Figure 21, where it is clear that the viscosity varies over time for the higher thickener concentration formulations.

4.2.2 Shear stability

The shear stability of the different lubricant formulations has been studied, for the extensive data, see Appendix. By measuring the viscosity during acceleration and de-acceleration of the rheometer, we receive a representation of the lubricants behaviour and the influence of shearing. The shear stability results presented is the data from the 52 mPas formulations only.

The upper part of the cycle, seen in Figure 23, is the accelerating part of the rheometer study, where the rheometer is increasing its shear rate linearly from 0 to 500 s^{-1}. The lower part is for the de-acceleration of the study, where the rheometer is reducing its shear rate from 500 to 0 s^{-1}. This is illustrated in Figure 22:

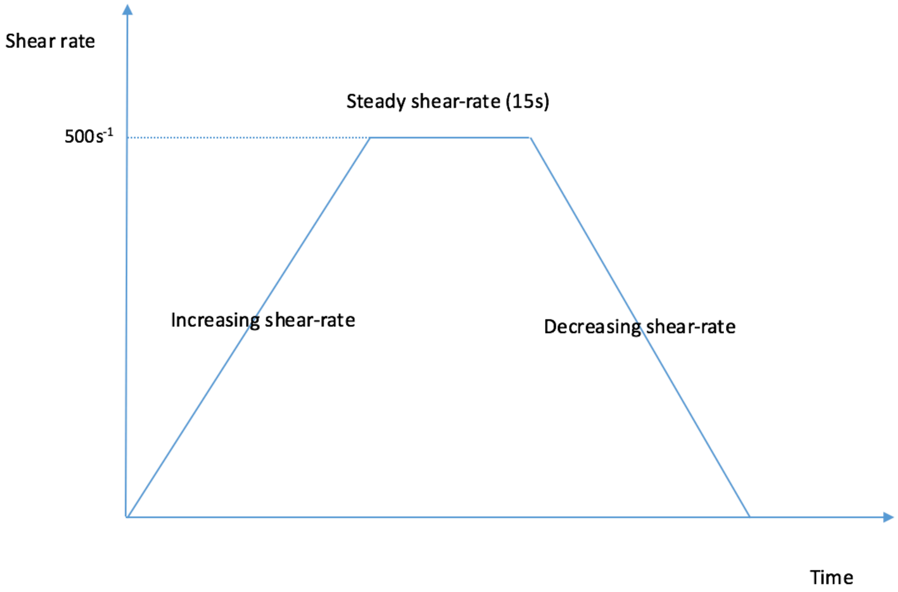


Figure 22 - Viscometer shearing procedure

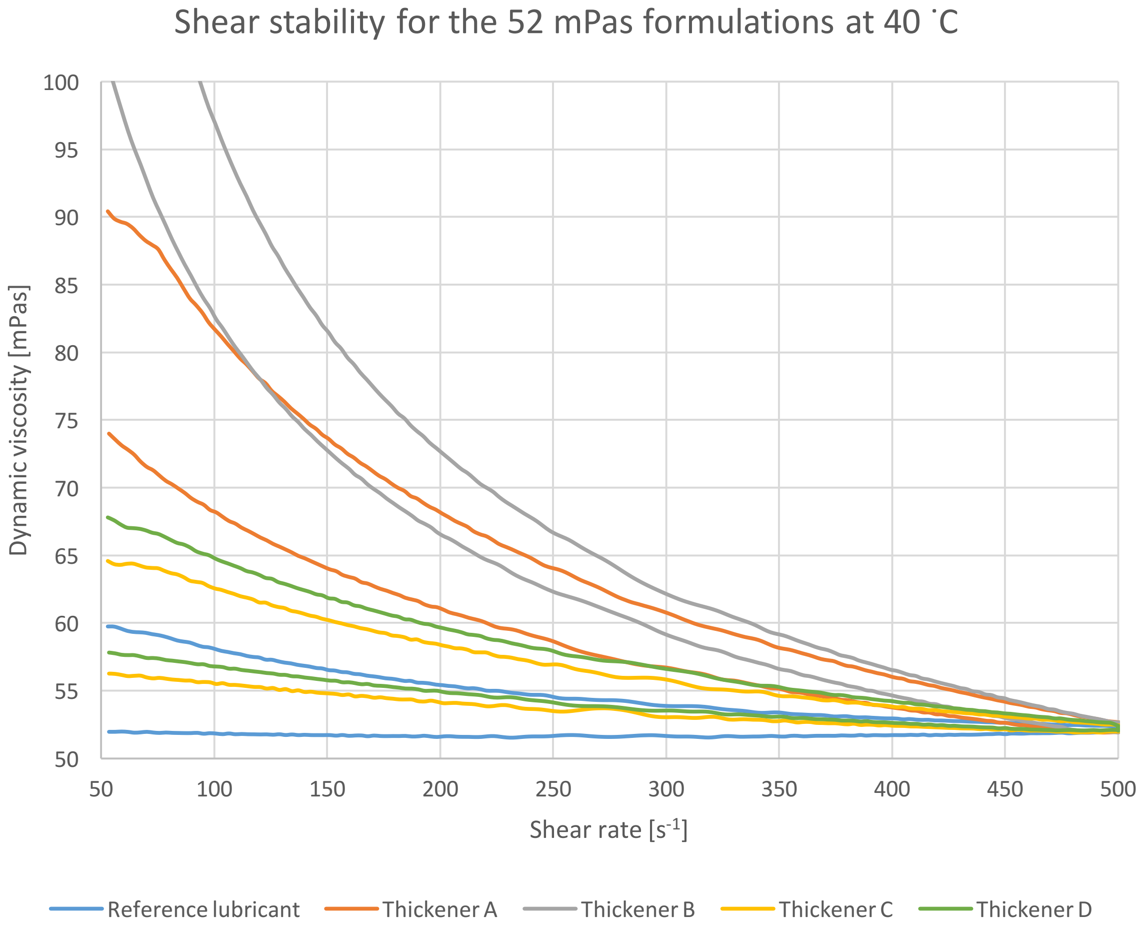


Figure 23 - Shear stability

In Figure 23, the shear stability of the 52 mPas formulations is presented. The data has been shifted in respect to the reference lubricant, and a moving average has been added to smoothen the graph. The results from the rheometer study of the formulated lubricants are showing clear signs on which thickeners are experiencing shear thinning behaviour. Thickener A and B is easily identified as highly shear thinning. For the thickener C and D, shear thinning is observed, but at a lower degree. The reference lubricant is showing close to Newtonian shear behaviour. It seems that the de-acceleration is not inflicted by the shear of the lubricant.

Thickener A is showing the highest deviation between the acceleration and de-acceleration, proving the thickener to be the one with the largest thixotropic properties. This can be seen by the large area between the graphs.

Table 5 - Degree of pseudoplasticity

	Viscosity at 50 s^{-1} [mPas]		Average of upper and lower viscosity at 500s^{-1} [mPas]	Average difference from 52 mPas
Reference lubricant	Upper	60	56	8%
	Lower	52		
Thickener A	Upper	90	82	58%
	Lower	74		
Thickener B	Upper	119	110	112%
	Lower	101		
Thickener C	Upper	65	60.5	16%
	Lower	56		
Thickener D	Upper	68	63	21%
	Lower	58		

The data presented in Table 5 is obtained from the data in Figure 23, where the viscosity obtained at the shear rate of 50 s^{-1} is in focus. The reason for this is to have a quantifiable representation of the pseudoplasticity of the different thickeners. It is observed from Table 5 that Thickener B is showing the highest deviation from the 52 mPas value at 50 s^{-1} shear rate. The deviation is represented in percentage, and for Thickener B the dynamic viscosity at 50 s^{-1} is 112% higher than at 500 s^{-1}. It is also noted that the viscosity of Thickener B during de-acceleration is lower, indicating hysteresis. This is observed for all cases in Table 5. This means that the polymer thickeners possess thixotropic behaviour. For the reference lubricant the change of the viscosity between 50 s^{-1} and 500s^{-1} shear rate is equal to 8%.

The data presented in Figure 24 is calculated by filtering out the data with a shear rate in between 30 s^{-1} and 499 s^{-1}. The reason for this is to receive a representation of the average viscosity which the lubricant is providing in this region. Due to the pseudoplastic behaviour of the thickeners, the viscosities presented below are larger than the viscosity received at 500 s^{-1}. An average viscosity higher than the formulated viscosity indicates a shear thinning behaviour of the lubricant. The spread of the data is represented by the standard deviation, and indicates the stability of the viscosity in the lubricant. A high standard deviation indicates that the viscosity is varying over the volume of the lubricant. The data below 30 s^{-1} is filtered out due to uncertainties related to the rheometer accuracy at lower shear rates.

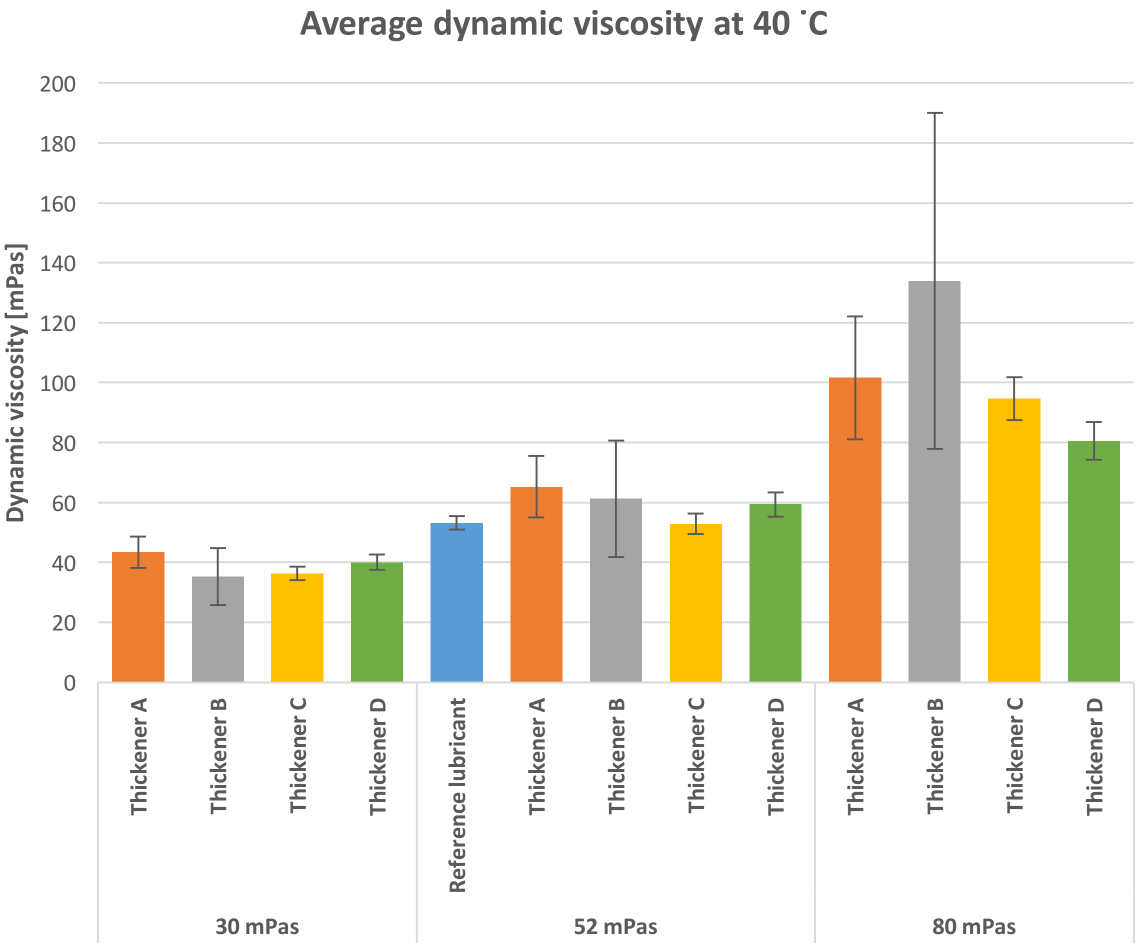


Figure 24 - Average dynamic viscosity for the different formulations

As seen in Figure 24, the diversity of the average viscosity for the different formulated fluids are high and increasing with higher concentration/formulated viscosity. For the 30 mPas formulations, the viscosities are rather homogenous with a small spread in the data. The difference in standard deviation is significant between the different thickener types. Thickener B shows a large variation of viscosity during shearing. This is also the case for thickener A, but at a lower degree. In the case of Thickener C and D, the viscosity - shear-rate dependency showed the most promising results. Under both cases, the shear thinning behaviour was dramatically lower as compared to Thickener A and B.

Thickener B deviates with a high average viscosity and standard deviation. The average viscosity is 134 mPas, which is 60% higher than the viscosity at 500 1/s (84 mPas). It is also noticeable that the average viscosity of Thickener C is slightly higher than thickener D. For lubricants formulated with Thickener B, there was a very high effect of thickening, where low concentrations increased the lubricant viscosity at a very high rate. However, the standard deviation of the viscosity indicates that the thickener contains a large variety of different viscosities over the bulk of the fluid.

A study done by Isaksson [29] showed that non-Newtonian VI – improvers loses its advantages under high shear rate applications. This means that the polymers used for hydraulic applications needs to be less shear thinning. The lubricant is required to be circulated in the hydraulic system, where the fluid will encounter the forces from the hydraulic pump. To achieve a functioning riser tensioner system, the oil is in need of being pressurised for the system to maintain its tensioning abilities. This requires a pump to pressurize the hydraulic system, which means that the lubricant must withstand this pressure. As the pressure increases, the shear forces met in the system increases, and the pseudoplastic lubricants will change their viscosity.

Together with the permanent viscosity-losses found for high-molecular weight polymers, the lubricants may not be applicable for hydraulic applications. Considerable shear breakdown was found for Thickener B in Brophy and Fitzsimmons [15] due to high shear rates.

Figure 24 is presenting the average viscosity of the lubricants and the results are greatly influenced by the pseudoplastic behaviour of the thickeners. This is noticeable because there is no clear distinction between the different formulation viscosities. If the lubricants had ideal Newtonian behaviour, the average viscosities would be equal to the initially formulated viscosities, 30, 52 or 80 mPas. The values would then show a staircase presentation with 30 mPas as the first step, following 52 and 80 mPas. This is not the case for the formulations presented. The degree of pseudoplasticity is in this case represented by a higher dynamic viscosity than the initial formulated viscosity at 500 1/s.

The reference lubricant is showing close to Newtonian shear behaviour. It seems that the de-acceleration is not inflicted by the shear of the lubricant. This may come from a permanent thickener orientation. This is most likely not caused by a polymer based thickener due to the low reduction in viscosity observed at higher shear rates. This is also observed in Figure 23. The behaviour of the reference lubricant observed in Figure 23, is indicating that there are thickeners that are maintaining the viscosity of the lubricant during shear. This may be because there are thickeners of Newtonian behaviour or modified polymers, i.e. crosslinked.

4.2.3 Temperature stability

The temperature stability of the thickeners is presented in three different figures below; Figure 25-27. The data presents the influence of temperature on the viscosity of the lubricant, at a shear rate of 500 s^{-1} for the temperatures; 20, 40, 60 and 80˚C.

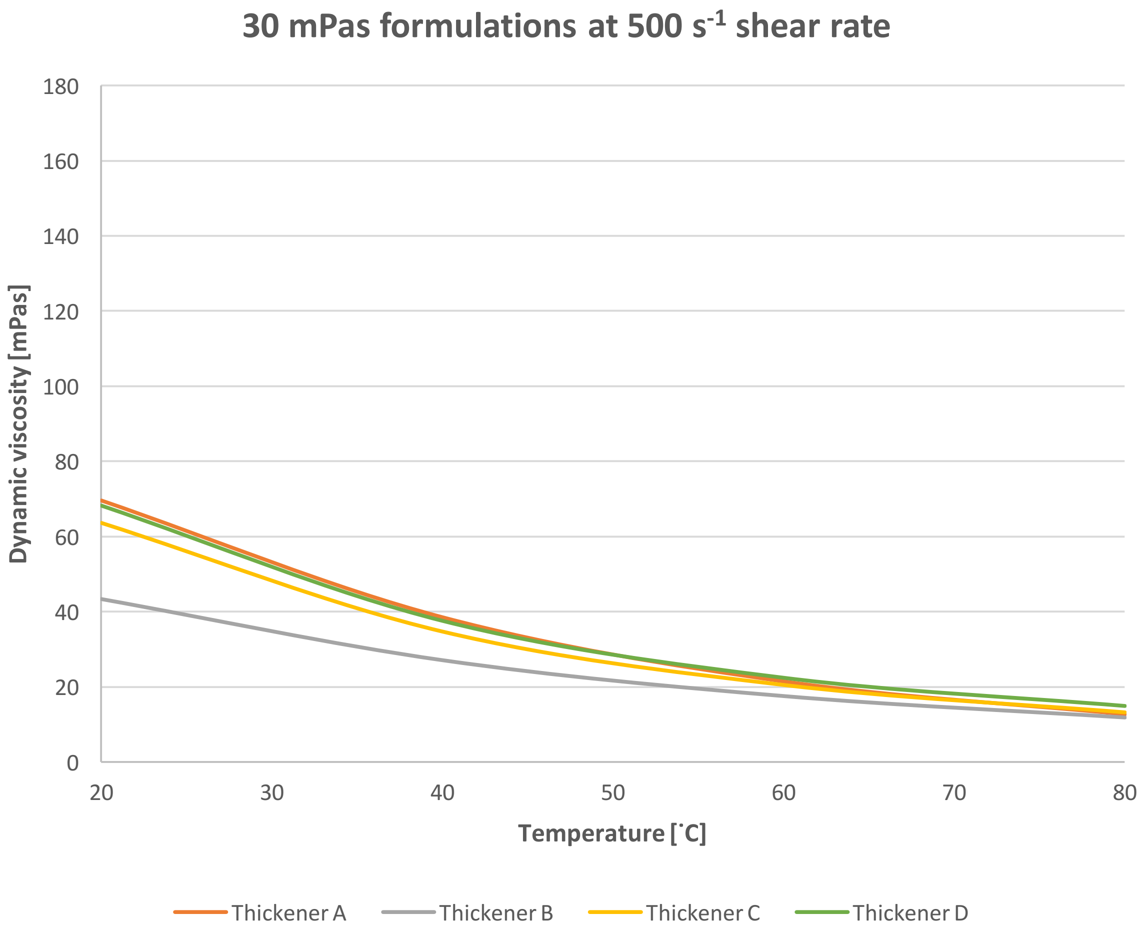


Figure 25 - Temperature stability of the 30 mPas formulations

The 30 mPas formulations are showing a decrease in viscosity over temperature. This is expected, as almost all lubricants show a decrease of viscosity when the temperature increases. The effect of temperature of the viscosity is the lowest for thickener B, as compared to thickener A, C and D. It needs to be clarified that Thickener B is the thickener with the lowest formulated viscosity (26 mPas) of the 30 mPas formulations, and that the degree of temperature-viscosity dependence is increasing with viscosity. This correlates with the results observed in Figure 25-27.

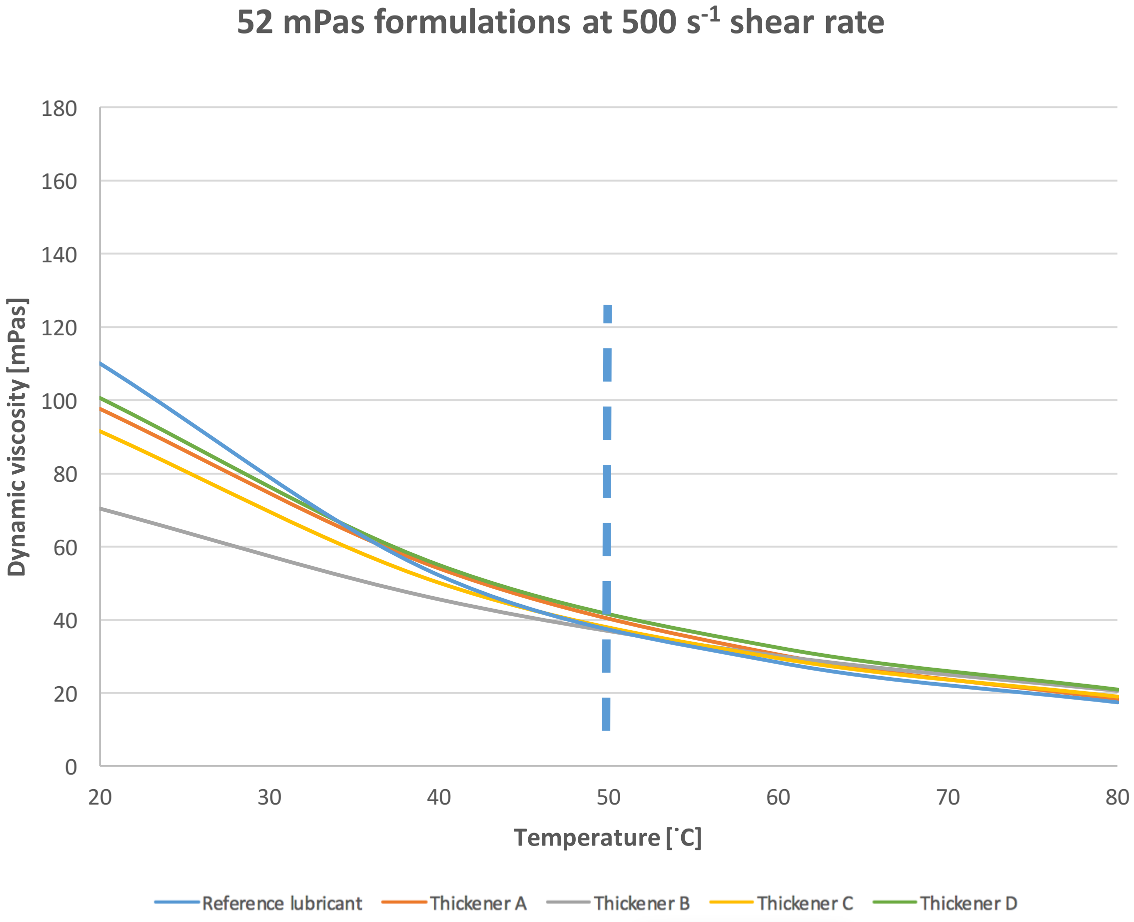


Figure 26 - Temperature stability of the 52 mPas formulations

The influence of temperature on viscosity for the 52 mPas formulations is presented in Figure 26. Even though the different formulations had different viscosities, the difference in viscosity became irrelevant after 50 ˚C. The thickeners are more or less providing the same viscosities from 50˚C and above. The variation is larger in the lower temperature range. This is also observed for the 30 mPas formulations in Figure 25. Thickener B deviates from the rest with the lowest temperature-viscosity dependability. It shows a decrease from 70 to 20 mPas over the temperatures: 20-80 ˚C. The reference lubricant is showing a higher influence of temperature on viscosity at lower temperatures than the other formulated lubricants.

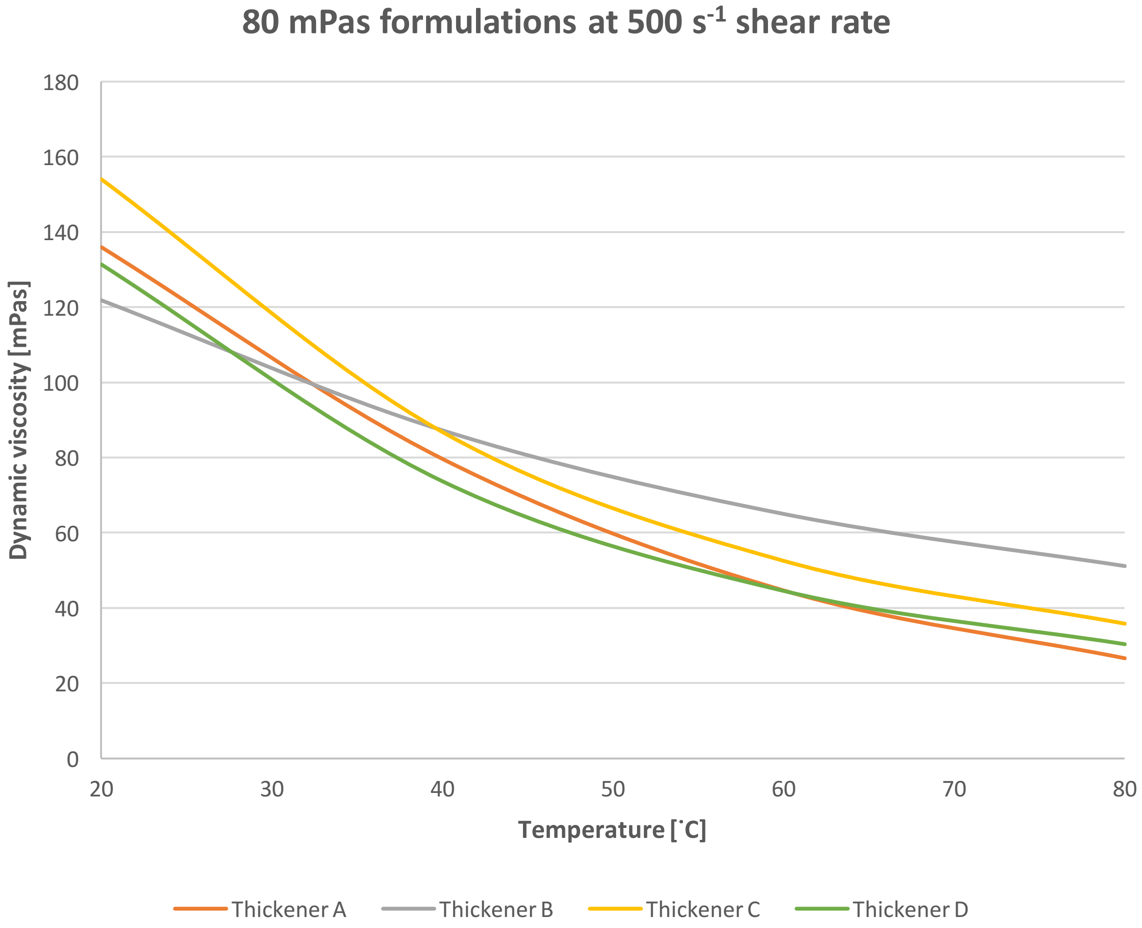


Figure 27 - Temperature stability of the 80 mPas formulations

All of the 80 mPas formulations are varying more in terms of temperature-viscosity than the lower formulated lubricants, seen in Figure 25-26. Instead of converging at increasing temperatures, the different thickeners are reaching different viscosities. Thickener B deviates with a higher linearity than the other thickeners, meaning that it might be a good additive for a high-temperature application. This behaviour is observed, but not very pronounced.

We notice that all lubricants are experiencing a decline in viscosity with increasing temperature. Figure 25, 25 and 26 also indicates that the non-Newtonian behaviour is reduced at higher temperatures. This is typical for polymer based thickeners [29]. For the 52 mPas formulations, the reference lubricant is showing a temperature-viscosity relationship that is slightly higher than the rest. This is a positive observation in terms of the formulations industrial applicability.

The low influence of temperature on the viscosity of the lubricants is expected due to the polymers VI – improver behaviour. Since this is a behaviour that also is observed for the reference lubricant, it is safe to assume that the reference lubricant contains polymer thickeners functioning as VI improvers. This is interesting due to the fact that very low pseudoplastic behaviour was found in the shear stability studies. If the thickener used in the reference lubricant was a polymeric type, pseudoplastic behaviour could have been expected. In other words, the reference lubricant may contain VI – improvers that are providing the low influence of temperature on viscosity, and also a rheology modifier that is maintaining a Newtonian behaviour during shear. A combination of several rheology modifiers is not uncommon for industrial lubricants, but it separates the reference lubricant from the formulated lubricants in this thesis, which only contains a single type of thickener.

4.3 Hydrodynamic lubrication

The hydrodynamic testing of the lubricants is presented in Figure 28-30. For Figure 28, each plot represent frictional performance of lubricants thickened with thickener A, B, C and D to the viscosity equal to 30 mPas.

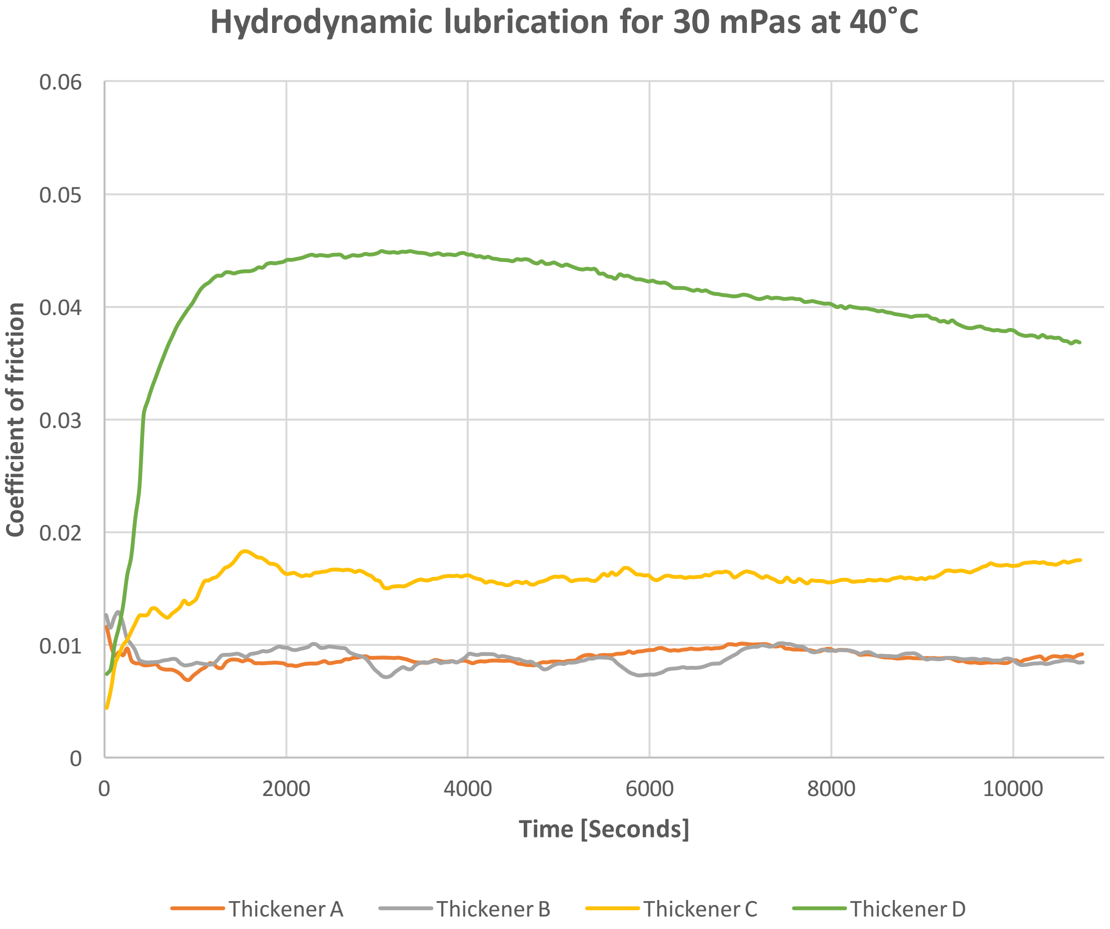


Figure 28 - Hydrodynamic lubrication for 30 mPas formulations

In figure 28, the hydrodynamic lubrication for the 30 mPas formulations is presented. There is a noticeable behaviour where the COF lay between 0.019 and 0.08 for Thickener A, B and C, but not thickener D. Thickener D is showing a very different behaviour than the other three lubricants. It has a large rise in COF over 1000 seconds where it stabilizes on the value equal to 0.044 and slowly decreases over time. This behaviour might be explained due to the water evaporation of the lubricant, as observed in Skjerstad [5]. Water evaporation increases the viscosity of the lubricant by reducing the base volume. This viscosity increase may lead to a reduction of the COF.

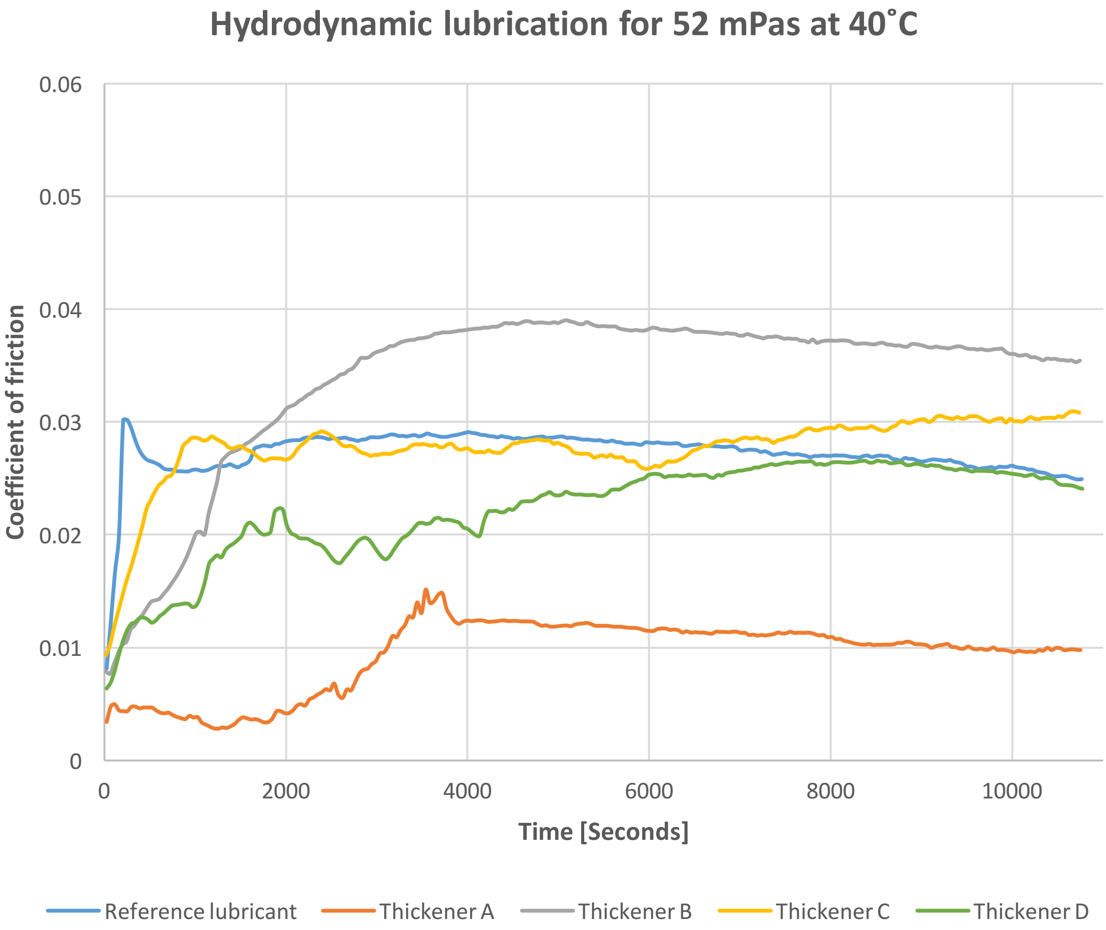


Figure 29 - Hydrodynamic lubrication for 52 mPas formulations

The 52 mPas lubricants are presented in Figure 29. All lubricants are showing slightly stable lubrication after 4000 seconds. The reference lubricant is showing a short running-in period and receives more or less stable COF at 0.029 after 2000 seconds. However, a slight decrease of the COF appears over time. The COF of Thickener A is increasing until 4000 seconds, where it enters a stable phase with a slight decrease over time. The COF of Thickener B is increasing gradually until 4000 seconds, where it also decreases over time. Thickener C is providing a promising behaviour where the COF more or less stabilizes after a small running-in. The COF is varying over time, where it lay between 0.025-0.030. Thickener D is showing a long period of instability, where it reaches some stability after 8000 seconds. The performance of Thickener D in this formulation indicates that the lubricant is not reaching any equilibrium and longer studies are necessary to confirm its behaviour.

The increase in COF that is observed after the running-in period for Thickener C and D, may be the result of an increased water content in the lubricant. This may be inflicted due to the uncertainties involved with using the water-drip system. If the water added to the lubricant is more than the water evaporating over time, the viscosity may fall and COF may increase.

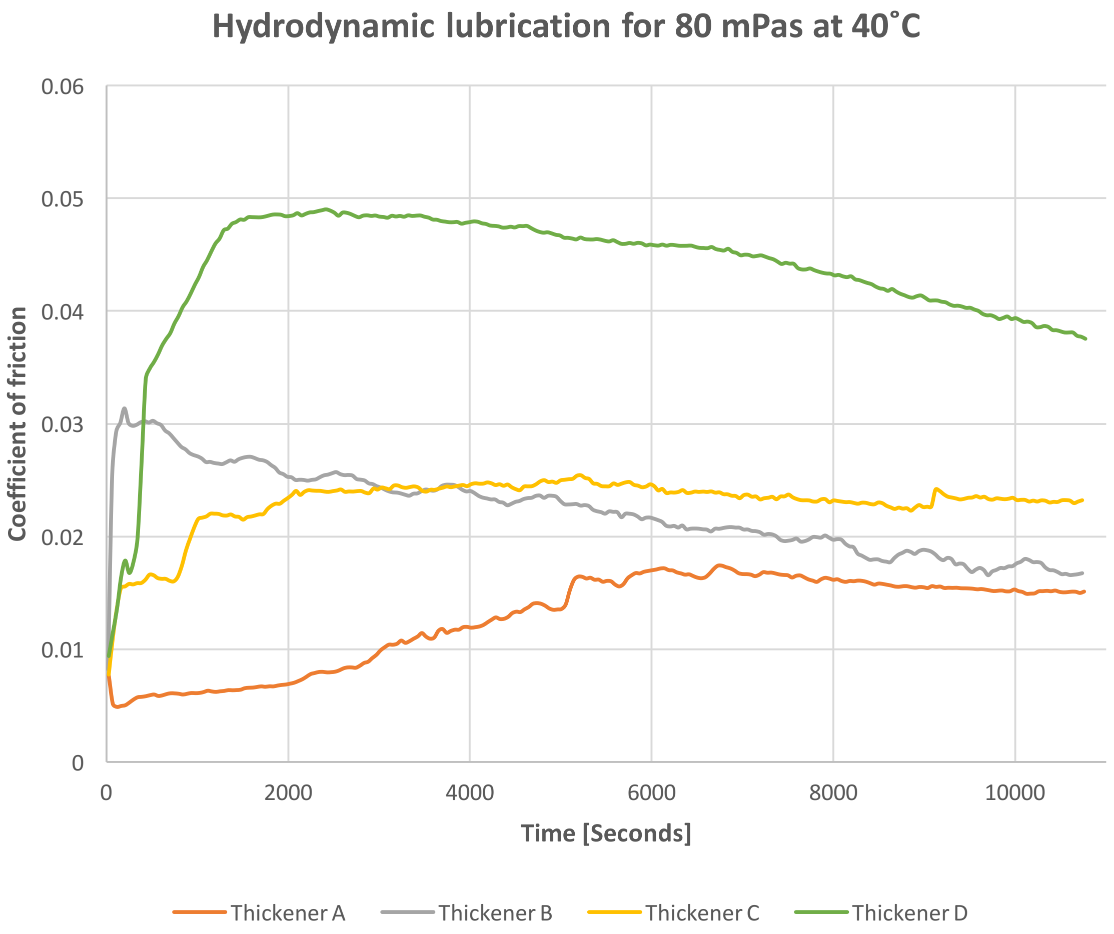


Figure 30 - Hydrodynamic lubrication for 80 mPas

In Figure 30, a large variation in the running-in observed between the different lubricants. The COF of Thickener A is increasing linearly from start to roughly 6000 seconds, where it stabilizes, reaching a COF = 0.018. Thickener B is not characterized by a run in period but a slow decrease in COF over time. Thickener C is showing a stepwise increase in COF until it has reached a stable COF around 0.025 after 2000 seconds. Thickener D is showing a large increase in COF during its running-in period and stabilizes after 1800 seconds. The COF then gradually decreases over time.

In Figure 31, the average COF of the different lubricant formulations is presented. The data from 6000 seconds and above have been averaged to receive a representation of the stable period where it is observed that the running-in period is over. The averaging is done by including the data from both repetitions.

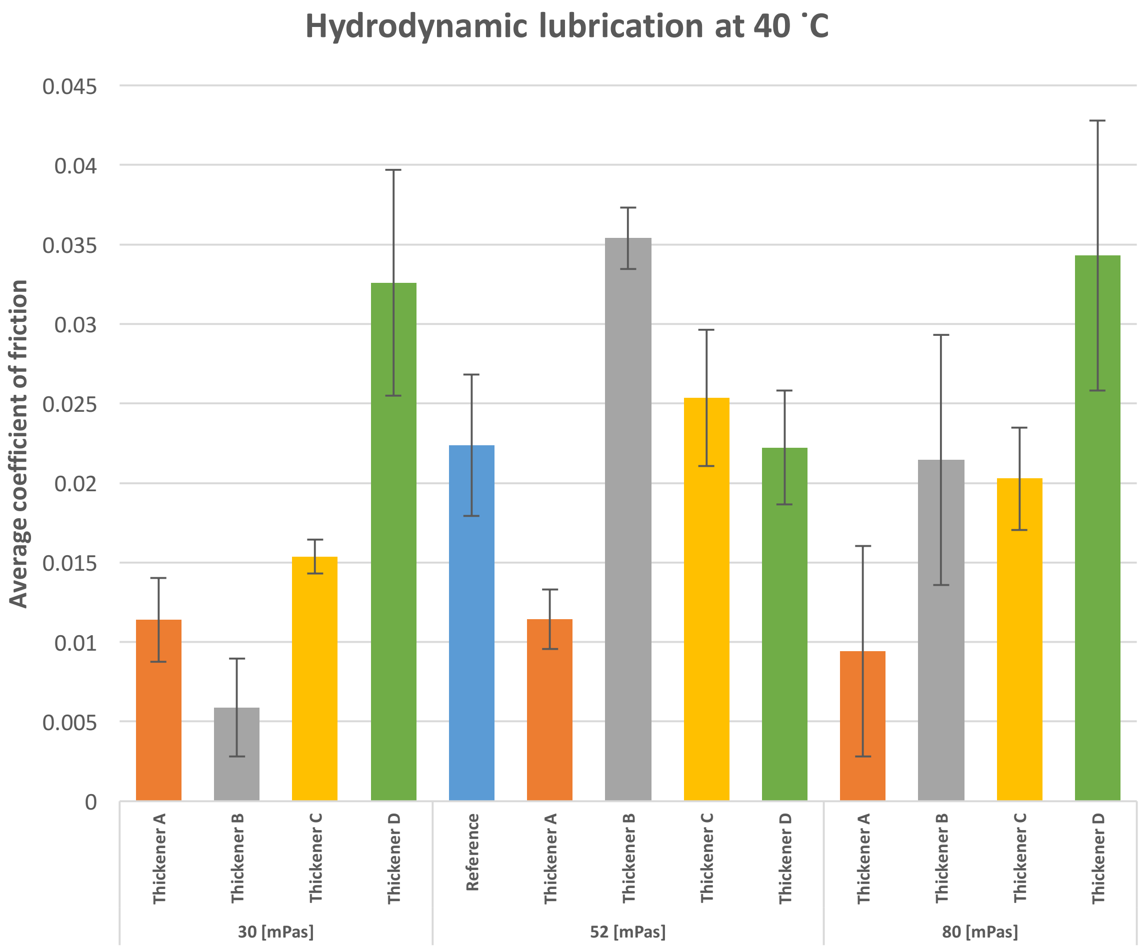


Figure 31 - Average data for hydrodynamic lubrication

By looking on the hydrodynamic results for thickener A, as seen in Figure 28-31, it is noted that the stability of the lubricant formulated to 30 mPas is higher than the one formulated to the viscosity of 52 mPas and 80 mPas. The low viscosity formulation is not experiencing a running-in period and is providing a stable COF over the entire test time with a low spread in the data. This is presented in the column representation seen in Figure 31. Both the 52 mPas and 80 mPas viscosity formulations are characterized with a running-in period, where the running-in time is increasing at higher viscosity. It is observed that the running-in period of the medium viscosity formulation is close to 4000 seconds, while the high viscosity formulation is around 6000 seconds.

The COF is decreasing slightly for thickener A with increasing viscosity. It is also noted that the standard deviation of the three different formulations of thickener A is high, placing the COF for the formulations almost at the same level. Relative to the reference lubricant, only Thickener A is providing a lower COF for the medium viscosity. For the polymeric thickeners B, C and D, no correlation between the COF and viscosity is observed. Thickener B is showing the highest variation in COF between the different viscosities.

The results from the TE88 reciprocating tribometer is indicating that the formulated lubricants are stable in terms of viscosity and COF. Figure 31 is giving no clear correlation between the performance of the polymers, and the thickeners used must therefore be analysed individually.

Thickener A is the only thickener that is independent of viscosity. This may be due to the low-molecular, nano-metre structures that are providing a thin surface film on the SDSS substrate. These molecules are providing a low COF, independent of the thickener concentration in the base fluid. When the concentration increases, the swelling of the water molecules are provided by weak hydrogen bonds which are easily broken by shear, but the abundance of functional groups gives the thickener the possibility to always be able to react with the substrate surface. When the seal is being slided up- and down the SDSS substrate, the thin film is resisting the shear forces due to the hexatomic rigid structure of the molecules.

Thickener B is, on the other hand, very dependent on the viscosity of the bulk lubricant. This may be seen in Figures 29-31, where the run-in period increases with concentration of the thickener. It is highly swelling and the candidate with lowest concentrations of the lubricants. This swelling effect makes the thickener difficult to formulate, and its reliability as a stable thickener is therefore in question. Further research regarding the formulation procedure should be considered. By looking at the standard deviation in Figure 31, it is easily observed that there is large variations in the viscosity. This is more or less confirming the theory mentioned in chapter 3.3.5, where the viscosity of the bulk lubricant consists of several different domains with different thickening. Together with its vulnerability in terms of mechano-degradation, the thickener is experiencing a change in bulk viscosity over the service, leaving it unable to perform in a hydraulic fluid application.

Thickener C is providing a low COF for the three different viscosity formulations, and shows some promising results due to its stability and low variability in COF. The concentration of the thickener is influencing the COF at a low degree and the relation of this is not linear. It is also seen that the standard deviation is increasing with the average COF, which indicates that there is a complex relation between the frictional forces and the amount of thickener present at the contact surface.

Thickener D is performing poorest in terms of hydrodynamic lubrication, where the COF is highest of the candidates. The presence of high-molecular weight polymers may be unable to lubricate the contact area, or the force of the reciprocating pin is able to remove the lubricating abilities of this thickener under these conditions. The lower COF provided by Thickener C, indicates that the lower molecular-weight is giving better lubricating properties.

It is noted that only thickener A is experiencing a slight drop in COF with increasing viscosity. This may be explained by the fact that only Thickener A is made of cellulose, and the relative high independency of viscosity may be related to this. Thickener B, C and D are polymeric thickeners and are not behaving in the same way in terms of COF. This may be due to the difference in molecular weights, thus leading to a difference in shear breakdown. It is assumed that the high shear forces experienced under the hydrodynamic testing are actively shearing the polymer chains. These results are indicating that the high molecular weight lubricants are behaving in an unstable manner under hydrodynamic lubrication, and should be avoided for hydrodynamic application. If not, stabilizing additives may improve the properties of the lubricant. It is also noted that some studies show [25] [30], that adding additives will change the molecular interactions, thus improving some and reducing other properties.

Thickener C is in this case not related to the high-molecular weight polymer behaviour mentioned above. Even though it has a molecular weight of 360000, which is higher than the shear stable limit mentioned in Brophy and Fitzsimmons [15], it is providing a promising performance. Its properties under hydrodynamic lubrication together with the promising low degree of shear thinning, makes this thickener attractive for hydraulic cylinder application.

Improving the formulation procedure with heating, longer stirring and lower shear, will probably increase the dispersion of the thickeners in the base. This may reduce the instability in COF observed in the hydrodynamic lubrication studies and provide lubricants that will perform better. The importance of lubricant homogeneity is seen in the variable viscosities and the performance of the different lubricant.

4.3.1 The influence of viscosity

Low viscosity lubricants are known to provide a lower film thickness between the surfaces in contact. A lower lubricant film thickness will lead to more surface asperities come in contact thus increasing the COF. For the tribological contact in focus; high alloy steel (SDSS) versus UHMWPE lubricated with water-glycol lubricant, a lowering of the viscosity may not lead to a higher COF. In Figure 31, it is noted that the influence of viscosity is not unambiguously. The different lubricants are not providing a clear answer to which viscosity provide the lowest COF. In other means it shows us which viscosity that is best suited for the tribological system in question.

For Thickener A, the average COF is more or less not influenced by the viscosity of the lubricant. This is the only thickener type of the four formulations that is showing this behaviour. The COF of thickener A is to some extent independent of the viscosity of the lubricant. This means that increasing the concentration of thickener, will lead to an insignificant reduction in COF. The large difference between the repetitions for the 80 mPas formulation is observed in the large standard deviation.

One of the reasons the COF is not showing any consistency between the different viscosity formulations may be due to the viscosity variations that may be present in the lubricant. When there is a difference in polymer chain lengths, the smaller, shorter polymer chains may be the only parts being able to be transferred between the mating contact area. This will then lead to a situation where only the shorter polymer chains will contribute to the lubrication of the contact, leaving the larger chains unable to enter the contact area.

If this is the case, then the small polymer chains will be the only parts providing the lubrication for the different viscosity formulations. This would result in a COF that is independent of the lubricant viscosity. Due to the high contact pressure and speed of the hydrodynamic test, the parts of higher viscosity will rather be pushed aside due to the higher inertia and physical volume of the longer, heavier polymer chains. This characteristic has been proved for Thickener B in Yoshida and Hosonuma [20], and may be true for the other polymers.

Due to the mechanical breakdown of the polymer chains experienced in moving contacts [21], the run-in period may be a seen as a deprivation of short polymers in the contact area. After shearing of the polymer chains, an increase of short polymer chains is made, and the equilibrium necessary to supply the lubricated contact [20], is achieved when the running-in period is over.

This inclines that using a low viscosity lubricant may in fact not be that bad. The low COF provided by Thickener A at low viscosity may be sufficient for a well operating lubricant. However, water-glycol lubricants with low viscosities are related to lower service life of hydraulic pistons. This is an effect that comes from the lubricants ability to flow into smaller cracks. When these cracks are confined in closed areas in the hydraulic piston, the pressure build-up is so high that the lubricant induces an increase in the crack propagation. This is called the wedge effect [3], and is also related to an increase in pitting corrosion observed in steel rods offshore.

Wenchao found [26] that Thickener A is experiencing an increase in wear when the concentration of thickener exceeds 0.7 wt%. The results given in Figure 30 shows that the COF is slightly reduced from low viscosity (0.66 wt%) to high viscosity (1.2 wt%), which may indicate that the wear is decreasing. This is true if the increase in COF results in increased wear, which contradicts Wenchao [26].

4.4 Boundary lubrication

The pin on disc results are presented in Figure 32 and 33. Due to the reduced influence of viscosity at boundary lubricated situations [9], only the 52 mPas formulations was studied. The study was performed at room temperature.

The boundary lubrication for the 52 mPas formulations is presented in Figure 32. The lowest COF is observed for the reference lubricant. The reference lubricant is also providing a stable COF of 0.14 after 100 seconds. The running-in period of the reference lubricant is comparable to the running-in period of the formulated lubricants for the first 100 seconds. After 100 seconds the friction of the lubricants starts to deviate from each other. The formulated lubricants are showing similar behaviour over the entire test time, where small variations in friction are present.

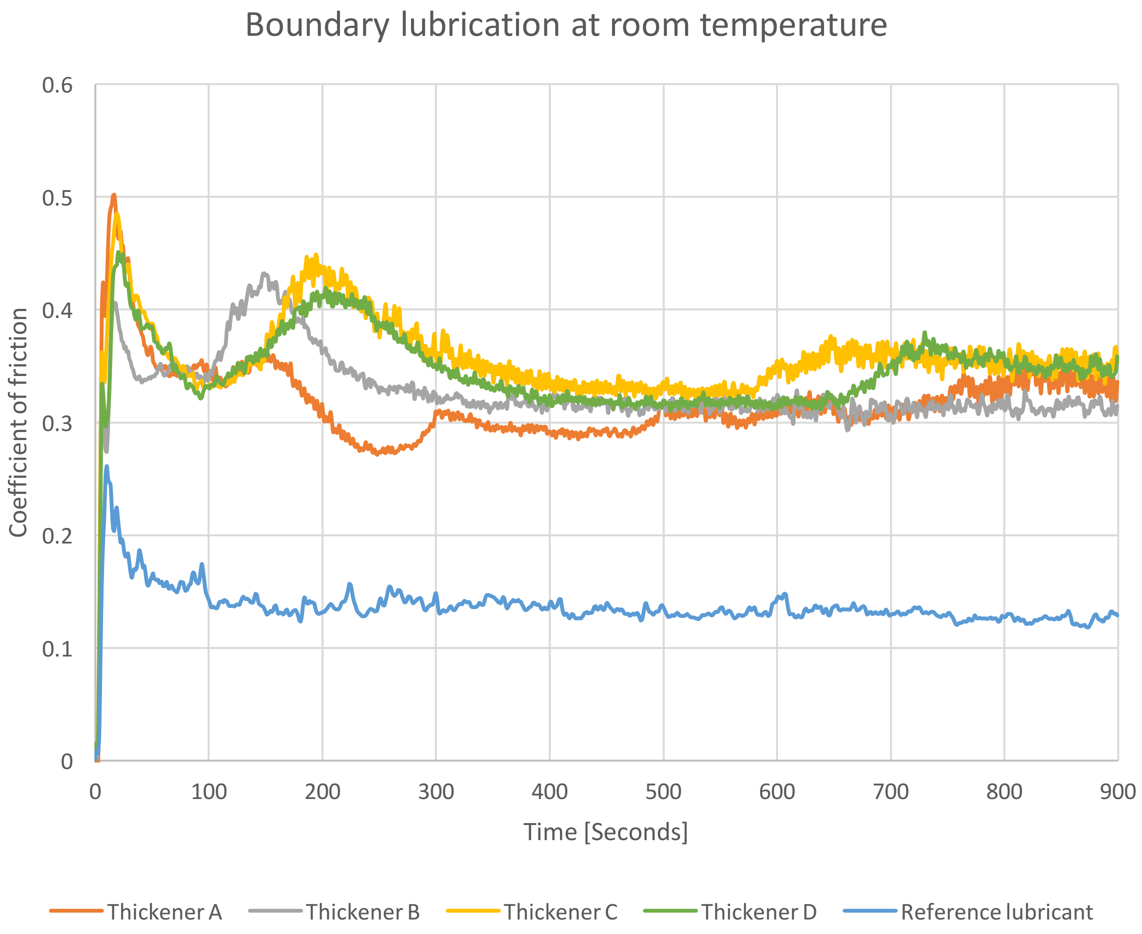


Figure 32 - Boundary lubrication at RT of the 52 mPas formulations

In Figure 32, boundary lubrication study show a clear difference between the tribological performance of the reference lubricant and the formulated ones. As seen in Figure 33, the reference lubricant is providing a COF which is nearly three times lower than the other formulations. There is a noticeable repeatability of the results, where test 1 and test 2 are showing near identical values.

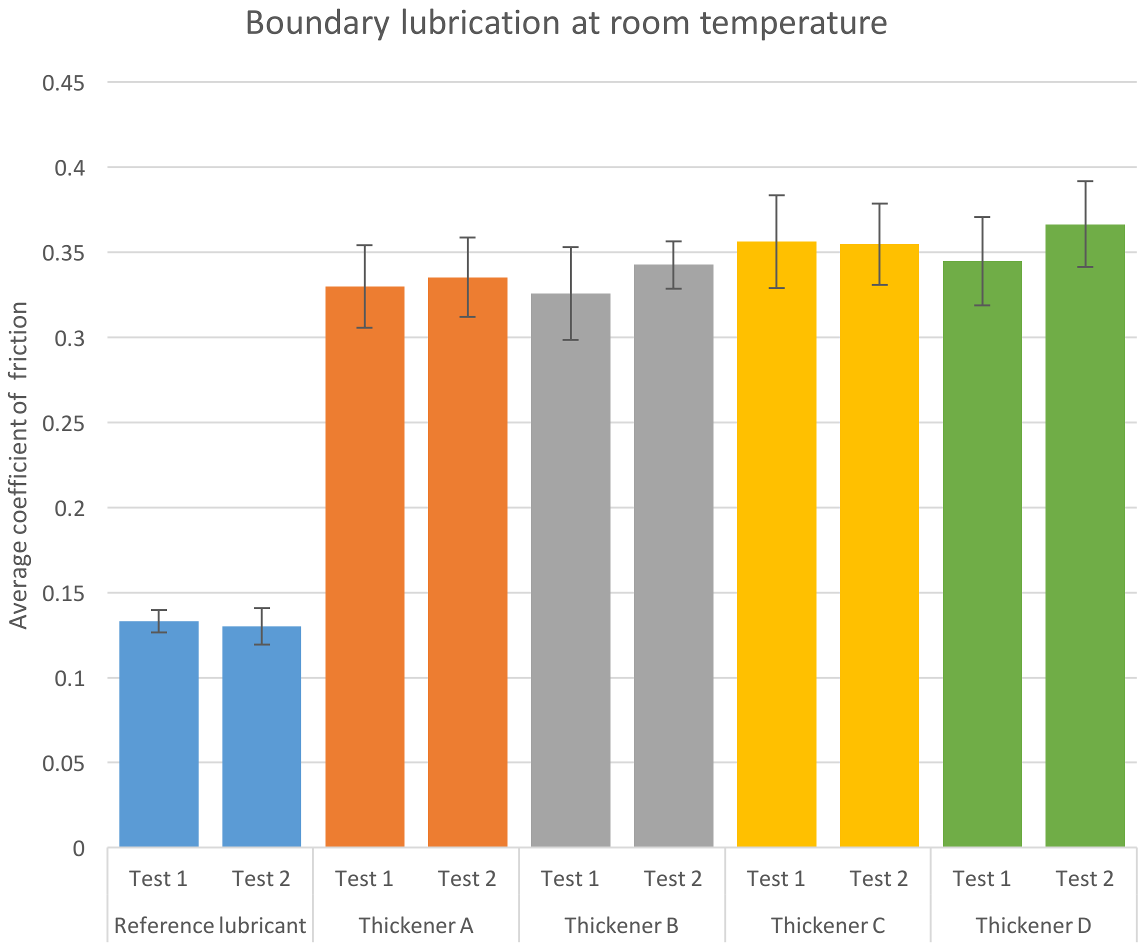


Figure 33 - Boundary lubrication at RT for 52 mPas formulations

The boundary lubricating studies are showing some very similar trends in terms of COF and standard deviation of the average results, as seen in Figure 32 and Figure 33. This indicates that the lubricating behaviour related to polymer-thickened water-glycol lubricants under high contact pressure conditions is quite similar. It also indicates that the thickeners in the formulated lubricant does not influence the COF under boundary lubrication, meaning that the lubricant should be modified with additional additives. The high contact pressure forces the lubricant out of the wear track, leaving the plate exposed and rapid wear is expected.

This indicates that the difference in the polymer molecular weight does not affect the COF during boundary lubrication. If this is true, then the shear breakdown of the polymer is irrelevant in terms of boundary lubricating properties for the lubricant.

The reference lubricant is providing a lower COF than all of the candidates. This lower COF is probably provided by chemical reactive additives that are activated under the boundary conditions. An additive known to do this is extreme-pressure additives, which are generally used for reducing the COF at boundary lubricating conditions. This is an additive that is not used for the formulated lubricants. Using an extreme-pressure additive may be a viable solution to reduce the COF under boundary lubrication for the formulated lubricants. This will of course need to be studied further due to the synergistic effects found between additives in lubricants [25] [30].

The temperature increase experienced in high friction contact areas is not believed to influence the boundary lubrication results in a large extent. The results from the temperature-viscosity stability, as seen in
Figure 26, indicated that the thickener showed stable behaviour during temperature increase. With this in mind the volatile behaviour of the COF observed in the running-in is probably influenced by other factors. This instability observed in the running-in period may be related to the lack of proper mixing of the thickener in the formulation. The degree of thickening homogeneity of the lubricant may influence the COF in the boundary regime.

4.5 Wear of the SDSS

This chapter shows the wear of the SDSS under boundary lubrication conditions. The wear volume from the wear tracks was calculated with the use of confocal microscope and the MountainsMap Universal, a surface analysis software. The figures below, Figure 34-38, are extracted from this software and the area of the wear profile is calculated. Three profiles were extracted for each repetition, the area was calculated for each profile and the area was then averaged. Only one of the profiles are presented in the thesis. The rest is attached in the Appendix.

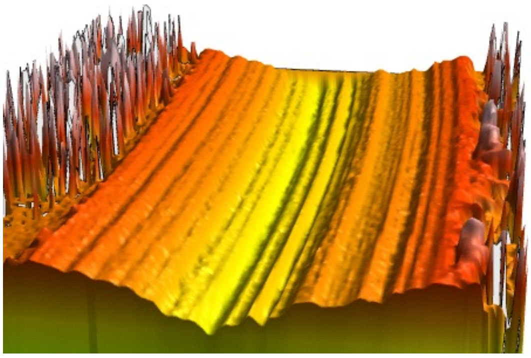
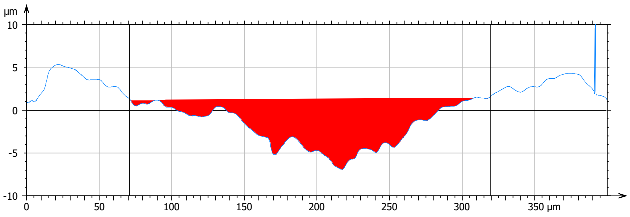
	
Wear track	Profile view

Figure 34 - Wear profile of the SDSS with the reference lubricant (R0)

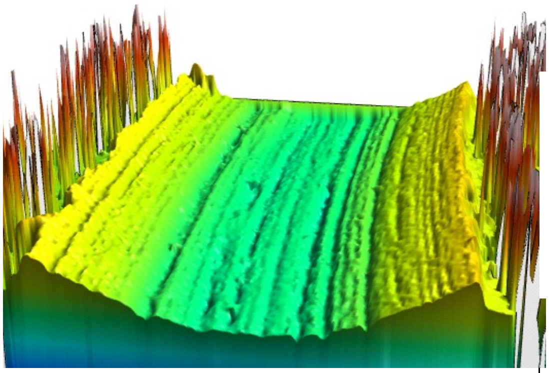
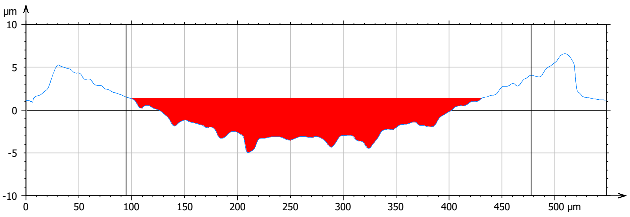
	
Wear track	Profile view

Figure 35 - Wear profile of the SDSS with the Thickener A lubricant

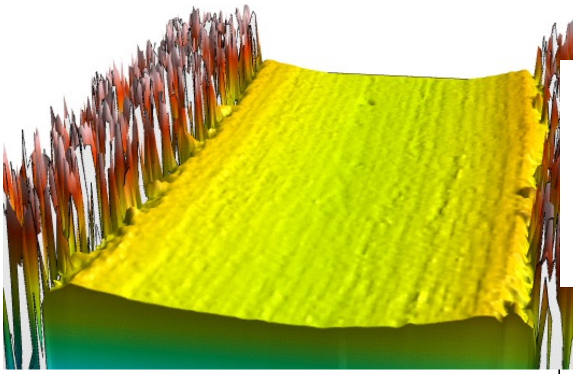
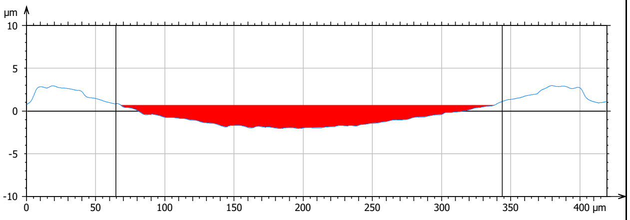
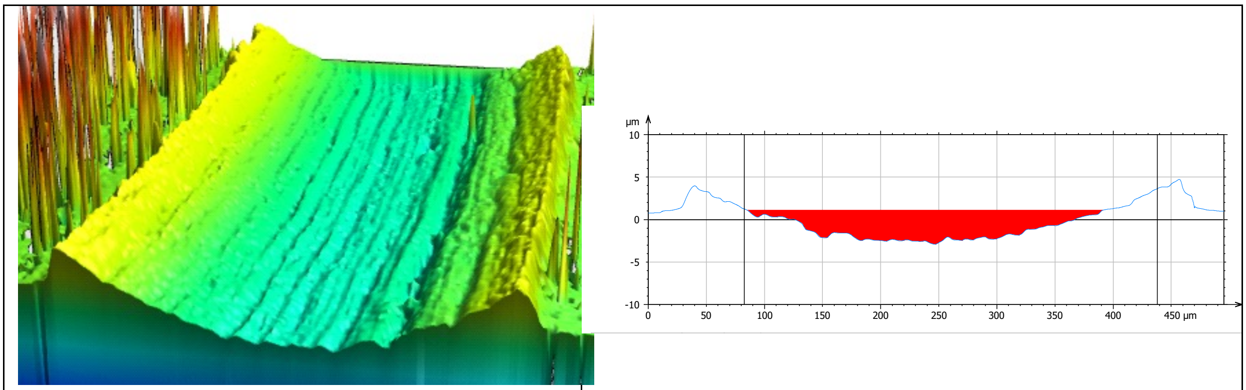
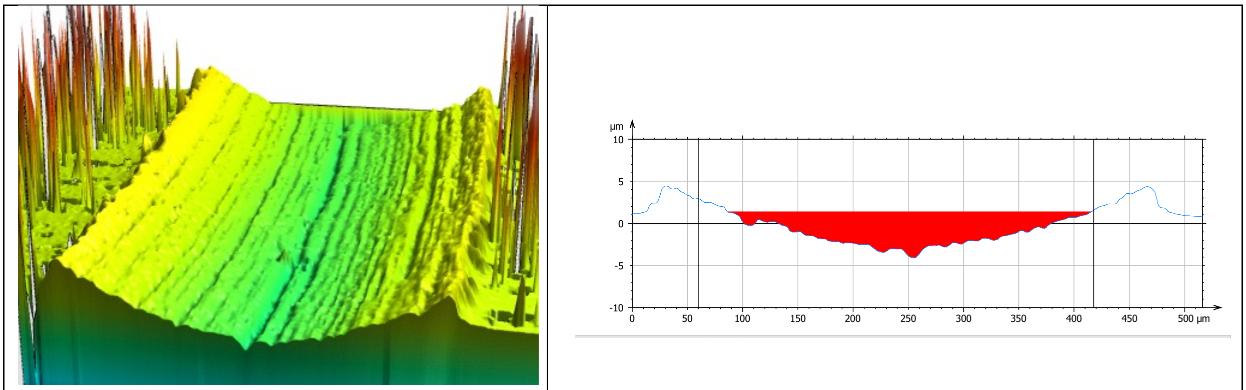
	
Wear track	Profile view

Figure 36 - Wear profile of the SDSS with the Thickener B lubricant



Wear track
Profile view

Figure 37 - Wear profile of the SDSS with the Thickener C lubricant



Wear track
Profile view

Figure 38 - Wear profile of the SDSS with the Thickener D lubricant

The wear volume of the wear track was calculated from the average area from the profile views and the circumference of the wear track. By relating the sliding distance of the experiment to the volume loss, Archards equation; $K = \frac{VH}{F_N S}$, is used to calculate the K – value of each repetition. K is the wear-coefficient of the softer material in the contact. In this situation the softer material is the SDSS.

The parameters used for this is given in Table 6 and Table 7:

Table 6 - Wear calculation parameters

Parameter	*Value*	*Unit*
Load	3.36	Kg
Radius	5	mm
Circumference	31.4	mm
Hardness of the SDSS	101	$\frac{kg}{mm^3}$

Table 7 - Wear volume data

Lubricant	***Test number***	***Sliding distance [mm]***	***Wear volume [mm^3]***	***K - value***	***Average K***
Reference lubricant	Test 1	5777.6	0.01293	1.35E-04	0.0001272
	Test 2	6876.6	0.01096	1.20E-04	
Thickener A	Test 1	14506.8	0.01615	7.57E-05	7.46283E-05
	Test 2	14506.8	0.01966	7.36E-05	
Thickener B	Test 1	8321	0.00700	5.61E-05	6.23881E-05
	Test 2	7284.8	0.00668	6.86E-05	
Thickener C	Test 1	10048	0.00915	6.53E-05	5.82972E-05
	Test 2	14538.2	0.00958	5.12E-05	
Thickener D	Test 1	14506.8	0.01024	6.39E-05	7.51488E-05
	Test 2	7912.8	0.00750	8.64E-05	

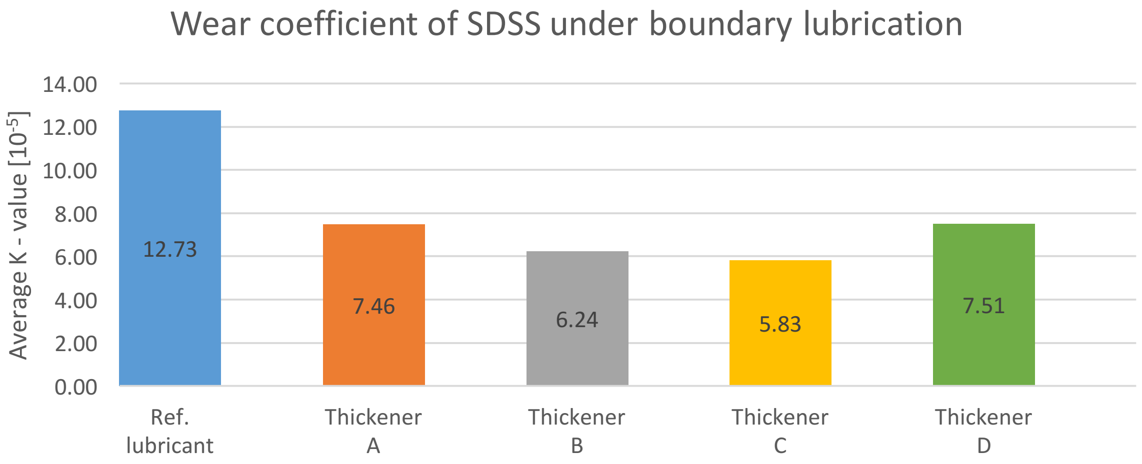


Figure 39 - K -value from Archard's wear volume calculations

In Figure 39, the wear coefficient of the different lubricants is presented. Based on the lubricants performance under severe boundary conditions, the reference lubricant show a higher wear coefficient than the formulated lubricants. All formulated lubricants are experiencing less wear than the reference lubricant, where thickener C is providing the lowest wear of SDSS. The wear with Thickener C which is 54% of the wear experienced with the reference lubricant.

A very interesting discovery regarding the wear of the SDSS material was that the reference lubricant delivered the poorest performance, according to the Archard calculations and the boundary lubrication studies. As the wear-performance of the lubricant depends on the constituent molecules that are present in the contact [30], an additive supplying a lowering of COF in expense of the wear may be assumed to be present. This additive is probable softening the surface of the SDSS substrate, leading to a lowering in COF. This softening is again leading to an increase in abrasive wear, as the hard alumina counter-surface will plough and remove the soft material. When the softer material is removed, the additive will again react with the fresh surface, supplying a new soft surface. This means that the additive will gradually degrade the surface as long as there are enough additive-reactive molecules in the lubricant.

The objective of this thesis was to formulate lubricants with COF and wear reducing properties, but the importance of them is not specified. Reducing the COF in expense of increased wear is not negative for the compensating mechanism the DRTS is supplying. A higher COF will reduce the compensating abilities of the tensioner system, which may lead to detrimental situations for the riser. The increase in COF will make the piston rod harder to move and the compensation of the riser will be reduced. If the compensated forces are lower than the required forces of the system, the integrity of the riser may be damaged. This is turn will result in failure of the riser. This means that the properties of low COF and low wear may not be obtainable for the lubricant in question, and a compromise between the two must be considered. The choice between the two needs to take into consideration the effect between the COF and the compensating abilities of the tensioner system. This can only be done by simulation and experimental studies, which means that this needs to be further assessed.

Due to the short test time for the boundary lubrication studies, it is difficult to say for certain which thickener results in the lowest wear in extended service. This is because the studies performed in this thesis may not describe the full service of the lubrication. The run-in period and other characteristics may influence the wear and friction of the system, thus leading to other results then presented in this thesis. The time is important due to the irregularity of the COF noticed in Figure 32, and longer test studies would provide a more accurate, and clearer result.

4.6 Summary

The thickener properties are summarized in Table 8 and Figure 40. The sole purpose of Figure 40 is to show the differences between the thickeners. The foundation of the scale is not clearly defined and cannot be read as is. It is only for illustrative purposes.

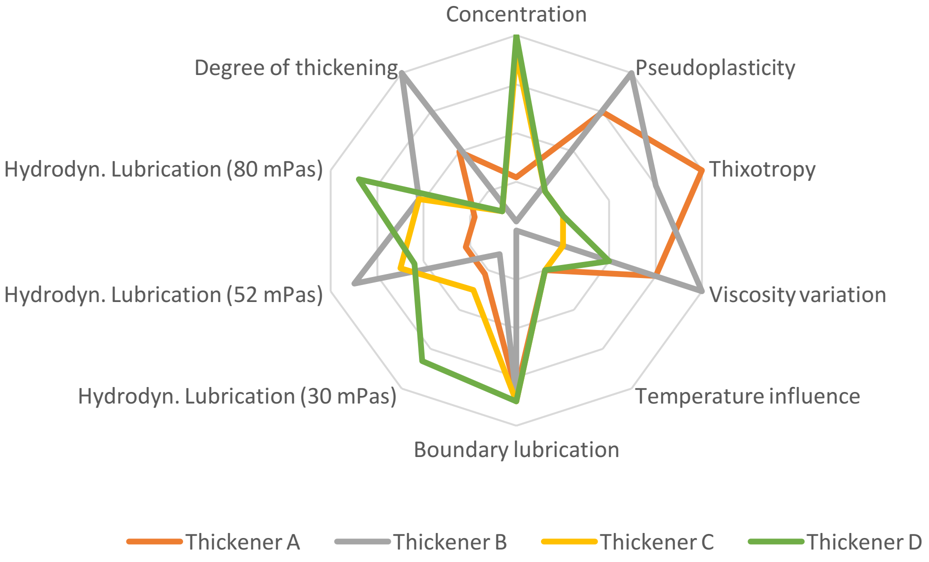


Figure 40 - Thickener properties

In Table 8, the most important properties of the thickeners are ranged from very low, low, medium, high and very high. The table is colour-labelled for showing what properties are prioritized in a hydraulic cylinder application.

Table 8 - Qualitative representation of the thickener properties

	Thickener A	**Thickener B**	**Thickener C**	**Thickener D**
Concentration	Low	Very low	High	High
Pseudoplasticity	High	Very high	Low	Low
Thixotropy	Very high	High	Low	Low
Viscosity variation	High	Very high	Low	Medium
Temperature influence on viscosity	Low	Very low	Low	Low
COF at boundary lubrication	High	High	High	High
COF at hydrodynamic lubrication (30 mPas)	Low	Very low	Medium	High
COF at hydrodynamic lubrication (52 mPas)	Low	Very high	High	Medium
COF at hydrodynamic lubrication (80 mPas)	Low	Medium	Medium	High
Degree of thickening	Medium	Very high	Low	Low

5 Conclusions

The best thickener for the DRTS, N-line application is not easily identified. By analysing the results, there is not a clear candidate. Thickener A is showing some very promising results in terms of hydrodynamic lubrication. Under hydrodynamic lubrication, Thickener A is showing a very low change of COF with viscosity. This behaviour is desired because it reduces the negative effects of shear thinning. Especially since shear-thinning behaviour is not a property that is desired. This indicates that the high pseudoplasticity observed, may not accelerate wear over time.

Thickener B is showing the most unstable results, highest pseudoplasticity and high thixotropic characteristics. With the poor results observed from the hydrodynamic and boundary lubrication studies, Thickener B is not an ideal candidate for the lubricant used in the hydraulic application. More studies with Thickener B needs to be performed, in order to decide if this modifier can be discarded. The formulation procedure is probably a key factor to improve the stability of this thickener. The main advantage of Thickener B is the low concentrations required to thicken the fluid.

The last thickeners, C and D are showing some very promising results, where Thickener C is the best alternative of the two. This is quite interesting, as the high molecular weight is usually used for thickeners of this chemical [27]. The reason Thickener C is the preferred choice of the two, is based on the higher shear stability, the lower COF achieved under hydrodynamic lubrication and the lower wear at boundary lubrication.

The goal of this thesis was to investigate how to reduce the COF and wear of the piston cylinder. This is made possible by using the Thickener C as a thickener for the lubricant used in the riser tensioner system. Thickener C provides low COF at hydrodynamic lubrication, low wear at boundary lubrication, low influence on temperature on viscosity and near-Newtonian shear behaviour.

6 Further work

In order to formulate a fully functioning lubricant that may be applied in a hydraulic application, several steps need to be investigated and studied. The lubricant may be further developed by improving the lubricating properties. This can be done in several ways.

The promising features of Thickener C may be used further where modified types are tested. Additionally, the Thickener C is in need of extreme-pressure additives, which will change the overall behaviour of the lubricant. This change may be positive or negative and this effect is necessary to investigate. Other thickener types that have not been tested in this thesis is also interesting to study. In example polyalkylenglycol. Combinations between thickeners is also important, as it is widely used to achieve the properties desired. Thickener C is a good candidate for this.

The tribo-chemical conditions that takes place during boundary lubrication for water-glycol lubricants is an important topic to study. The results could provide an understanding on how well the lubricant is behaving in this contact and could help reduce both the COF and wear.

The effect of polymer network-structures on the lubrication of the hydraulic cylinder may also be studied. Zhain et al [31], found that Thickener A and C in aqueous solutions formed complex network-structures in the fluid. The structures depended on the formulation parameters as stirring time, rate, concentration and molecular weight. These factors were also recognized as important when formulating the different lubricants in this thesis. The viscosity, time dependency and pseudoplastic behaviour showed sign of variation when the formulation factors were altered. The importance of the polymer network-structures on COF, wear and lubricant properties needs to be further assessed to understand the complex lubricating mechanisms that occur.

7 References

[1] C. B. von der Ohe, R. Johnsen og N. Espallargas, «A review of piston rod failure cases and alternative concepts,» *OMAE,* 2009.

[2] C. B. von der Ohe, «Complex degradation mechanisms,» NTNU, 2011.

[3] C. B. von der Ohe, R. Johnsen og N. Espallargas, «Premature failure of riser tensioner piston rods exposed to offshore splash zone operation - status and review of critical multi-degradation factors,» i *NACE*, 2009.

[4] M. Tyrhaug, «Study of the tribological degradation mechanisms in offshore hydraulic cylinders,» NTNU, 2013.

[5] P. Skjerstad, «Tribological performance of polymers and lubricants used in offshore compensating hydraulic cylinders,» NTNU, 2014.

[6] J. Iversen, «Complex degradation mechanisms in offshore conditions,» NTNU, 2015.

[7] B. Stachowiak og A. Batchelor, Engineering tribology, Elsevier Science Publishers B.V., 1993.

[8] B. Stachowiak og A. Batchelor, «Chapter 16 - Wear of non-Metallic Materials,» i *Engineering tribology*, Elsevier Science Publishers B.V., 1993, pp. 679-705.

[9] B. Bhushan, «Modern tribology handbook,» CRC press, 2001.

[10] R. Flitney, «Chapter 4 - Reciprocating seals,» i *Seals and sealing handbook*, 5 red., Oxford, Elsevier Science, 2007.

[11] F. Cardarelli, «Materials handbook,» Arizona, Springer, 2005, pp. 702-703.

[12] K. Markus og C. Allen, «The sliding wear of ultrahigh molecular weight polyethylene in an aqueous environment,» *WEAR,* vol. 178, pp. 17-28, 1994.

[13] S. Materials, «Sandvik Materials Technology,» 1 September 2015. [Internett]. Available: http://smt.sandvik.com/en/materials-center/material-datasheets/tube-and-pipe-seamless/sandvik-saf-2507/. [Funnet 2015].

[14] MatWeb, «Alumina material data sheet,» [Internett]. Available: http://www.matweb.com/search/DataSheet.aspx?MatGUID=0654701067d147e88e8a38c646dda195&ckck=1. [Funnet March 2016].

[15] J. Brophy og V. Fitzsimmons, «Aqueous non-flammable hydraulic fluids,» *Industrial & Engineering Chemistry,* vol. 43, nr. 4, pp. 884-896, 1950.

[16] G. Totten og Y. Sun, «Chapter 18 – Water-Glycol Hydraulic Fluids,» i *Handbook of hydraulic fluid* , New York, Marcel Dekker, 2000, pp. 917-946.

[17] D. C. Rasp, «Water-based hydraulic fluids containing synthetic components,» *Journal of synthetic lubrication,* vol. 6, nr. 3, pp. 233-251, 1989.

[18] BASF, «BASF,» [Internett]. Available: https://www.dispersions-pigments.basf.com/portal/load/fid793184/BASF%20Rheology%20Modifiers%20 Practical%20Guide.pdf . [Funnet January 2016].

[19] DOW, «DOW Acrysol Rheology Modifiers,» [Internett]. Available: http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_08f8/0901b803808 f8b0d.pdf?filepath=coatings/pdfs/noreg/884-00076.pdf&fromPage=GetDoc . [Funnet January 2016].

[20] CONFIDENTIAL.

[21] R. Mortimer og O. ST, Chemistry and technology of lubricants, London: Blackie and Son Ltd, 1992.

[22] L. Rudnick, Lubricant additives chemistry & applications, New York: Marcel Dekker, 2003, pp. 338-345.

[23] K. Mackenzie og J. AE, «Polymer shear stability,» *WEAR,* vol. 17, pp. 389-398, 1971.

[24] G. Totten, «High performance thickened water-glycol hydraulic fluids,» i *The expo and technical conference for electrohydraulics and electropneumatic motion control technology*, Milwaukee, 1994.

[25] A. Tomala og A. Karpinska, «Tribological properties for additives for water-based lubricants,» *WEAR,* vol. 269, pp. 804-810, 2010.

[26] CONFIDENTIAL.

[27] CONFIDENTIAL.

[28] CONFIDENTIAL.

[29] O. Isaksson, «Rheology for water-based hydraulic fluids,» *WEAR,* vol. 115, pp. 3-17, 1987.

[30] A. Misra, M. AK og Srivastava, «Antiwear characteristics of additives: synergistic and adverse effects,» *WEAR,* vol. 31, pp. 345-357, 1975.

[31] CONFIDENTIAL.

[32] CONFIDENTIAL.

Appendix

Rheology

The rheological study of the lubricants was done by using a rheometer. The rheometer in use was a HAAKE mars rotational rheometer.

Two types of studies were performed; a viscosity measurement at 40 ˙C and 500 s^{-1}, and a full rheological study, where several temperatures was tested. This study consisted of a several steps that are elaborated below.

Table 9 - Viscosity measurement at 40 ˙C

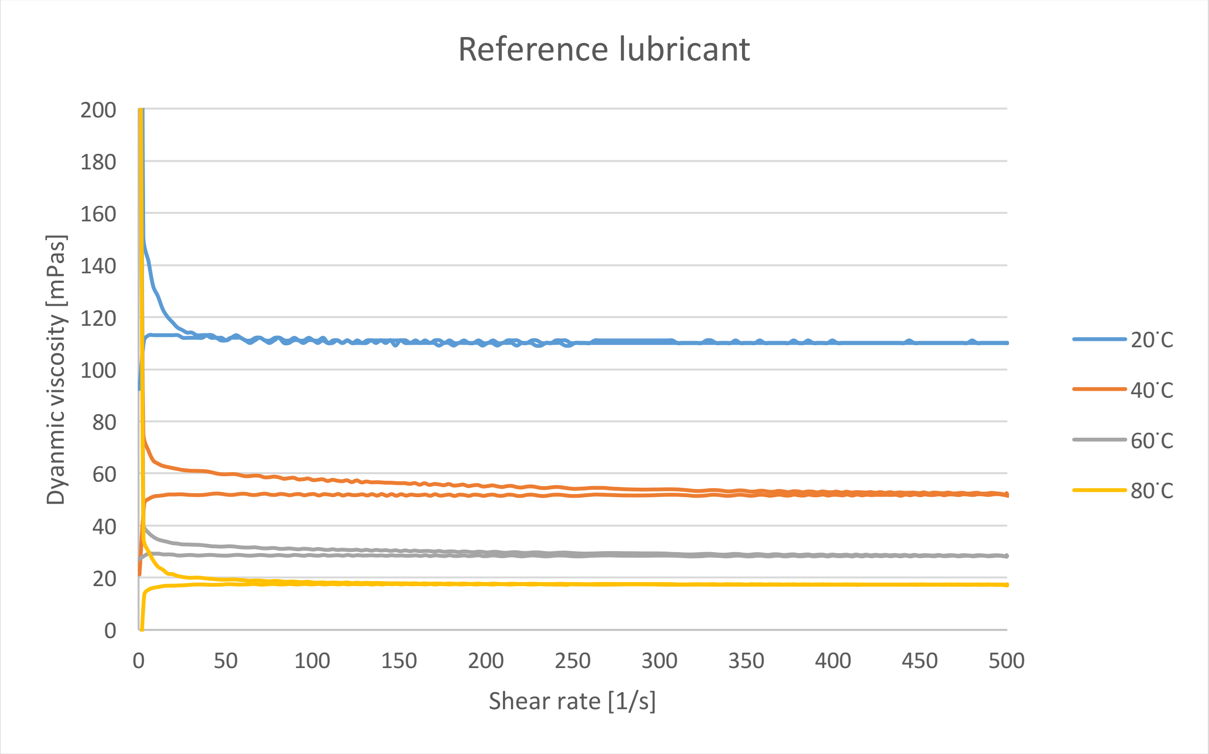
Step	**Description**	**Shear rate [s^{-1}]**	**Temperature [˙C]**
1	Heating of the lubricant	0	40
2	Linear increase of shear rate over 180 seconds	0 → 500	40
3	Constant shear rate over 30 seconds	500	40
4	Linear decrease of shear rate over 180 seconds	500 → 0	40

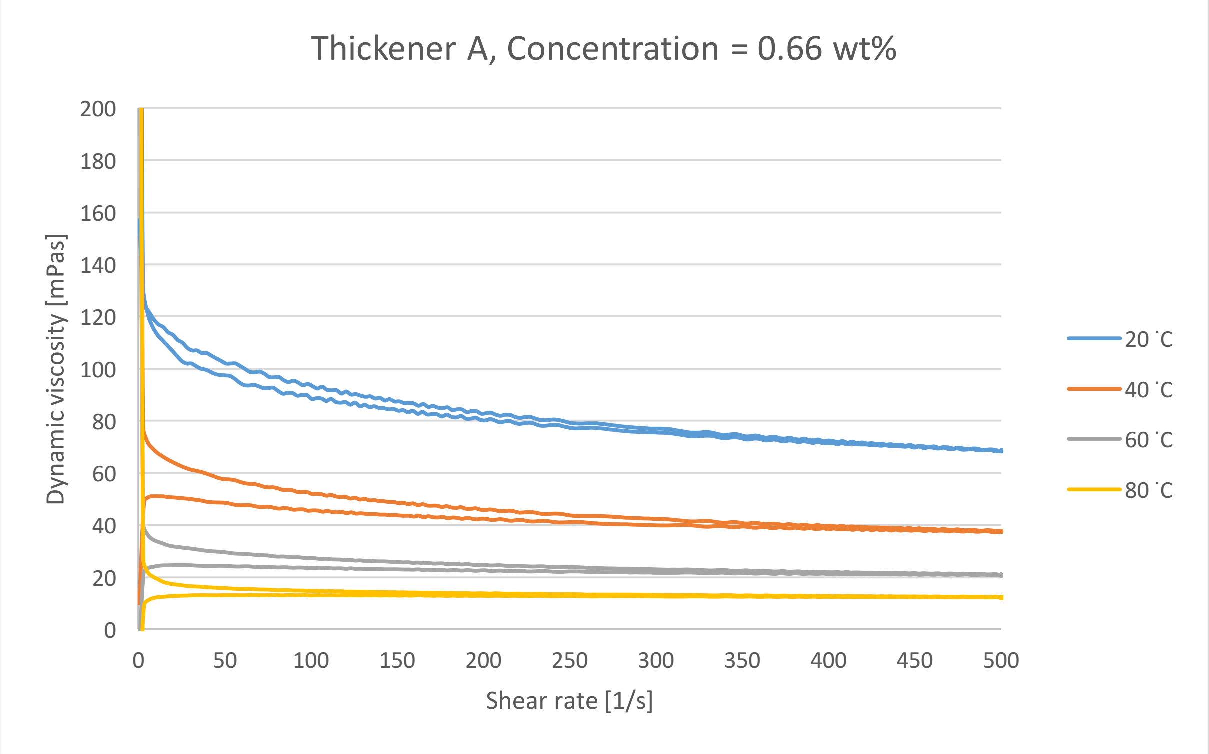
Table 10 - Full rheological study

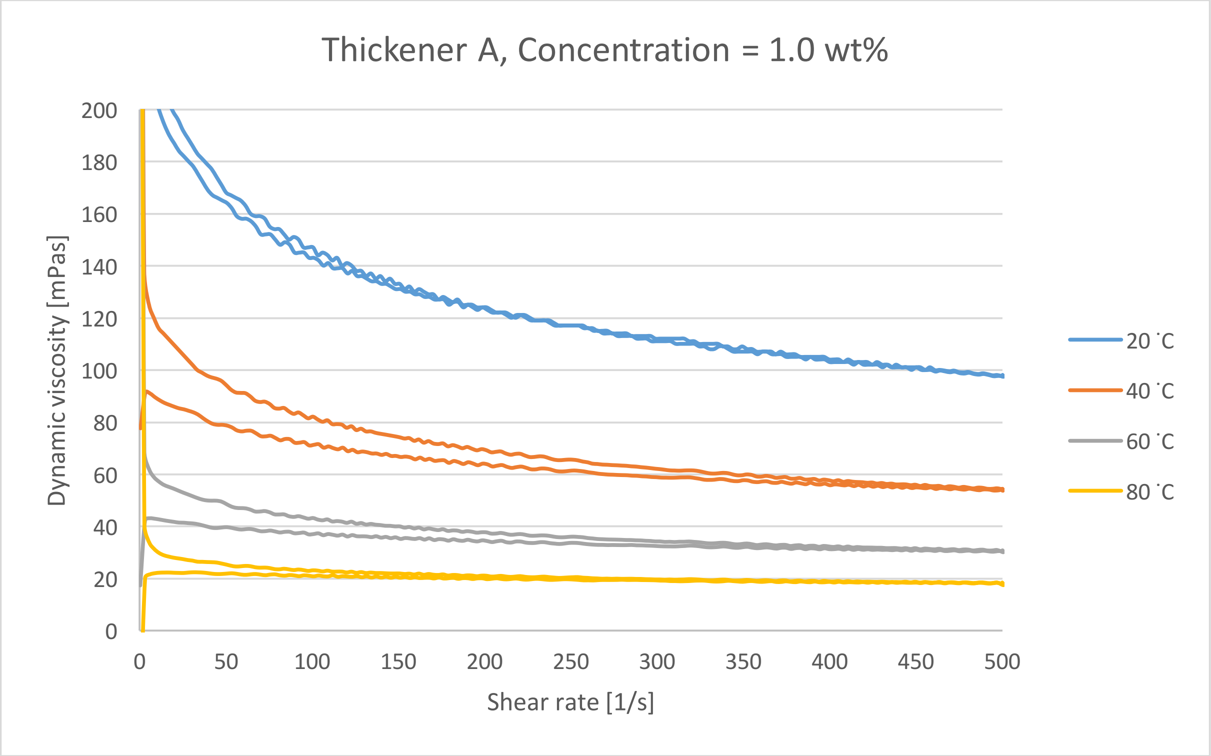
Step	**Description**	**Shear rate [s^{-1}]**	**Temperature [˚C]**
1	Heating of the lubricant	0	20
2	Linear increase of shear rate over 180 seconds	0 → 500	20
3	Constant shear rate over 30 seconds	500	20
4	Linear decrease of shear rate over 180 seconds	500 → 0	20
5	Heating of the lubricant	0	40
6	Linear increase of shear rate over 180 seconds	0 → 500	40
7	Constant shear rate over 30 seconds	500	40
8	Linear decrease of shear rate over 180 seconds	500 → 0	40
9	Heating of the lubricant	0	60
10	Linear increase of shear rate over 180 seconds	0 → 500	60
11	Constant shear rate over 30 seconds	500	60
12	Linear decrease of shear rate over 180 seconds	500 → 0	60
13	Heating of the lubricant	0	80
14	Linear increase of shear rate over 180 seconds	0 → 500	80
15	Constant shear rate over 30 seconds	500	80
16	Linear decrease of shear rate over 180 seconds	500 → 0	80

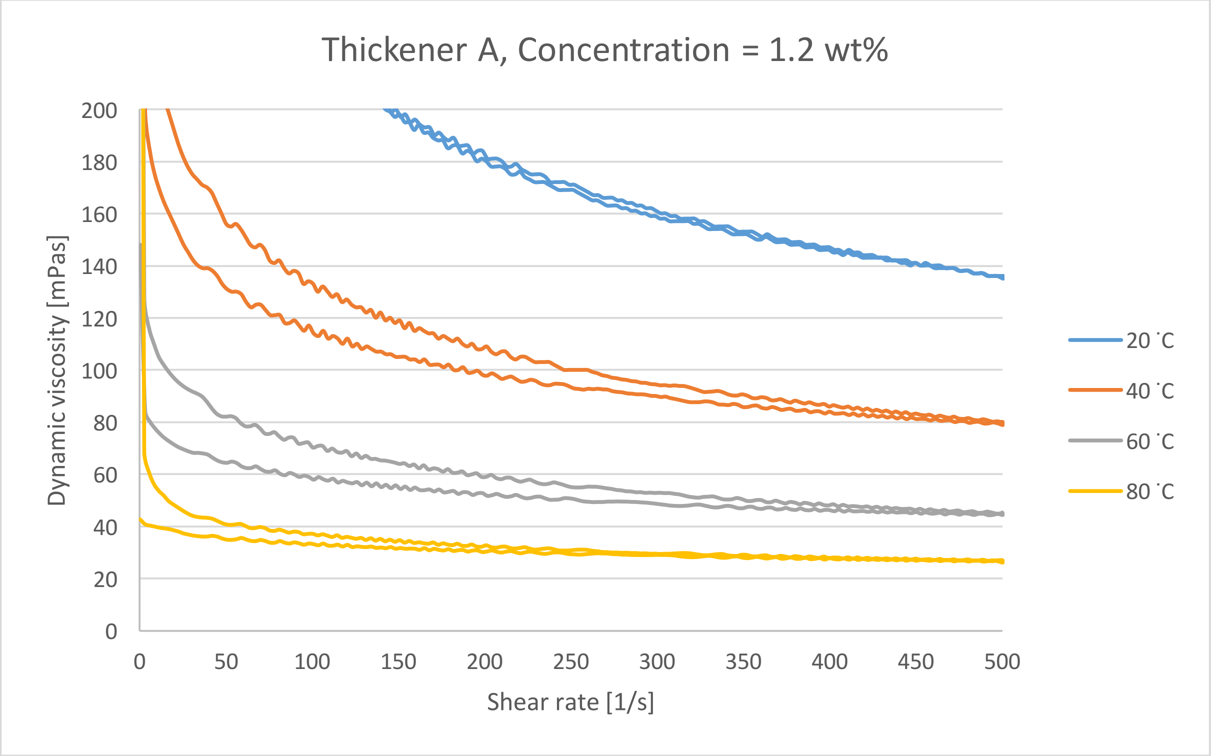
Figure 41 - Full rheological profile study

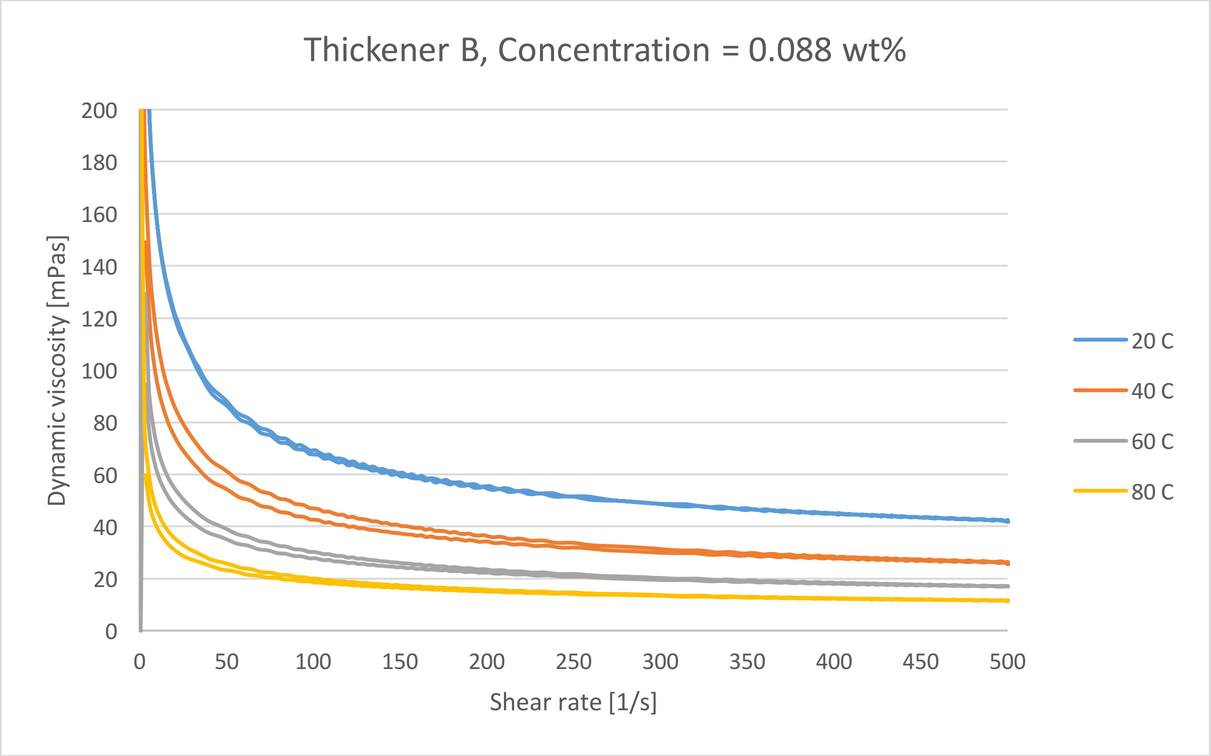
Rheology study

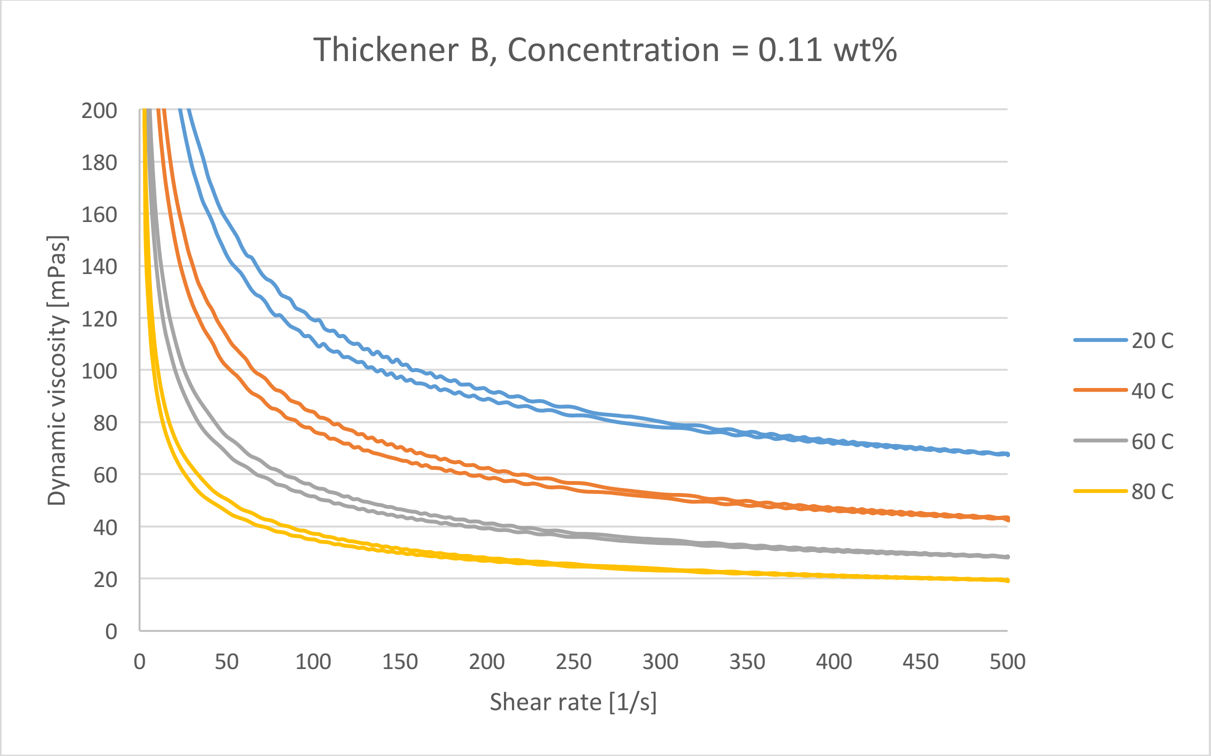


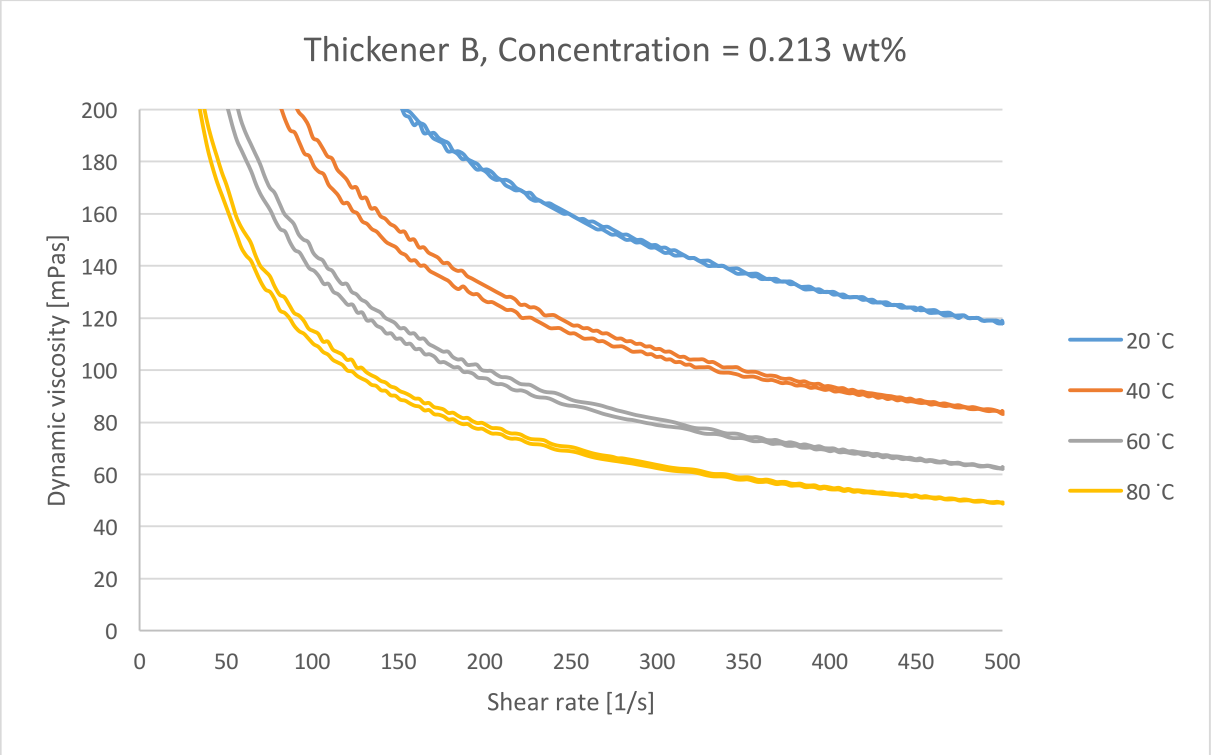


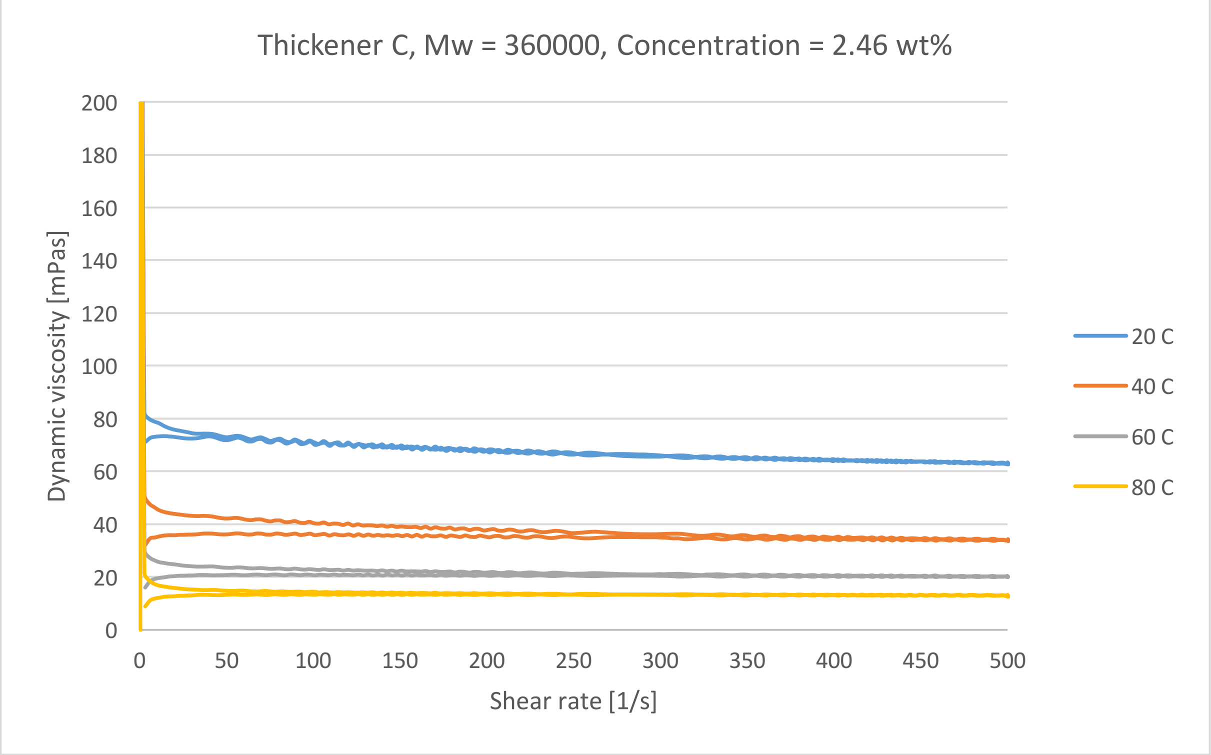

Thickener A, Concentration = 1.0 wt%
Dynamic viscosity [mPas]
200
180
160
140
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
450
500
Shear rate [1/s]
20 ˚C
40 ˚C
60 ˚C
80 ˚C

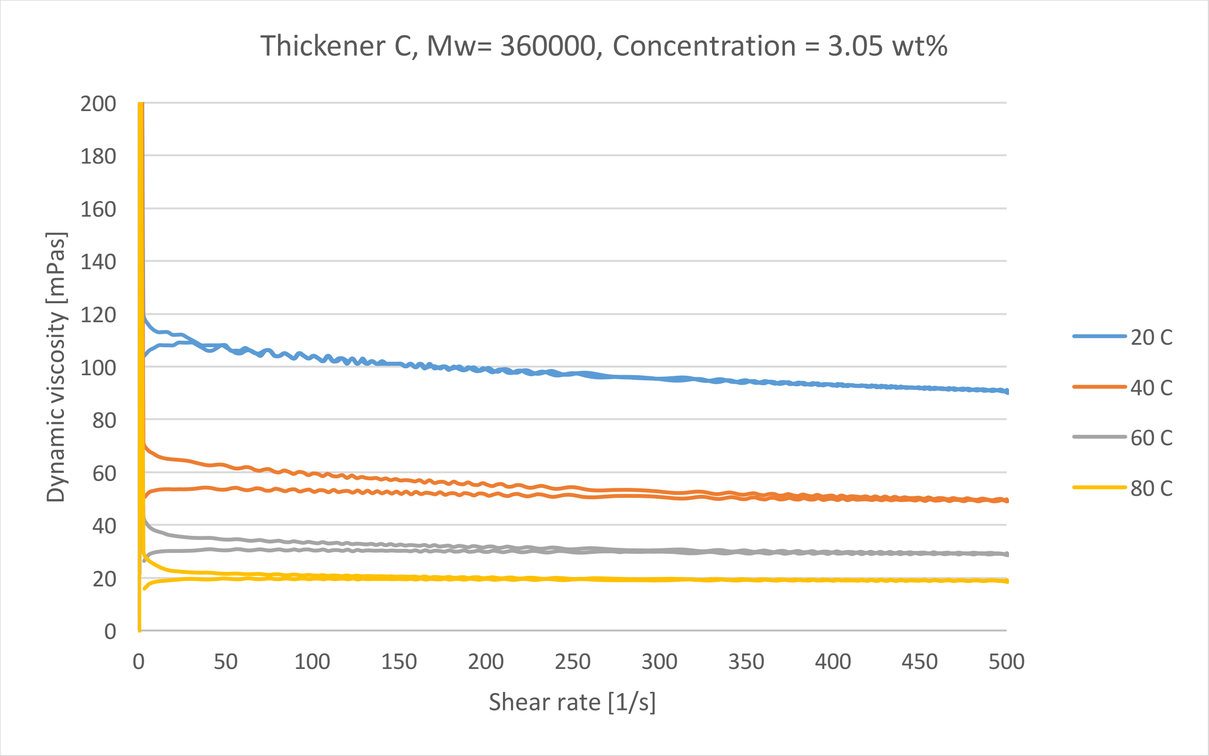

Thickener A, Concentration = 1.2 wt%
Dynamic viscosity [mPas]
200
180
160
140
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
450
500
Shear rate [1/s]
20 ˚C
40 ˚C
60 ˚C
80 ˚C

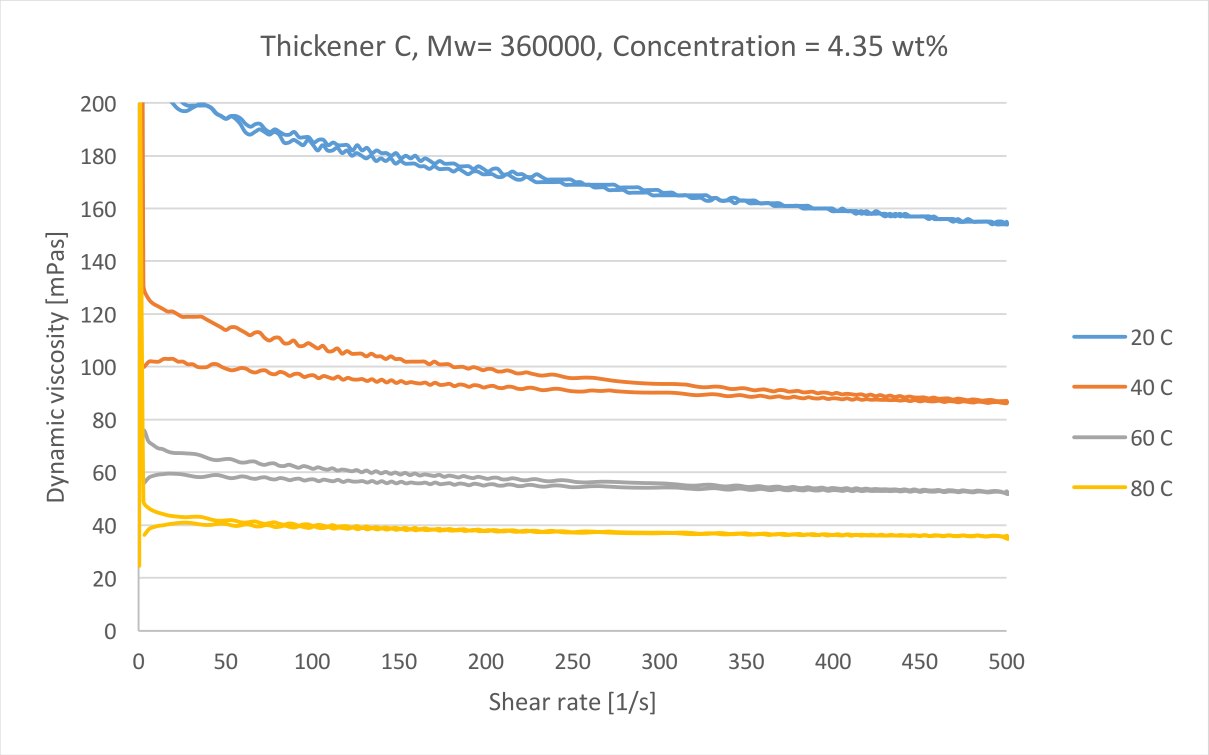

Thickener B, Concentration = 0.088 wt%
Dynamic viscosity [mPas]
200
180
160
140
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
450
500
Shear rate [1/s]
20 C
40 C
60 C
80 C

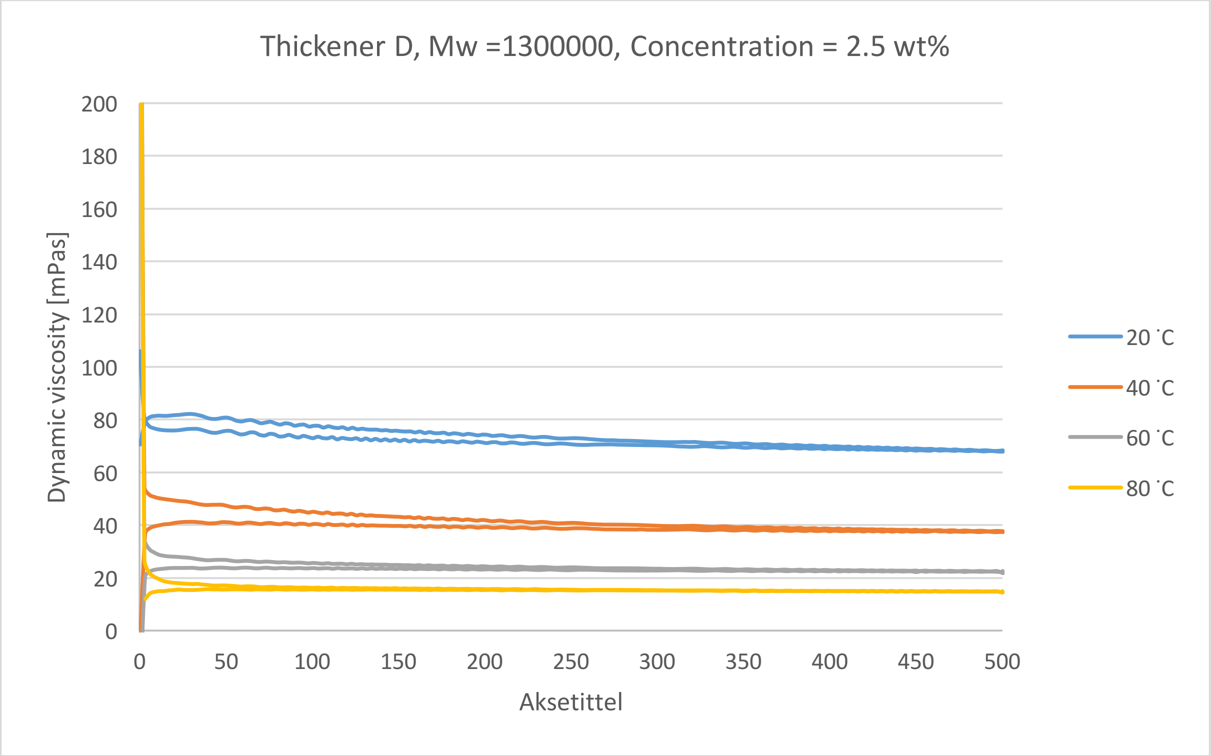

Thickener B, Concentration = 0.11 wt%
Dynamic viscosity [mPas]
200
180
160
140
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
450
500
Shear rate [1/s]
20 C
40 C
60 C
80 C

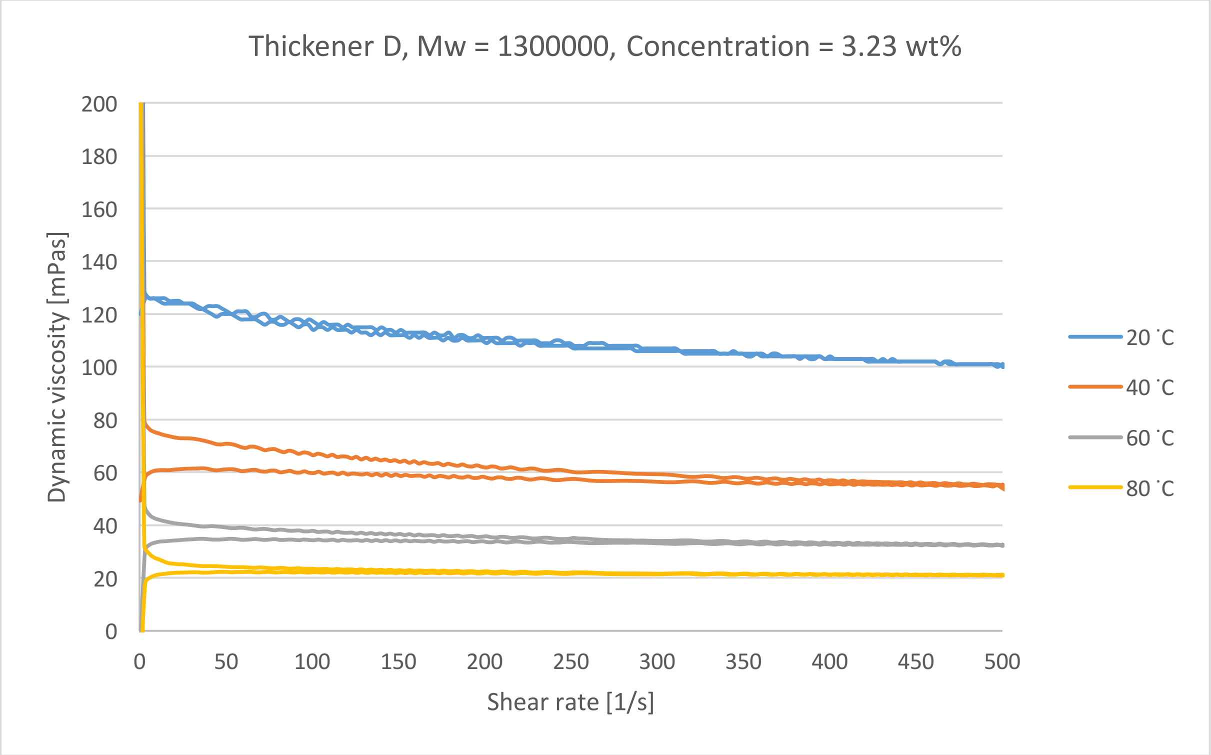

Thickener B, Concentration = 0.213 wt%
Dynamic viscosity [mPas]
200
180
160
140
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
450
500
Shear rate [1/s]
20 ˚C
40 ˚C
60 ˚C
80 ˚C

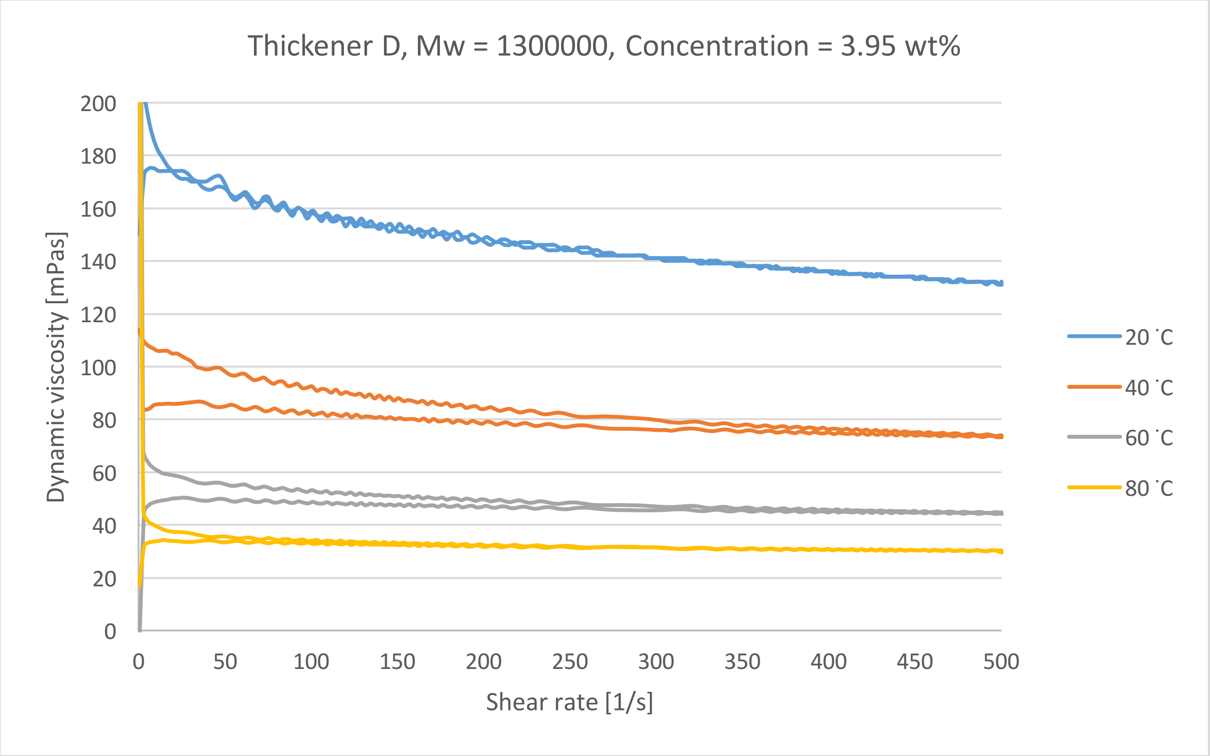

Thickener C, Mw = 360000, Concentration = 2.46 wt%
Dynamic viscosity [mPas]
200
180
160
140
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
450
500
Shear rate [1/s]
20 C
40 C
60 C
80 C


Thickener C, Mw= 360000, Concentration = 3.05 wt%
Dynamic viscosity [mPas]
200
180
160
140
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
450
500
Shear rate [1/s]
20 C
40 C
60 C
80 C

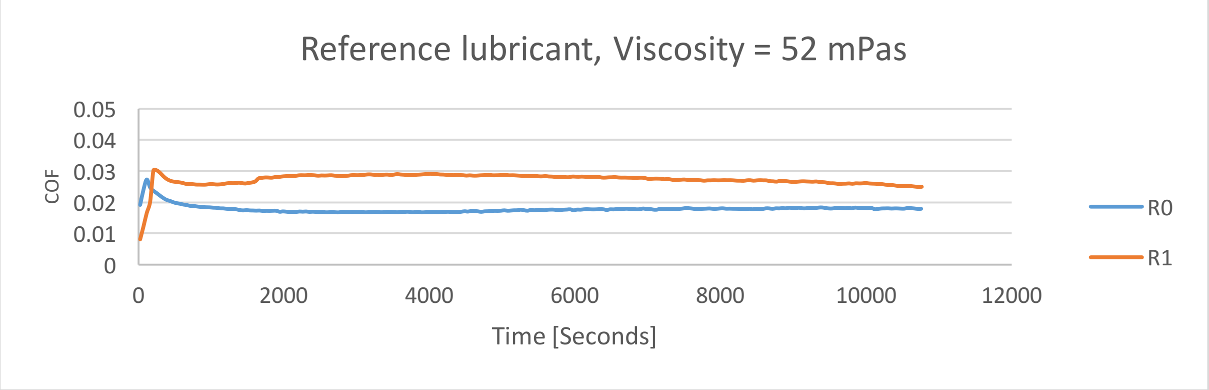

Thickener C, Mw= 360000, Concentration = 4.35 wt%
Dynamic viscosity [mPas]
200
180
160
140
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
450
500
Shear rate [1/s]
20 C
40 C
60 C
80 C

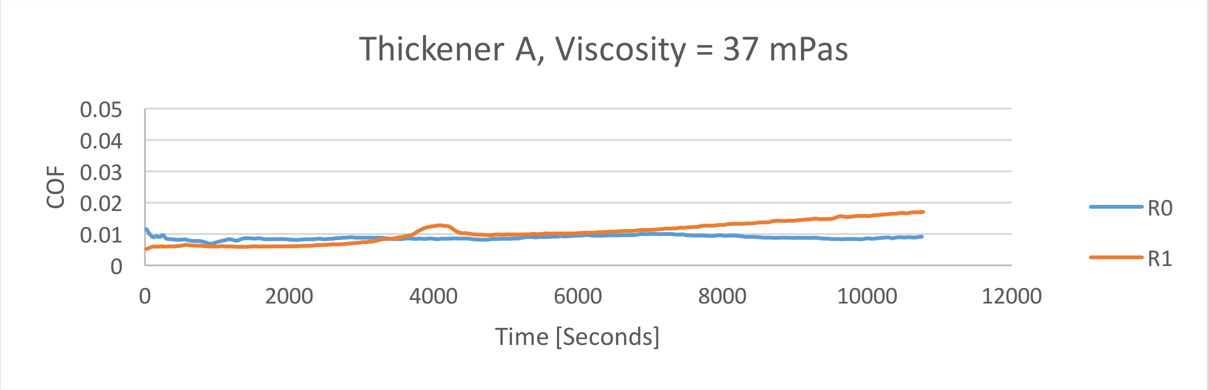

Thickener D, Mw =1300000, Concentration = 2.5 wt%
Dynamic viscosity [mPas]
200
180
160
140
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
450
500
Aksetittel
20 ˙C
40 ˙C
60 ˙C
80 ˙C

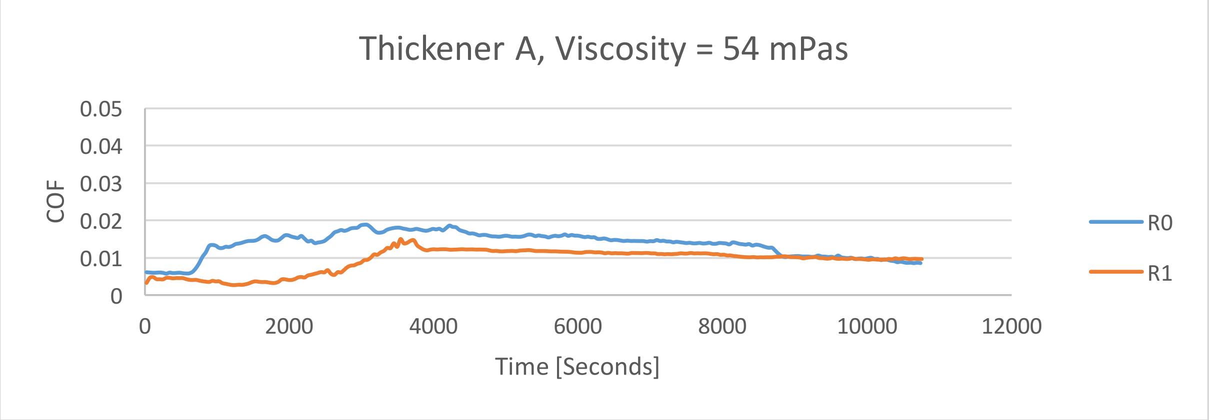

Thickener D, Mw = 1300000, Concentration = 3.23 wt%
Dynamic viscosity [mPas]
200
180
160
140
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
450
500
Shear rate [1/s]
20 ˙C
40 ˙C
60 ˙C
80 ˙C

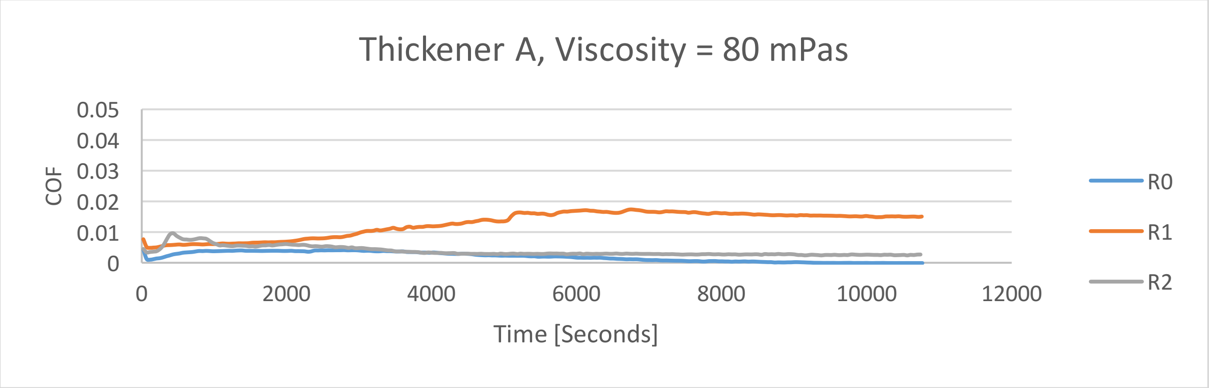

Thickener D, Mw = 1300000, Concentration = 3.95 wt%
Dynamic viscosity [mPas]
200
180
160
140
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
450
500
Shear rate [1/s]
20 ˙C
40 ˙C
60 ˙C
80 ˙C

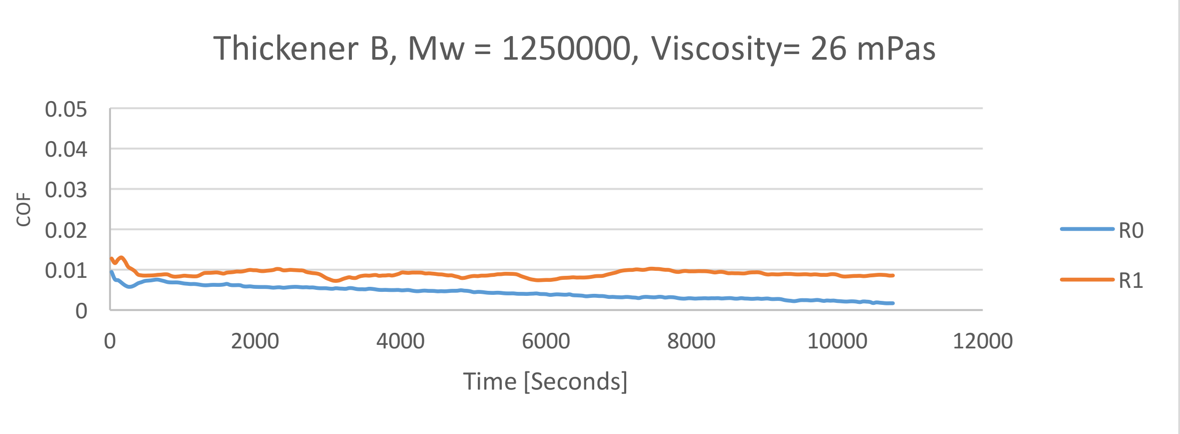
TE88 results

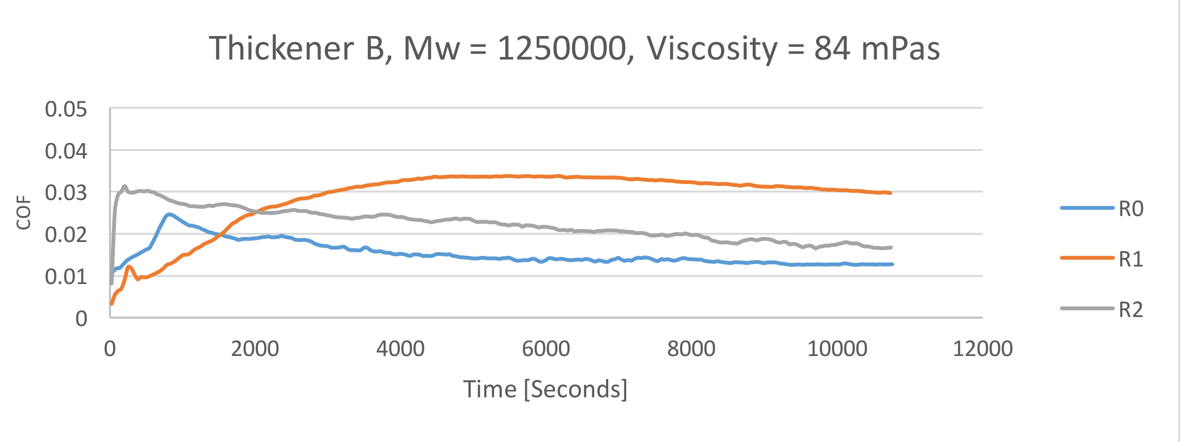


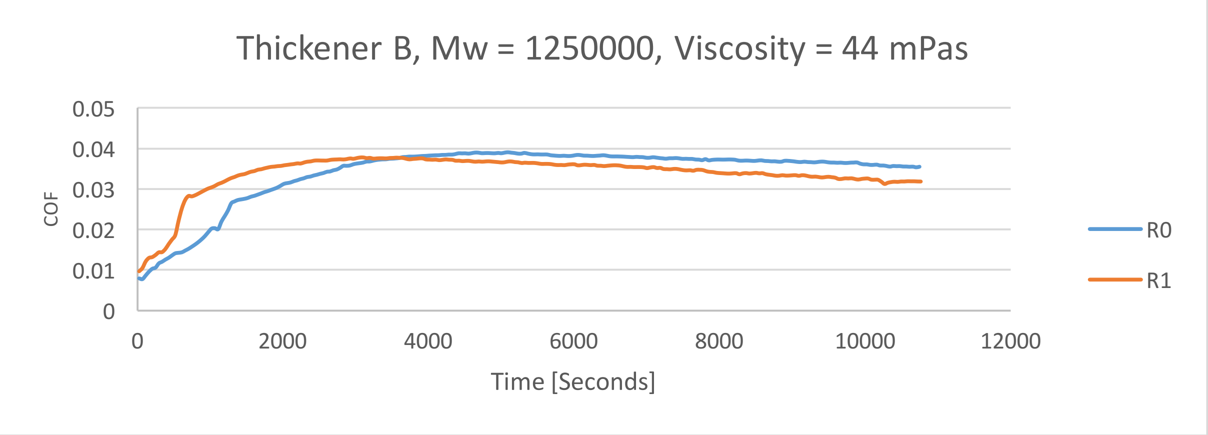


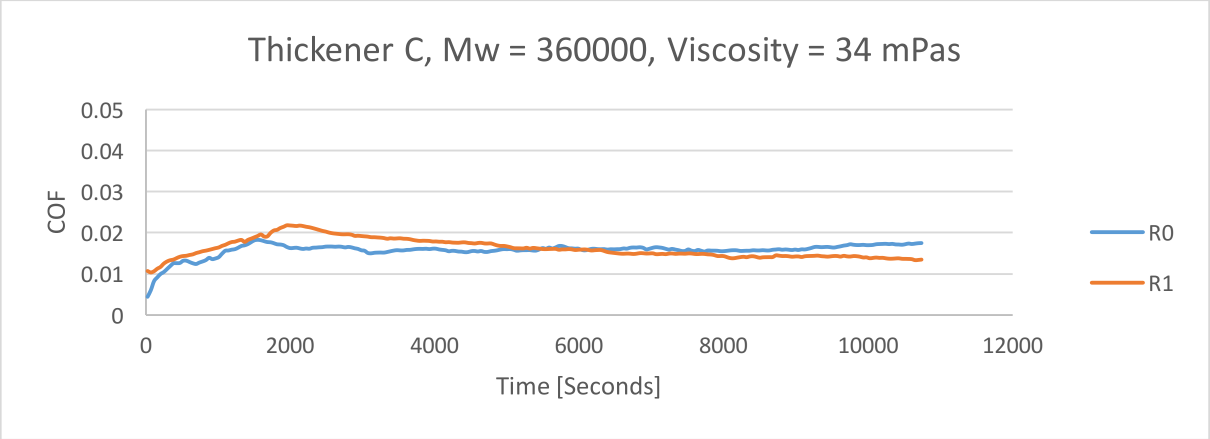


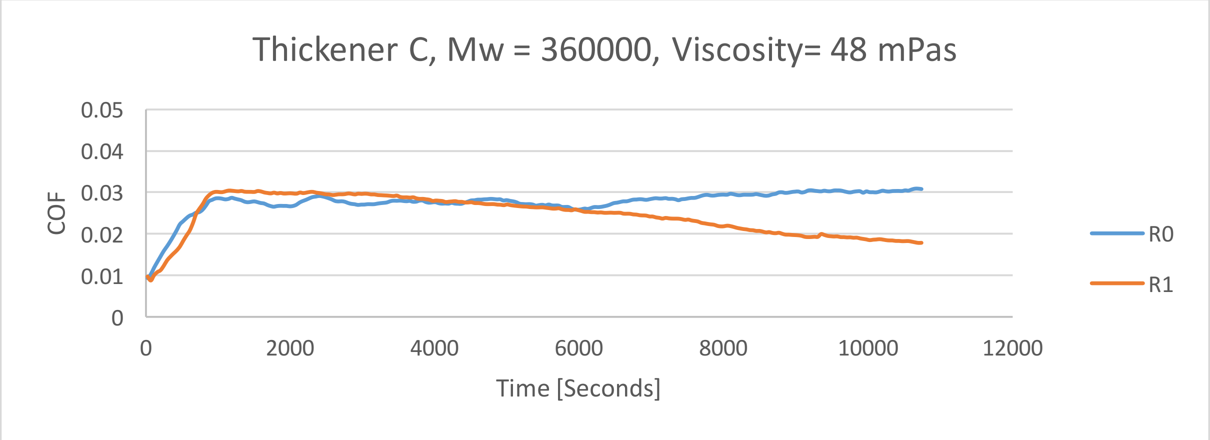


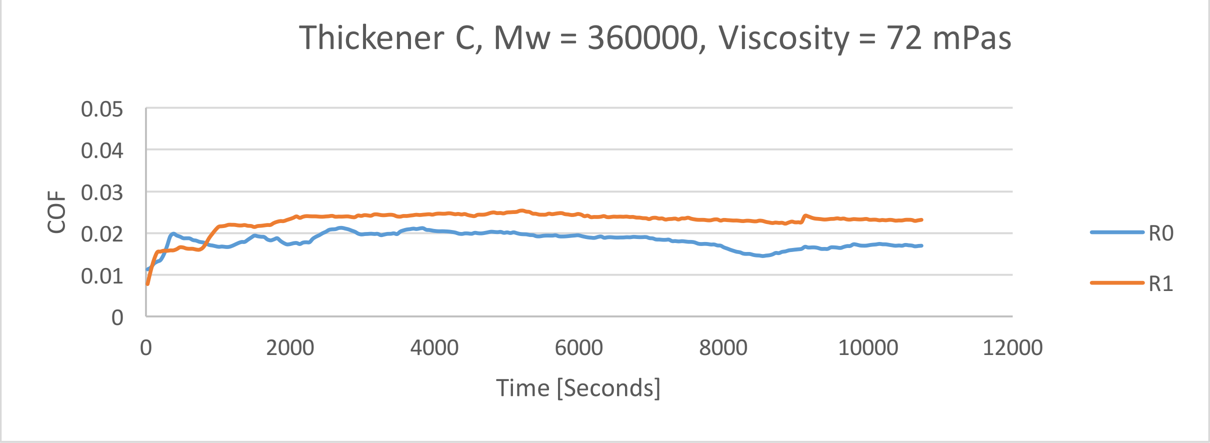

Thickener B, Mw = 1250000, Viscosity= 26 mPas
COF
0.05
0.04
0.03
0.02
0.01
0
0
2000
4000
6000
8000
10000
12000
Time [Seconds]
R0
R1

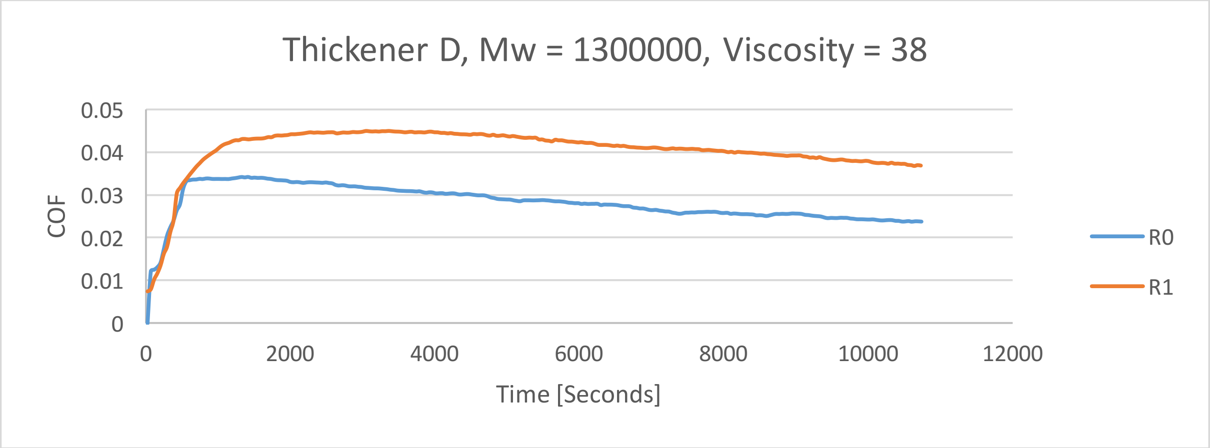

Thickener B, Mw = 1250000, Viscosity = 84 mPas
COF
0.05
0.04
0.03
0.02
0.01
0
0
2000
4000
6000
8000
10000
12000
Time [Seconds]
R0
R1
R2

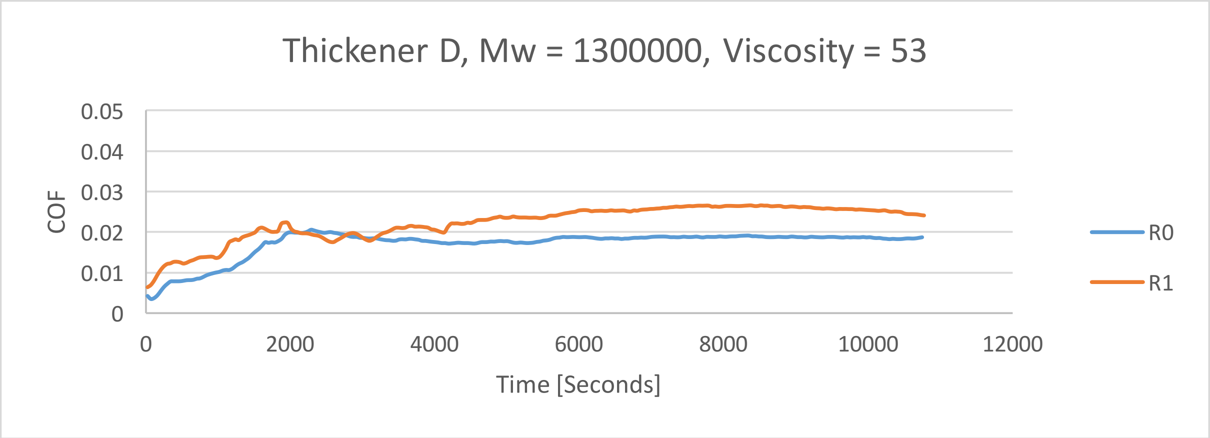

Thickener B, Mw = 1250000, Viscosity = 44 mPas
COF
0.05
0.04
0.03
0.02
0.01
0
0
2000
4000
6000
8000
10000
12000
Time [Seconds]
R0
R1

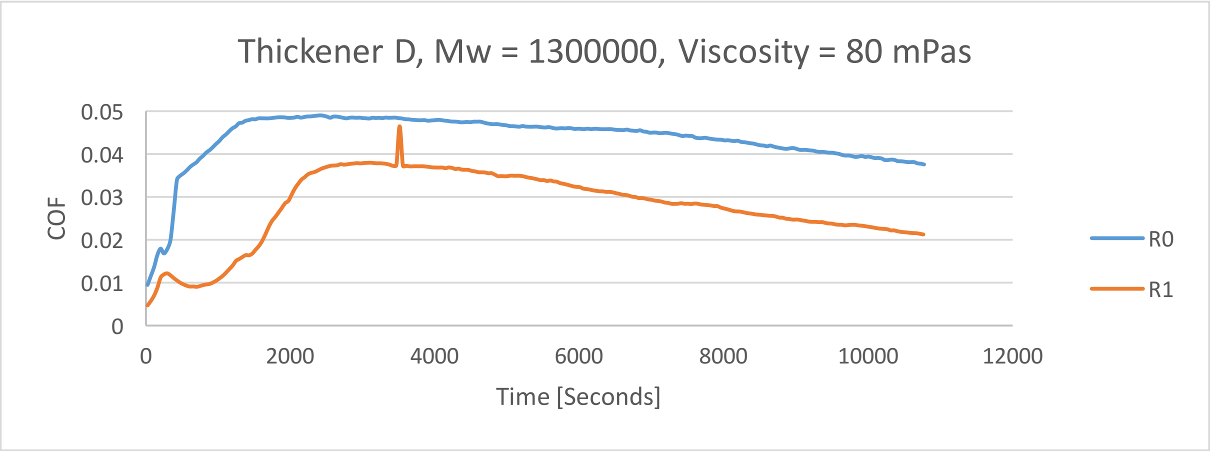

Thickener C, Mw = 360000, Viscosity = 34 mPas
COF
0.05
0.04
0.03
0.02
0.01
0
0
2000
4000
6000
8000
10000
12000
Time [Seconds]
R0
R1


Thickener C, Mw = 360000, Viscosity= 48 mPas
COF
0.05
0.04
0.03
0.02
0.01
0
0
2000
4000
6000
8000
10000
12000
Time [Seconds]
R0
R1


Thickener C, Mw = 360000, Viscosity = 72 mPas
COF
0.05
0.04
0.03
0.02
0.01
0
0
2000
4000
6000
8000
10000
12000
Time [Seconds]
R0
R1


Thickener D, Mw = 1300000, Viscosity = 38
COF
0.05
0.04
0.03
0.02
0.01
0
0
2000
4000
6000
8000
10000
12000
Time [Seconds]
R0
R1


Thickener D, Mw = 1300000, Viscosity = 53
COF
0.05
0.04
0.03
0.02
0.01
0
0
2000
4000
6000
8000
10000
12000
Time [Seconds]
R0
R1


Thickener D, Mw = 1300000, Viscosity = 80 mPas
COF
0.05
0.04
0.03
0.02
0.01
0
0
2000
4000
6000
8000
10000
12000
Time [Seconds]
R0
R1

Hertzian pressure calculations

The input and output for the pin-on-disc experiment and the material data used, is shown below. In this case the number 1 is for the SDSS and number 2 is for the alumina.

Reduced radius:

$$\frac{1}{R'} = \frac{1}{R_x} + \frac{1}{R_y}$$

Reduced Youngs modulus:

$$\frac{1}{E'} = \frac{1}{2}\left(\frac{1 - v_A^2}{E_A} + \frac{1 - v_B^2}{E_B}\right)$$

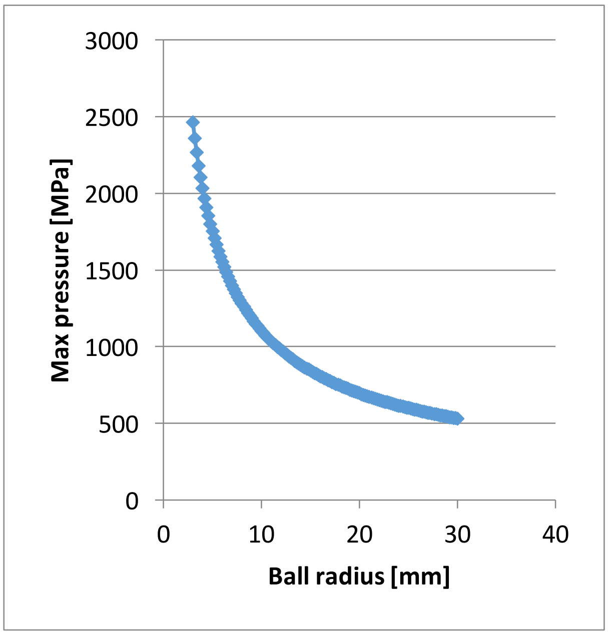
Contact surface:

$$a = \left(\frac{3F_N R'}{E'}\right)^{1/3}$$

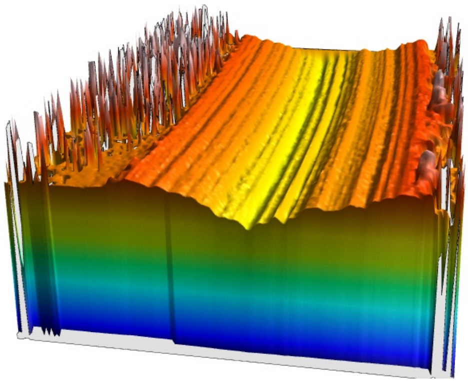
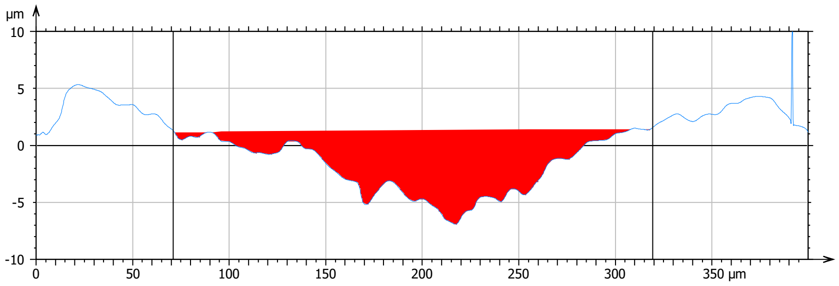
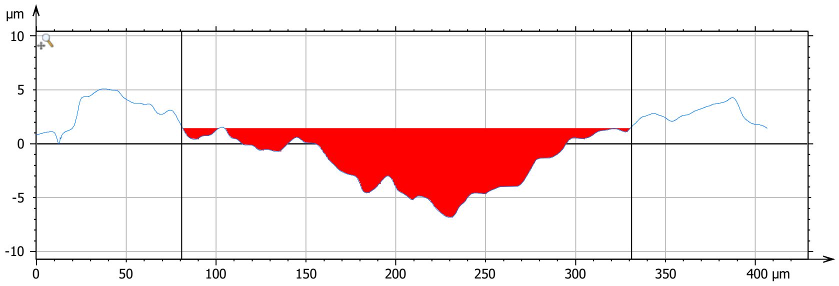
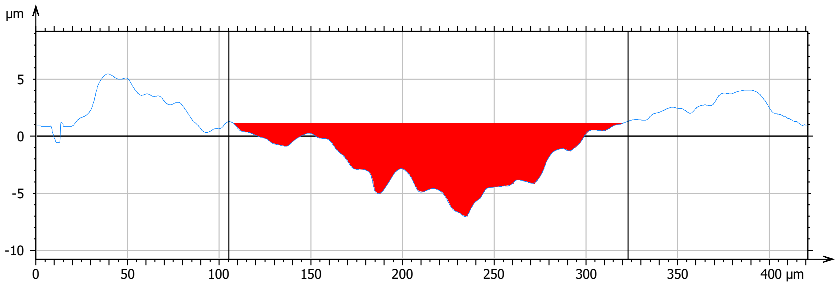
Maximum pressure:

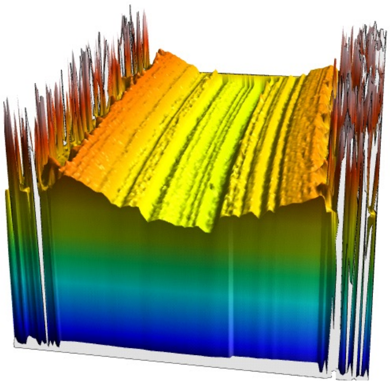
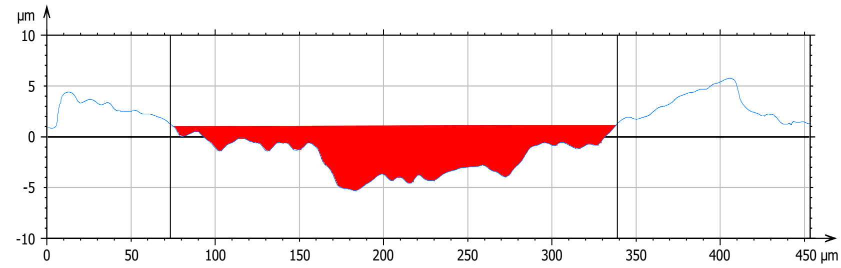
$$P_{Max} = \frac{3F_N}{2\pi a^3}$$

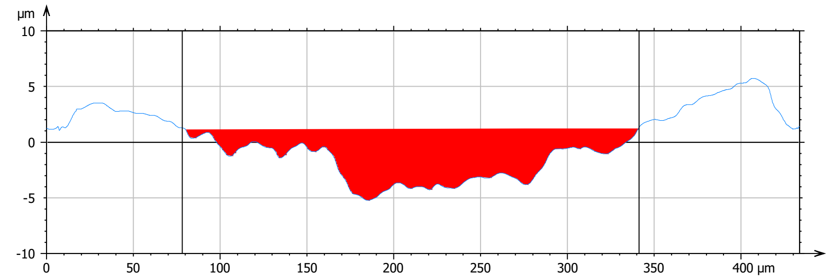
	Ball on Plate		
Input	R ball	3	mm
	Rb	1E+14	mm
	E1	210000	MPa
	E2	370000	MPa
	F	33	N
	v1	0.3	
	v2	0.22	
Output	R`	3	mm
	E`	289636	MPa
	Rcontact	0.0800	mm
	Acontact	0.020114652	mm^2
	Pmax	2460.892711	MPa
	Pmean	1640.595141	MPa

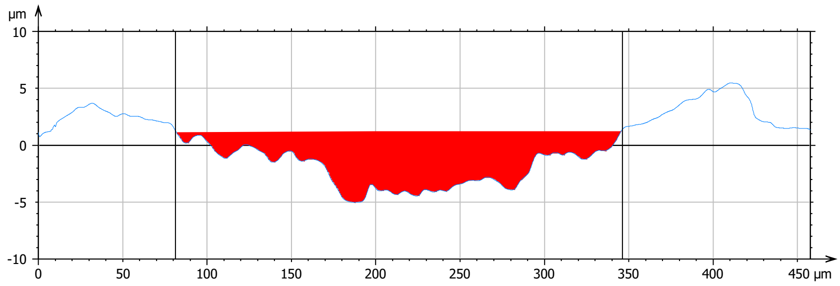


Wear results

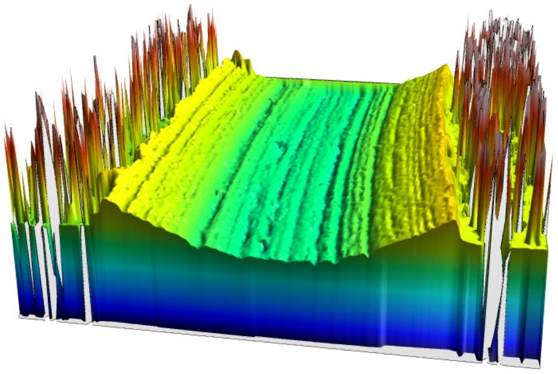
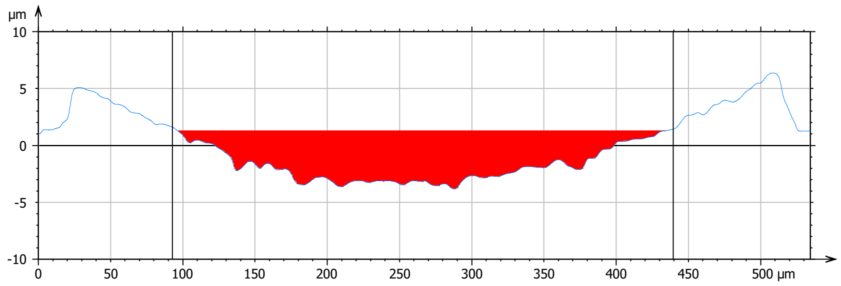
	Reference lubricant R0
 **Parameters** Value Unit Maximum depth 8.37 µm Area of the hole 831 µm²	Wear profile 1
 **Parameters** Value Unit Maximum depth 8.41 µm Area of the hole 860 µm²	Wear profile 2
 **Parameters** Value Unit Maximum depth 8.33 µm Area of the hole 780 µm²	Wear profile 3

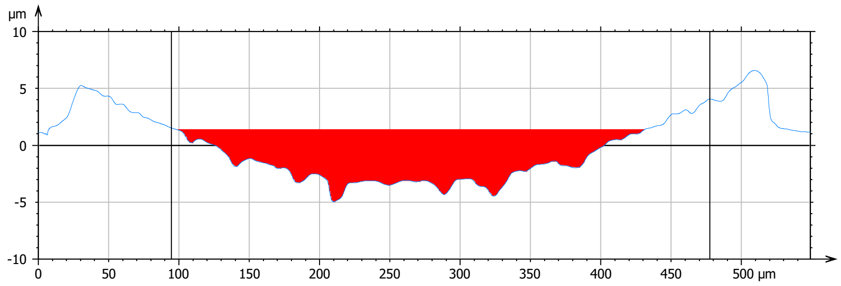
<table>
<tr><td></td><td>Reference lubricant
R1</td></tr>
<tr><td>

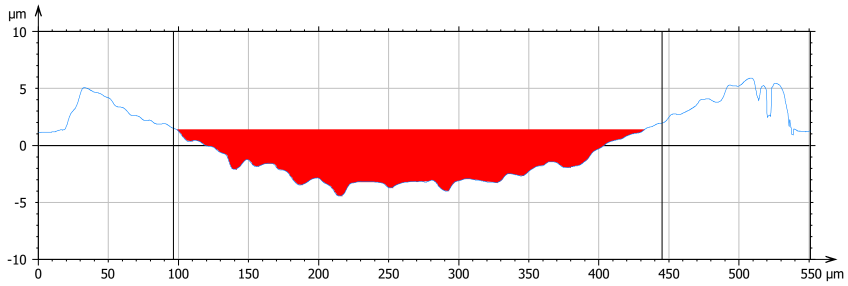
<table>
<tr><th>Parameters</th><th>Value</th><th>Unit</th></tr>
<tr><td>Maximum depth</td><td>6.55</td><td>µm</td></tr>
<tr><td>Area of the hole</td><td>878</td><td>µm²</td></tr>
</table></td><td>Wear profile 1</td></tr>
<tr><td>

<table>
<tr><th>Parameters</th><th>Value</th><th>Unit</th></tr>
<tr><td>Maximum depth</td><td>6.53</td><td>µm</td></tr>
<tr><td>Area of the hole</td><td>853</td><td>µm²</td></tr>
</table></td><td>Wear profile 2</td></tr>
<tr><td>

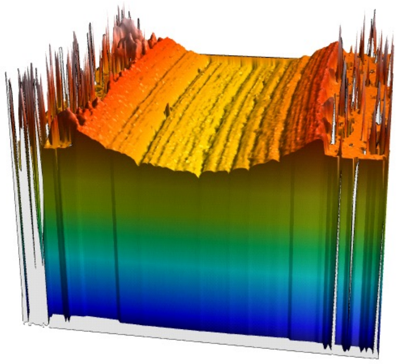
<table>
<tr><th>Parameters</th><th>Value</th><th>Unit</th></tr>
<tr><td>Maximum depth</td><td>6.34</td><td>µm</td></tr>
<tr><td>Area of the hole</td><td>891</td><td>µm²</td></tr>
</table></td><td>Wear profile 3</td></tr>
</table>

<table>
<tr>
<td></td>
<td>Thickener A R0</td>
</tr>
<tr>
<td>

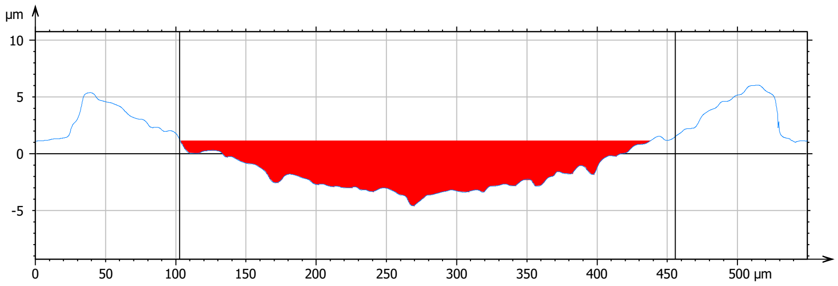
<table>
<tr><th>Parameters</th><th>Value</th><th>Unit</th></tr>
<tr><td>Maximum depth</td><td>5.25</td><td>µm</td></tr>
<tr><td>Area of the hole</td><td>1117</td><td>µm²</td></tr>
</table></td>
<td>Wear profile 1</td>
</tr>
<tr>
<td>

<table>
<tr><th>Parameters</th><th>Value</th><th>Unit</th></tr>
<tr><td>Maximum depth</td><td>6.48</td><td>µm</td></tr>
<tr><td>Area of the hole</td><td>1186</td><td>µm²</td></tr>
</table></td>
<td>Wear profile 2</td>
</tr>
<tr>
<td>

<table>
<tr><th>Parameters</th><th>Value</th><th>Unit</th></tr>
<tr><td>Maximum depth</td><td>5.95</td><td>µm</td></tr>
<tr><td>Area of the hole</td><td>1186</td><td>µm²</td></tr>
</table></td>
<td>Wear profile 3</td>
</tr>
</table>

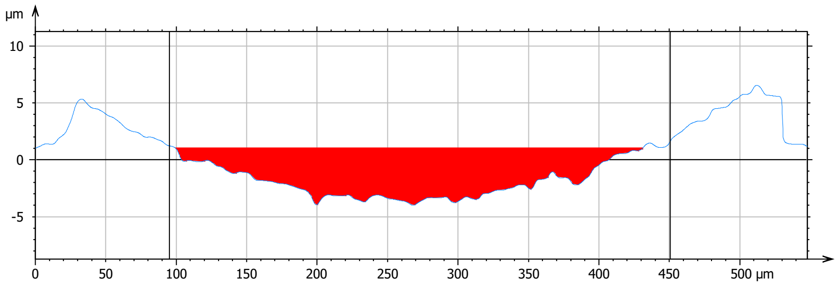


Thickener A R1



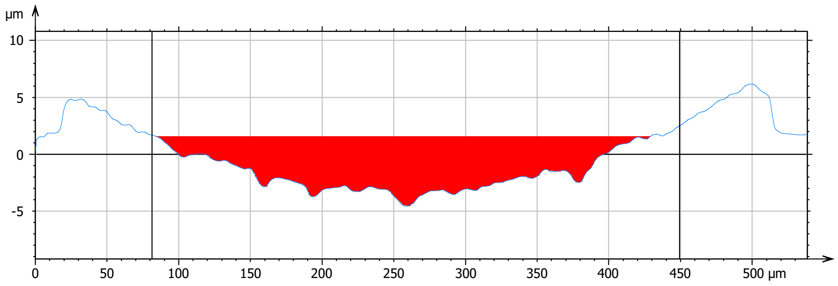
Parameters	Value	Unit
Maximum depth	5.84	µm
Area of the hole	1084	µm²

Wear profile 1



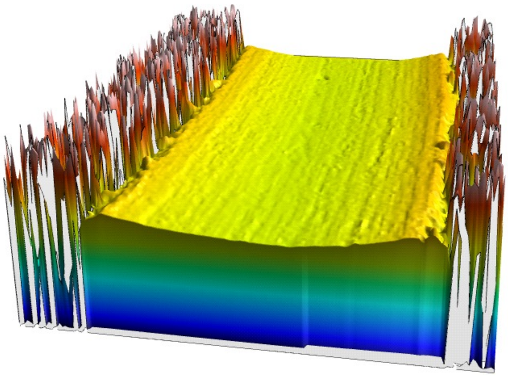
Parameters	Value	Unit
Maximum depth	5.21	µm
Area of the hole	1093	µm²

Wear profile 2

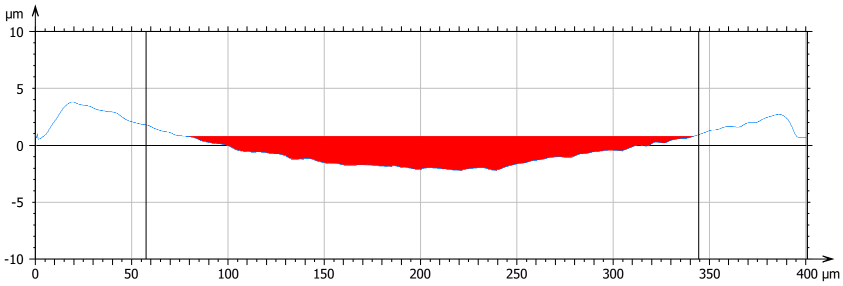


Parameters	Value	Unit
Maximum depth	6.25	µm
Area of the hole	1216	µm²

Wear profile 3

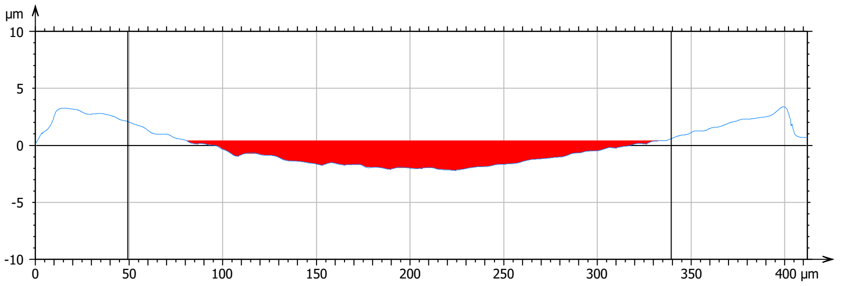


Thickener B R0



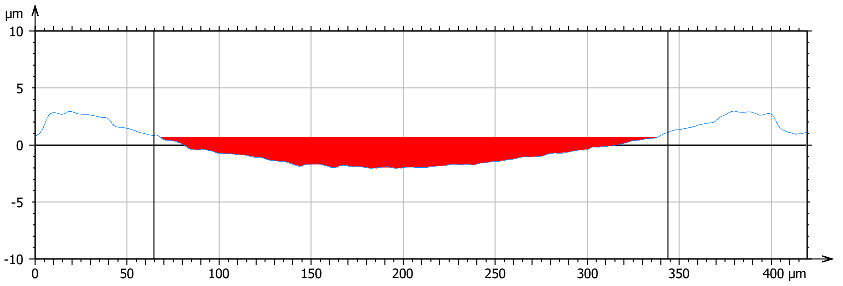
Parameters	Value	Unit
Maximum depth	3.12	µm
Area of the hole	518	µm²

Wear profile 1



Parameters	Value	Unit
Maximum depth	2.77	µm
Area of the hole	444	µm²

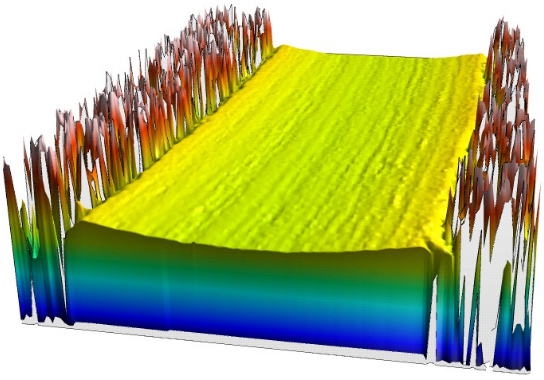
Wear profile 2



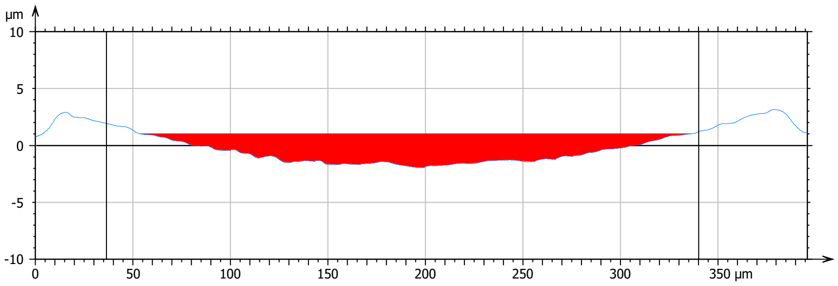
Parameters	Value	Unit
Maximum depth	2.90	µm
Area of the hole	523	µm²

Wear profile 3

Thickener B R1

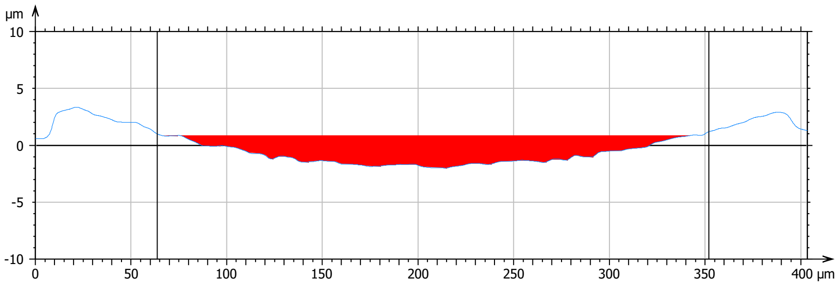


Wear profile 1



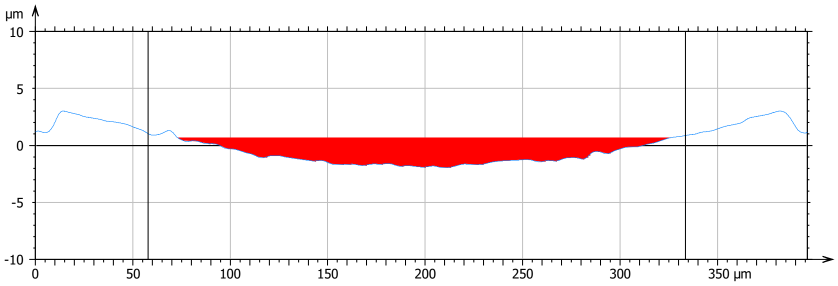
Parameters	Value	Unit
Maximum depth	3.17	µm
Area of the hole	578	µm²

Wear profile 2

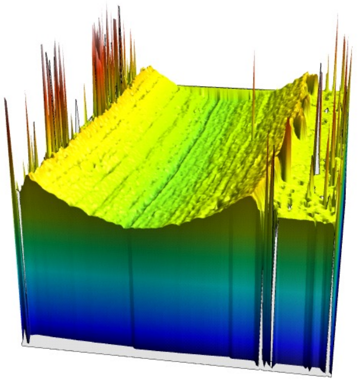


Parameters	Value	Unit
Maximum depth	2.99	µm
Area of the hole	531	µm²

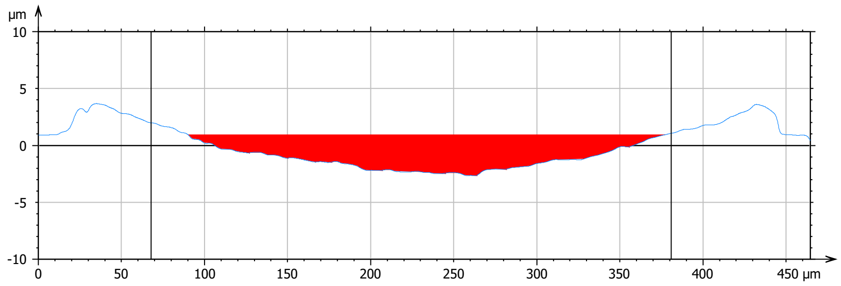
Wear profile 3



Parameters	Value	Unit
Maximum depth	2.81	µm
Area of the hole	480	µm²

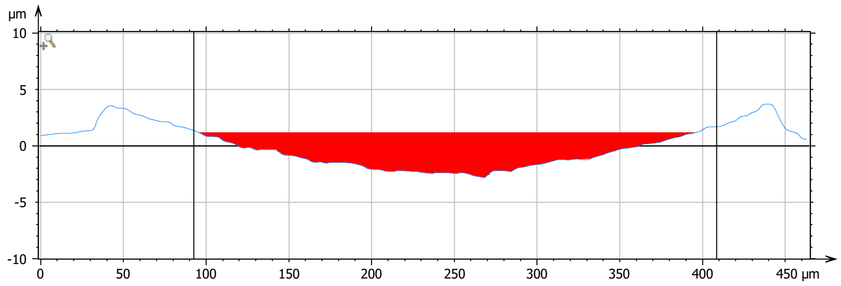


Thickener C R0



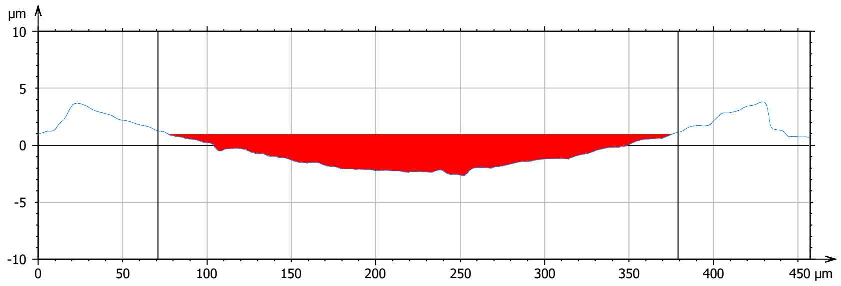
Parameters	Value	Unit
Maximum depth	3.73	µm
Area of the hole	670	µm²

Wear profile 1



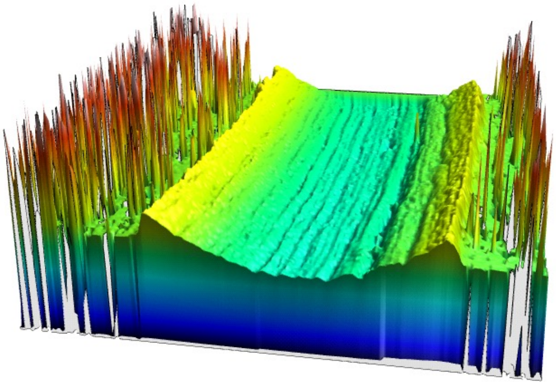
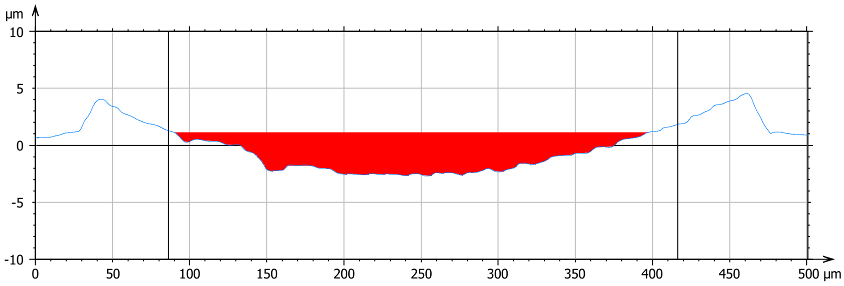
Parameters	Value	Unit
Maximum depth	4.16	µm
Area of the hole	744	µm²

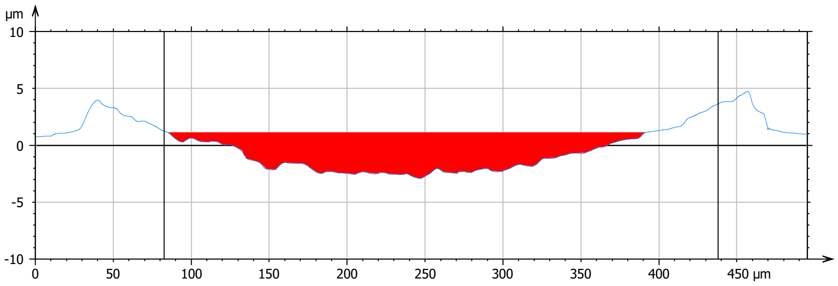
Wear profile 2

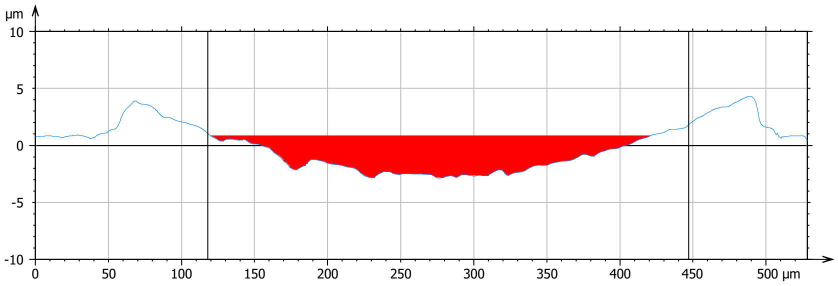


Parameters	Value	Unit
Maximum depth	3.80	µm
Area of the hole	673	µm²

Wear profile 3

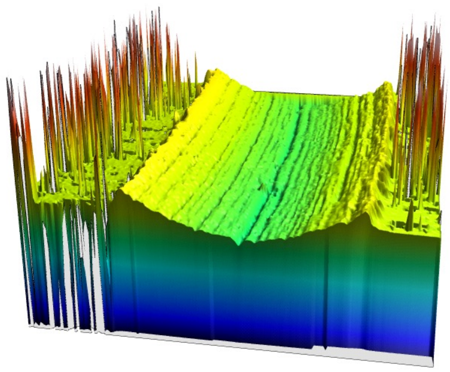
<table>
<tr><td></td><td>Thickener C R1</td></tr>
<tr><td>

<table>
<tr><th>Parameters</th><th>Value</th><th>Unit</th></tr>
<tr><td>Maximum depth</td><td>3.99</td><td>µm</td></tr>
<tr><td>Area of the hole</td><td>814</td><td>µm²</td></tr>
</table></td><td>Wear profile 1</td></tr>
<tr><td>

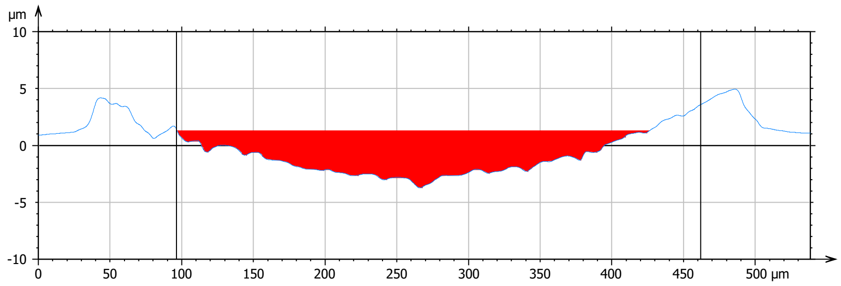
<table>
<tr><th>Parameters</th><th>Value</th><th>Unit</th></tr>
<tr><td>Maximum depth</td><td>4.15</td><td>µm</td></tr>
<tr><td>Area of the hole</td><td>800</td><td>µm²</td></tr>
</table></td><td>Wear profile 2</td></tr>
<tr><td>

<table>
<tr><th>Parameters</th><th>Value</th><th>Unit</th></tr>
<tr><td>Maximum depth</td><td>3.92</td><td>µm</td></tr>
<tr><td>Area of the hole</td><td>754</td><td>µm²</td></tr>
</table></td><td>Wear profile 3</td></tr>
</table>

Thickener D R0

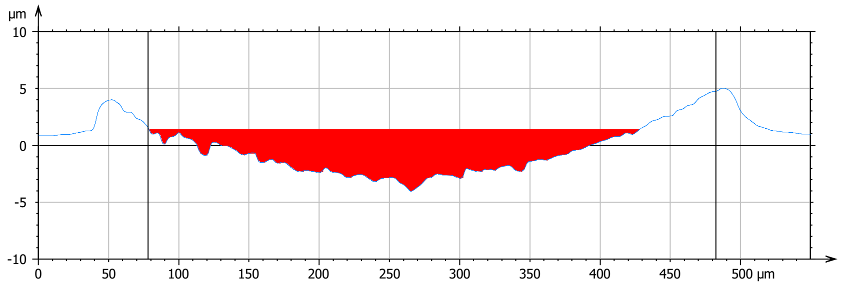


Wear profile 1



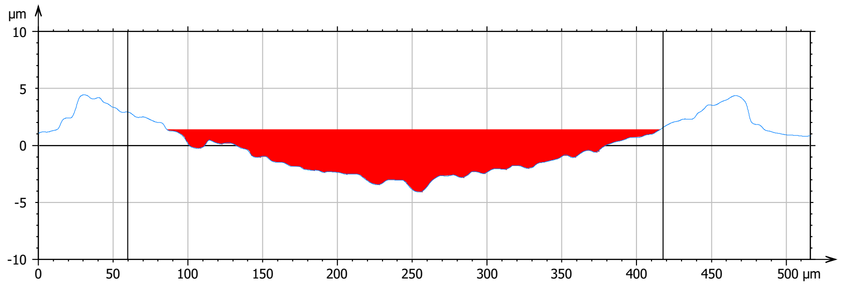
Parameters	Value	Unit
Maximum depth	5.15	µm
Area of the hole	952	µm²

Wear profile 2



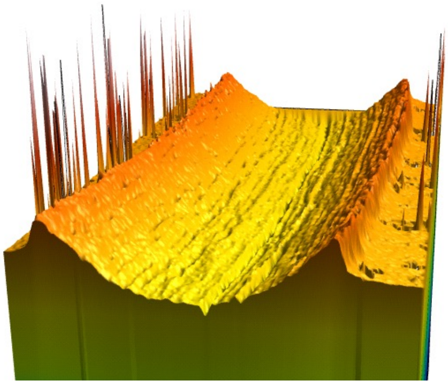
Parameters	Value	Unit
Maximum depth	5.57	µm
Area of the hole	1013	µm²

Wear profile 3

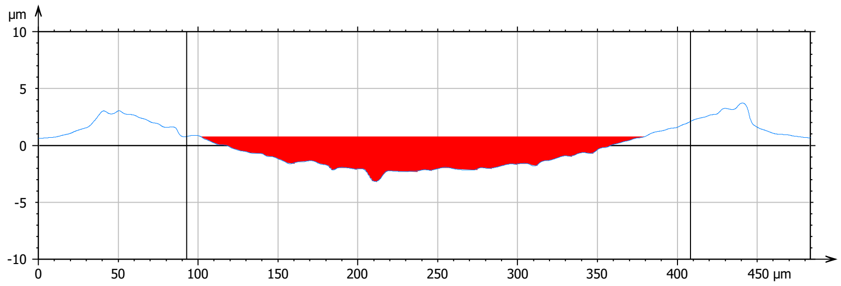


Parameters	Value	Unit
Maximum depth	5.67	µm
Area of the hole	983	µm²

Thickener D R1

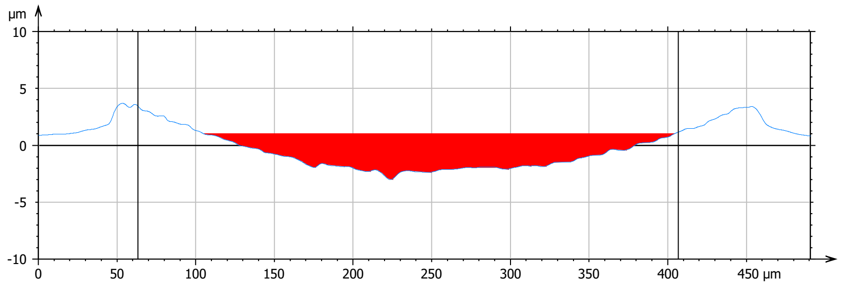


Wear profile 1



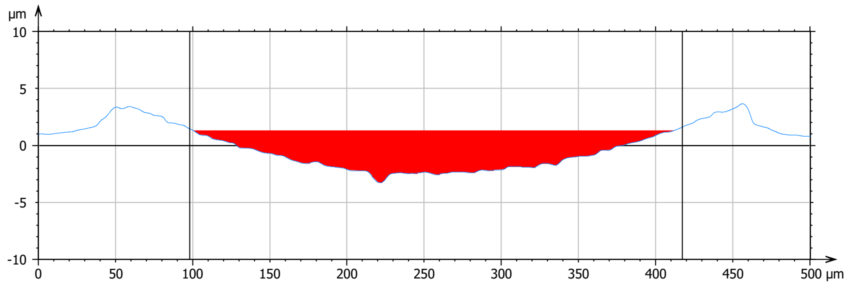
Parameters	Value	Unit
Maximum depth	4.05	µm
Area of the hole	611	µm²

Wear profile 2



Parameters	Value	Unit
Maximum depth	4.17	µm
Area of the hole	722	µm²

Wear profile 3



Parameters	Value	Unit
Maximum depth	4.74	µm
Area of the hole	839	µm²