

LABORATORY BENCH TESTS WITH IMPROVED ABILITY TO PREDICT GREASE LUBRICATION PERFORMANCE IN ROLLING BEARINGS

Rory McAllister

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Department of Mechanical Engineering

Imperial College London

Statement of Originality

I confirm that all work presented is my own, unless specifically noted. In these cases, the source is appropriately referenced.

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ABSTRACT

Frictional losses in rolling bearings produce an enormous quantity of wasted energy due to the abundance of bearings in the modern world. This loss can be reduced by improving the frictional performance of the lubricating greases that are the primary lubricant of bearings. A vital part of this improvement, and of developing new greases, is the test system used. It can provide deep insight into the observed phenomena, or potentially mislead, if the relevant lubrication mechanisms are not accurately emulated.

Bearing tests were conducted under conditions representative of typical applications, with a set of greases containing some of the most common thickener types. The bearings were dismantled post-test and imaged, and the lubricant films were analysed in-situ using IR spectroscopy to assess their chemical composition. The bearings showed a typical grease distribution, with the majority situated at the raceway shoulders and shields and only a small quantity of ‘active’ lubricant remaining in the raceway. Certain IR changes were associated with shear degradation, and these were used in a novel way to assess the extent of degradation. The active lubricant was found to be oil-rich and heavily shear-degraded.

Rheometry and conventional ball-on-disc testing of friction and film thickness were applied to the fresh test greases, as well as shear degraded and thermally aged samples. The degraded samples behaved very differently to fresh grease, suggesting that testing of fresh grease does not represent the friction, film thickness and rheology of the active lubricant observed in bearings. Degradation during ball-on-disc testing was compared to that of bearing tests and was found to be far more limited. Inherent problems with the ball-on-disc geometry were also identified that limit applicability to the contacts of bearings.

From these findings, a novel barrel-on-ring test device was developed which aimed to replicate bearing conditions in the most salient ways. Comparison of film thickness in the new device, a ball-on-disc machine and bearings under the same starvation conditions showed that the new rig allowed reflow of grease at a much greater rate than the ball-on-disc device, approaching the film thickness of the bearings. This suggests that the novel device is more representative of bearing lubrication than standard tests, and therefore may provide better predictions about bearing performance, as well as better understanding of lubrication phenomena.

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LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
AISI	American Iron and Steel Institute
ASTM	ASTM International, formerly known as American Society for Testing and Materials
AW	Anti-wear
CAD	Computer-aided design
CCD	Charge-coupled device
CLA	Centre-line average
COF	Coefficient of friction
DAC	Digital-to-analog converter
DAQ	Data acquisition
DGBB	Deep-groove ball bearing
DIN	Deutsches Institut für Normung (German Institute for Standardisation Registered Association)
DSC	Differential scanning calorimetry
EHD	Elastohydrodynamics
EHL	Elastohydrodynamic lubrication
EN	Europäische Norm (European Standards)
EP	Extreme pressure
EV	Electric vehicle
FTIR	Fourier-transform infrared
HDI	Hexamethylene diisocyanate
Li-12HSA	Lithium 12-hydroxy-stearate
IP	Energy Institute (originally Institute of Petroleum)
IR	Infrared
IRRAS	Infrared reflection-absorption spectroscopy
ISH	Inlet shear heating
ISM	Industrial, scientific and medical (RF frequency bands)
ISO	International Organisation for Standardisation
LVE	Linear visco-elastic

MCT	Mercury cadmium telluride
MDI	Methylene diphenyl diisocyanate
MTM	Mini traction machine
NLGI	National Lubricating Grease Institute
OTM	Optical transfer matrix
PAO	Polyalphaolefin
PDSC	Pressure differential scanning calorimetry
PETG	Polyethylene terephthalate glycol-modified
PID	Proportional, integral, derivative
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PU	Polyurea
RF	Radio frequency
RGB	Red, green, blue
RMS	Root mean square
RPM	Revolutions per minute
SCBR	Single-contact bearing rig
SD	Starvation degree
SDK	Software development kit
SEM	Scanning electron microscopy
SIS	Swedish Institute for Standards
SLIM	Spacer layer imaging method
SRR	Slide-roll ratio
SRV	Schwingung, reibung, verschleiß (oscillating, friction, wear)
TDI	Toluene diisocyanate
TIG	Tungsten inert gas (welding)
TRIAC	Triode for alternating current
VI	Viscosity index
WAM	Wedeven associates machine
ZDDP	Zinc dialkyldithiophosphate

1 INTRODUCTION

This thesis is a study of the lubrication performance of grease in rolling element bearings and how best to assess this performance in the development of new greases. This chapter provides some essential background information on the topic of rolling element bearings and lubricating grease and explains the motivations of the project in this context. The objectives and expectations of this work are outlined, along with the structure of this thesis.

The work presented here is an effort to aid the development of greases optimised for friction or other properties, by providing an incremental improvement to the way greases are tested. By making these tests more applicable and representative of the bearings which they ultimately should emulate, the value of the test result is greatly improved, and new formulations can be developed in a cost-effective manner.

1.1 BACKGROUND

Rolling element bearings and their most commonly used lubricant, grease, play a vital but typically unseen role in modern society. Transport, manufacturing and the energy industry are some of the most important areas which rely on the low friction provided by rolling bearings. Rolling bearings are found in almost any device where objects are in relative motion, particularly those where precision, high load capacity, high speed and reliability are desired. Their abundance is, in part, due to the excellent performance typically provided by the lubricating grease they often contain, allowing a self-contained element of a machine that is capable of surviving beyond the life of the machine that relies on it.

1.1.1 Rolling Element Bearings

The sliding of objects in relative motion results in friction and wear at the contacting surfaces. Both can be reduced through the use of rolling elements that separate the surfaces, creating two rolling contacts. Such technology was presumably used in antiquity for the transport of heavy objects, though the earliest evidence for the use of such rolling elements was in a design for a battering ram by the military engineer of Alexander the Great, Diades, in 330 BC and recorded by Pollio Vitruvius in his treatise on architecture [1]. His design allowed for a faster

and more destructive ram by seating it on rollers located in grooved tracks that were separated from gathering by a form of cage [2].

Rolling element bearings have also been found in the remains of Greek, Roman, Chinese and Celtic civilization, but throughout the Middle Ages were little used. It was not until approximately 1500 AD that Leonardo Da Vinci produced designs for thrust bearings, some of which differ very little to those in use today, though impractical to manufacture at the time [2], [3]. Probably the first practical radial ball bearing, though cageless, was produced during the industrial revolution in England by Charles Varlo sometime before 1772, and used successfully in a horse-drawn carriage with little wear [2]. Fifteen years later John Garnett developed a similar design that included a cage, separating the balls from sliding at high speed against one another [4]. Reducing and controlling friction with such inventions were important steps in the path to modern technology.

Since then, rolling element bearings have been an integral part of machinery, now present in almost every instance of rotary motion, with more than 50 billion in operation around the world [5]. Given their abundance in the transmission of power, efficiency of a bearing is vital and can have a large influence on the overall energy consumption of a machine.

Bearing design and lubrication are the two design factors that can influence the frictional torque of a bearing and this project focusses on this influence of the lubricant, specifically grease, which is used to lubricate 90% of roller bearings [5].

1.1.2 Lubricating Grease

Grease originally, and still in a non-technical context, referred to animal fats which were used as effective lubricants for the plain bearings of axles, among other simple sliding contacts. There is evidence that animal and plant fats were partially saponified with bases such as lime by the ancient Romans to create a thickened mixture which was used as a topical remedy [6], but only when mineral oils began to be refined from crude oil in an industrial scale, beginning in 1859, was it common to thicken an oil using a soap for use as a lubricant [5]. An early deviation from the general trend of petrochemical lubricants was the use of black slugs as a form of axle grease in Sweden, prior to industrialisation [7].

The modern definition of a grease, according to the National Lubricating Grease Institute (NLGI) of the USA is: “A lubricant that is a solid to semi-fluid dispersion of a thickening agent (thickener) in a liquid. A lubricating grease may be formulated with additives that impart special properties such as resistance to oxidation or wear.” [8]. This definition does not highlight perhaps the most important feature of a lubricating grease - its dramatic shear-thinning behaviour. The presence of the thickener imparts a ‘yield stress’ that prevents the lubricant from flowing away from where it is needed as an oil may do, yet viscosity drops close to that of the base oil under high shear rate, providing low friction.

Base fluids include mineral oils of all refinement groups, natural oils and fats, synthetic oils such as polyalpha-olefins, esters, polyglycols, silicones, perfluoropolyethers and any other fluid used for lubrication. The most common base oils are refined mineral oils, group I, II and III, used primarily for their low cost. The other fluids are used in more demanding applications, with only 7% of greases produced in 2012 using synthetic or semi-synthetic base oils [9].

Similarly, though many grease thickeners are available, the majority of greases in production are lithium-based, comprising 77% of the total [9], ultimately originating from Clarence Earle’s 1942 patent [10]. Lithium and other metals are used in the form of a metal soap, ionically bonded to a molecule such as a hydroxystearate. Other thickener types include organophilic clays, fumed silica, polymers such as PTFE and polypropylene, as well as polyureas. These thickeners may be selected depending on the application demands such as chemical and physical resistance to temperature, water resistance, shear stability, chemical resistance and many others.

1.2 MOTIVATION

1.2.1 Modern Demands

When rolling bearings first entered use, their design was comparatively rudimentary. Bearing steels were impure, containing many inclusions which would initiate fatigue leading to failure [11] and operating temperatures and speeds were low by modern standards. This meant that the lubrication of such bearings was not so critical as it was less likely to be a cause of failure.

With developments in these other areas, lubrication has become increasingly important and now inadequate lubrication represents some 80% of bearing failures [12].

Developments in lubrication science have been significant but as a field, grease lubrication has been somewhat neglected. The mechanism of grease lubrication is certainly complex and there is no consensus on its nature. The most widely used model for grease lubrication describes the influence of the thickener as negligible, and its role is simply to retain the oil in the bearing and release it gradually which then provides lubrication as in the case of an oiled contact [13]. Analysis of the rolled tracks of dismantled bearings suggests this is a major oversimplification, and that the thickener plays a role not only in lubrication itself but, by its progressive destruction, it controls release of the oil from the thickener matrix [14]. In fact, the film thickness of a grease under the same conditions as an oil will typically be higher, but often subject to the additional effect of starvation which can drastically reduce film thickness [15]–[18]. The complexity of these processes and our limited understanding of them has produced the current situation in which demands on greases are stringent, but an understanding of how to improve formulation is lacking. In addition to this fundamental problem, there are contemporary issues that necessitate new formulations.

The burgeoning lithium-ion battery market, mainly driven by the transition to electric vehicles, has created a huge demand for lithium as a raw material. In 2008 lubricating greases represented an estimated 16% of global lithium consumption, with batteries at 20%. In 2022 batteries now consume 74% of global lithium production and lubricating greases have fallen to 3% [19]. Figure 1.1 shows the rise in the price of Li_2CO_3 , one of the most common sources of lithium used in lubricating greases. A dramatic rise around the year 2016 almost tripled the cost of the material. It has since fallen from its peak but is likely to remain at an elevated level. This has led to a search for a cheaper alternative to the common lithium thickener, as the traditional grease becomes less economically feasible.

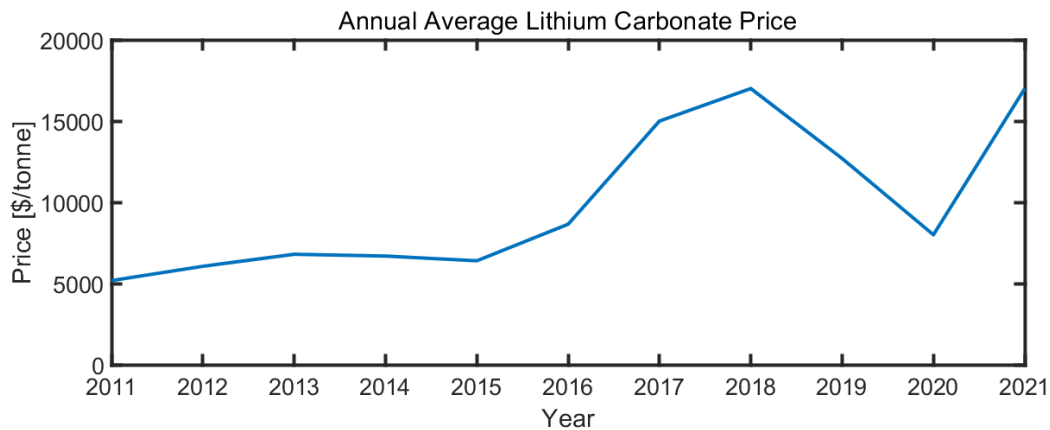


Figure 1.1: Average lithium carbonate price over the last decade, showing a significant increase after 2016 [19]. The sharp decrease in 2020 is an anomaly caused by the COVID-19 pandemic.

New technical and environmental requirements are also driving the development of new grease technologies. Electric vehicles have simpler transmissions than those of internal combustion-powered vehicles. This results in a larger proportion of frictional losses originating from bearings as well as making bearings proportionally a more common failure mode. Lubrication of these bearings is therefore a higher priority in electric vehicles. Novel grease development is also motivated by a demand for more eco-friendly lubricants that will biodegrade if released into the environment. These require careful formulation to mitigate the problems associated with these base oils such as high pour point and low oxidation stability. In many applications the expectation is now for grease life to exceed machine life: “greased for life”.

1.2.2 Grease Qualification

There is wide variety of test methods used to both assess the performance of a grease in a specific aspect, and to qualify it for a certain application. The former might be used in research and development while the latter are used by manufacturers on their finished products in order to prove the suitability for an application, demonstrate value to the customer, and aid sales. Ultimately, many of these tests have a similar purpose and it is only by convention that the qualification tests have achieved the status they have. This convention constrains manufacturers to a standard set of tests that both they and, more importantly, the customers are familiar with. A customer is less likely than the manufacturer to be aware of the suitability of the tests, but will inevitably provide significant inertia against developments.

Unfortunately, many of the common tests performed on greases are flawed. A common flaw is that they do not represent realistic application conditions and do not provide meaningful information about the expected performance or lifetime of the grease in a bearing. They are therefore difficult to use in grease selection for an application. A pervasive issue is that tests developed by standards organisations are used beyond their intended scope in direct violation of the advice of the standards themselves.

The challenge is to develop these new grease formulations that have optimised lubrication properties and meet modern demands in a cost-effective and efficient manner. The main goal of this project is to develop effective techniques to assess the performance of novel grease formulations.

1.3 RESEARCH PROGRAMME

1.3.1 Aims

By testing a range of new formulations in a rapid way that provides a real prediction of performance, it would be possible to gain better understanding of how certain aspects of grease composition influence friction or grease life. It would also aid development of greases to meet the modern demands outlined above.

This thesis describes experimental testing undertaken to identify the most important aspects of rolling bearing lubrication, so that they can be emulated in a bench test setup. Existing tribological test equipment is used in carefully designed test procedures, and these are compared to real rolling bearings in terms of chemical composition of the lubricant in the rolled track, using identical greases. These findings and other observed weaknesses in the standard ball-on-disc tribological test setup informed the development of a new test rig to bring bench model testing of grease even closer to a true bearing emulation.

1.3.2 Thesis Structure

The following chapter reviews the literature available on greased lubrication of bearings and aims to identify the areas which can be improved. At the end of the chapter, the work of this thesis that was aimed at addressing these shortcomings is described. Chapter 3 describes the

experimental methods used, and Chapter 4 presents the findings of research into the state of the ‘active’ lubricant of operating bearings, in particular the state of degradation. The work in Chapter 5 assesses the effects of this degradation of grease on the film thickness and friction of model tribological tests. Chapters 6 and 7 describe the development and results, respectively, of a novel test rig which aims to better emulate the features of a bearing and provide a more accurate model test to assess the performance of greases. Finally, Chapter 8 discusses the findings of this work, what conclusions can be drawn, and how future work might further improve the new test rig.

2 LITERATURE REVIEW

This chapter provides a review of the literature relating to lubricating greases, starting by defining lubricating grease and emphasising the important role it plays in modern society and how our changing expectations of its performance necessitate detailed study and improvement. The fundamentals of grease lubrication are reviewed, before describing grease composition and structure.

2.1 INTRODUCTION – LUBRICATING GREASES

The NLGI defines lubricating grease by its composition: “A lubricant that is a solid to semi-fluid dispersion of a thickening agent (thickener) in a liquid. A lubricating grease may be formulated with additives that impart special properties such as resistance to oxidation or wear” [8]. It is also possible to define it by its characteristic properties of shear-thinning and yield stress. These are the two properties that distinguish it from lubricating oils and therefore are most relevant to the tribologist.

Any lubricant is applied primarily for the purposes of optimising friction and wear, with liquid oils being by far the most common lubricant in use. A semi-solid lubricating grease may be chosen over an oil in instances where solid behaviour is desired i.e. no flow under its own weight. This property is desirable in a wide range of applications, from open gearing where oil would fly off, to wire ropes where it is retained between the wires and prevents fretting wear. Many machines that are usually lubricated with oil such as gears or plain bearings may be better lubricated with grease if they operate intermittently. In such cases the oil would flow away from contacting parts when motion is stopped, and components would wear on each restart. Switches and threads may be lubricated with grease as it is retained, excluding oxygen and preventing corrosion. A lack of flow and leakage is desirable in applications where contamination is to be avoided such as the food, pharmaceutical or textile industries, and in fire-risk applications such as coal mining, aviation and chemical processing [20].

Rolling element bearings are a major application of lubricating greases and it is on this, specifically, that this project focusses. Harris' "Rolling Bearing Analysis" states that for most cases, lubricating grease can be used in rolling bearings, with the benefits of retaining its position as well as providing some sealing function against particulates and moisture [21]. An oil-lubricated bearing would require an oil sump or an expensive circulation system, filter, pump and possibly heat exchanger. For low-speed applications where relubrication interval for a grease would be too short, an oil sump might be employed. He cautions that grease is unable to cool a bearing in the same way an oil may, so at the highest speeds and in critical systems such as aircraft turbine bearings, a pumped oil system is used. Greases offer the simplest lubrication system, contained entirely within the bearing itself and as such are widely used for all but the highest speeds.

Reliance on the good performance of lubricating greases is immense, considering its ubiquity in rolling element bearings and their abundance in virtually all moving machinery. The expected operating conditions can vary drastically in terms of load, speed, temperature and cleanliness as the applications of greases are wide. The high-speed, precision spindles of machining centres, heavily loaded and dirty wheel bearings of earth movers and the huge bearings of wind turbines could all be lubricated with greases. Even more extreme conditions exist in aeronautical or space applications, where the operating temperature range can be hundreds of degrees Celsius, with fluid lubricants required to perform at their limits of pour point and evaporative loss [22]. In such applications, as well as others such as lubrication in nuclear power plants, reliability is critical. The operating lifetime of the grease must be very well understood. It may be possible to relubricate prior to failure but in many applications, it is impossible to do so. Here, the grease must be relied on to outlast other aspects of the system.

Modern trends are also influencing expected performance of lubricating greases. Electrification of the automotive sector not only forces grease manufacturers to reconsider their reliance on lithium thickeners, but also introduces new demands on lubricants. Powertrains are operating faster, requiring lower torque and hence size and weight for the same power production [23]. Bearings must therefore reduce in size and spin faster than in internal combustion vehicles. Properties such as copper corrosivity, electrical resistivity and

compatibility with plastics must now be considered [24]. A Fuchs investor presentation claims there are “more than 30 different types of greases” in passenger cars [25] but the removal of the internal combustion engine and its associated lubrication means greases play an even more dominant role in dictating transmission efficiency. With “range anxiety” a major obstacle to widespread EV adoption [26], it is more important than ever for car manufacturers to select an efficient lubricating grease.

Failures of grease lubrication are common and can have large associated financial cost. Holmberg and Erdemir estimated worldwide tribological wear and wear-related failures to cost 680 trillion Euros in 2017 [27] of which a crude estimate of 3% can be attributed to grease, based on its global demand as a proportion of all lubricants in 2018 [28]. Wind turbines represent an ever increasing proportion of the global electricity production but as much as one third of their cost is spent on operation and maintenance for off-shore farms [29], in large part due to mechanical failure in the gearbox, of which 76% is caused by bearings [30]. Even with the stringent maintenance procedures adopted in passenger airline travel there have been many failures where grease played a role. Alaska Airlines Flight 261 crashed into the Pacific Ocean, killing all 88 occupants, due to a failed trapezoidal thread nut. This failure “was caused by excessive wear resulting from Alaska Airlines’ insufficient lubrication of the jackscrew assembly” [31]. While it was primarily a failure to relubricate the jackscrew (shown in Figure 2.1) on the manufacturer’s recommended interval, an improved ability of the grease to be retained and reduce wear may have prevented the crash.

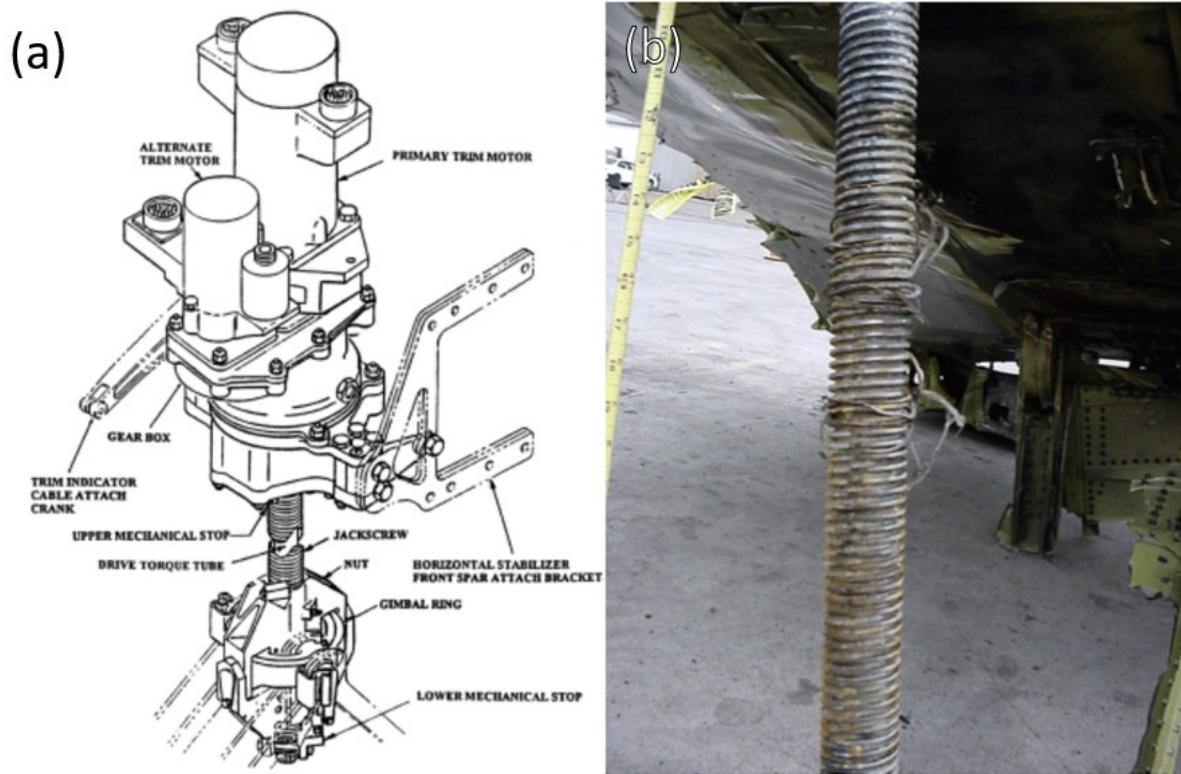


Figure 2.1: (a) Jackscrew assembly of MD-83 aircraft. (b) Recovered jackscrew showing remnants of the failed nut wrapped around the threads. Images from Aircraft Accident Report [31].

The abundance of grease and our reliance on it necessitate research and development to improve formulations and it is likely there remain significant improvements to be made. The addition of thickening agents to oils was first performed for the sole purpose of preventing flow. Some of the first greases were thickened using ‘fillers’ such as gypsum, mica or chalk, that added no lubricating value to the grease [32]. As grease technology has progressed, the filler has been replaced by thickeners that can offer lubricating ability of their own. Metal soaps were introduced as thickeners, with calcium soaps the first to be widely produced [33], and are effective boundary lubricants, used in applications such as wire drawing [34], metal injection moulding, pharmaceutical tablet pressing and as a lubricant in pencils and crayons [35]. The thickener can therefore be considered to offer an opportunity to enhance lubricating performance beyond that of the base oil. Not only is it possible to deliver a low-friction solid lubricant to prevent metal-metal contact should the film collapse, but the rheological characteristics can be tailored to reduce churning losses by ‘channelling’ [36] while also enabling sufficient resupply to prevent starvation of the contact at high speed. Through better testing and understanding, all these properties can be improved.

2.2 LUBRICATING GREASE COMPOSITION AND STRUCTURE

2.2.1 Grease Thickeners

There are many different thickener types in use, often used for specific applications, but by far the most common, with 91% of worldwide production in 2017 falling into this category, are the metal-soap greases [37], consisting of a carboxylate soap ionically bonded to a metal cation in the simplest case.

2.2.2 Metal-soaps

Calcium

These were the first greases to be developed, produced in 1845 by the simple addition of limestone (CaCO_3) and an animal fat triglyceride to mineral oil [38]. This produced a calcium carboxylate soap which acted as a thickener through mechanisms discussed in a later section of this review. Calcium soaps were the first to be used and very cheap to produce, but when made from animal fats, a small content of water is required to stabilise the structure [39], upon evaporation of this water the grease loses its consistency and fails. This leads to a relatively low operating temperature of 60-80°C. When made with a more refined source of fatty acid, the operating temperature is more reasonable [39]. As the ‘hydrated’ form of calcium greases are resistant to water, they are still in use today.

Sodium

In instances when the temperature limit of calcium greases was a problem, sodium greases were commonly used. Writing at the latest in 1911, Hurst describes the use of calcium “when crude, rough greases are required” and sodium “when better qualities are desired” [32]. Boner describes sodium greases as susceptible to water [39], and they represent just 0.4% of the 2017 worldwide production [37].

Aluminium, Barium etc

Aluminium greases are described as adhesive and water resistant, but lack shear stability, probably due to their unusually small particle size compared to other metal-soaps [39], [40]. They have a relatively low upper operating temperature of 80-90°C and are little used today.

Other metal cations such as barium, strontium, zinc etc have been used to make greases. Some such as strontium have attractive properties in terms of temperature and shear stability as well as water resistance [39], but have limited sale, presumably due to the unfavourable cost-benefit ratio.

Lithium

By far the most common metal cation used in lubricating greases in modern times is lithium. Figure 2.2(a) shows the most commonly used reaction to produce the thickener. Accounting for 53.7% of production in 2017, simple lithium soaps are regarded as a standard multi-purpose grease, applicable in all cases where another grease type is not required for specialist function. First developed and patented by Earle in 1942 [10], the extremely high dropping point of 190°C, good water resistance and exceptional shear stability lead to its adoption across industry, despite its higher cost compared to calcium or sodium [39]. An additional benefit is its apparently lower coefficient of friction compared to other greases, Horth finding that the friction coefficient of a journal bearing setup was minimum for lithium greases, though all greases tested showed lower friction than the base oil under their boundary lubrication regime [41]. This study also found the friction of a grease in boundary conditions to vary with shear strength of the thickener, appearing that Li soap occupied an optimum, between very low shear strength, Al soap for example, and very high such as Ca complex.

Fatty Acids

Historically any fatty acid used for lubrication might be used to make a grease. A fatty acid with 18 carbon atoms (stearic acid) achieves the maximum thickening effect after reaction to produce a soap [40], [42]. As the length of the hydrocarbon tail increases, so does the solvency in oils and this length achieves optimum interaction with the oil without dissolving the soap structure. Castor oil, obtained from the castor bean, produces mainly ricinoleic acid upon hydrolysis of the triglyceride. This may be hydrogenated to produce 12-hydroxystearic acid (12-HSA), having the additional benefit of a polar hydroxyl group, increasing the melting point and thickening ability [5]. For these reasons 12-HSA is the most common acid in use. For complex greases (discussed below), a wider variety of acids can be used, such as acetic, sebacic, azelaic, boric etc.

Complex Greases

Some grease properties, primarily temperature stability, can be drastically improved by the addition of multiple carboxylates to the metal cation. These may be fatty acids differing in chain length, hydroxyl groups or number of carboxyl groups, or inorganic acids such as boric or phosphoric acid [40]. Boner suggests calcium complexes were the first to be developed, almost all of which contain acetic acid [42], drastically improving its thermal stability [39]. Complexes show a slightly lower thickening effect than simple soaps and so must constitute a greater proportion of the grease for a given consistency, leading to a reduced rate of oil bleeding [40].

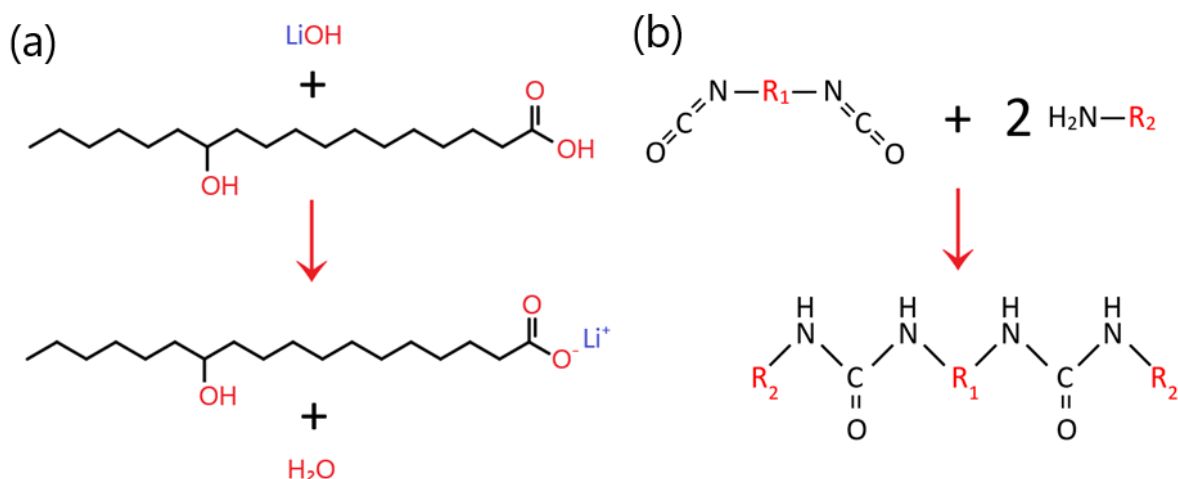


Figure 2.2: (a) The typical chemical reaction used to produce metal-soap greases, here showing production of lithium 12-hydroxystearate. (b) General reaction to produce a polyurea. R groups used vary widely and diamines may be used to produce longer chains.

2.2.3 Polyureas

First developed in 1954 by Swaken [5], polyureas are a relatively recently discovered class of thickeners that have inherent anti-oxidant abilities [5], [43] and do not contain metal ions which are usually catalysts of oil oxidation. As a result, they have good high-temperature performance [5] and are usually used in cases where this is necessary. One class of polyurea, diureas, can be produced through the reaction of one molecule of diisocyanate with two molecules of monoamine. This reaction is shown in Figure 2.2(b). Tetraureas and longer molecules can be made by linking diisocyanate molecules with diamines, and two monoamines to end the chain. In this sense polyureas should really be called oligoureas as they are hardly polymers by most standards, usually not having more than eight urea groups.

Liu and Sun found that the more urea groups were added the higher the dropping point and shear stability, as well as reduced oil separation [44]. However, they also found that more urea groups also reduced the consistency of the grease, especially moving from tetra to hexaurea. Not only can the number of urea groups be controlled, but the functional groups marked R_1 and R_2 in Figure 2.2b can be altered. Aliphatic, aromatic and other groups can be used to control interaction between thickener and oil. In practice just three diisocyanates are used: methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI) and hexamethylene diisocyanate (HDI).

2.2.4 Polymers

PTFE is used as a thickener in greases intended for extreme conditions such as very high temperature ($>200^{\circ}\text{C}$), acid or basic conditions as well as vacuum [45]. Polypropylene (PP) has also entered the market recently as a novel thickener, with favourable characteristics in bearing life tests [46] and very large increases in film thickness as compared to base oil at low speed [47]. They are, however, susceptible to softening [48]. Though they appear promising, these greases have not been widely adopted and there is relatively little research available on PP greases.

2.2.5 Inorganic Thickeners

Several inorganic materials can be used to thicken grease, performing well at high temperatures due to their oxidation resistance and extremely high melting points, stable at temperatures $>300^{\circ}\text{C}$ [40]. To thicken suitably, they must be treated with organic compounds in order to interact sufficiently with the base oil. Bentonite and other clays as well as fumed silica are examples of these thickeners. Clays were introduced to improve high temperature performance as they do not melt. They have poor shear stability as they lack a fibre matrix but are still used in some open gearing applications in combination with extremely viscous oils [49]. Silicas were developed for lubrication at low temperatures and are favourable in centralised lubrication systems as their lack of elasticity results in good pumpability according to Gow [49]. He goes on to say they are inherently unstable, separating over time and that they are not often used in bearings, exhibiting low shear stability but find application in polymer and aluminium lubrication.

2.3 BASE OILS

The base oil of a grease has a great influence on its characteristics as a lubricant. Some consider the purpose of the thickener to simply be in retaining the base oil at the point of application. Under conditions of high speed and fully flooded inlet, the base oil is indeed the dominating factor in controlling film thickness as measured in ball-on-disc configurations [16], [47], [50]–[52]. Its viscosity, viscosity index, oxidation resistance, pour point and many other properties of the oil will limit or enable its use under certain applications.

Any lubricating oil may be used in a grease, though grease production is almost entirely performed using conventional mineral oils, with 90% of greases produced in 2017 falling into this category. Only 6% utilised synthetic oils with the remainder semi-synthetic and bio-based oils (just 0.6%) [37].

Apart from influencing grease performance in the same ways that they would as pure oils, the base oil interacts with the thickener and grease consistency can be influenced in this way. In general, increased solvency of the base oil causes a higher consistency for a given mass content of thickener [53]. To a manufacturer this means less thickener is required for a given consistency which may mean significant cost savings as “the thickener is generally the highest priced component” [54]. For typical hydrocarbon oils, a high aromatic or naphthenic content increases solvency which can be approximately measured using the aniline point [42], the temperature at which equal parts aniline and oil separate into two phases. Low aniline point, indicating good solvency, has been correlated with higher thickening effect [54] as has naphthenic content, compared to paraffinic [33]. This has implications for the future of grease formulation as the demands on manufacturers to increase the operating temperature range and thermal oxidation stability of their greases forces them to select synthetic oils such as PAOs or hydrocracked group III oils. These formulations will require significantly more thickener to achieve the required consistency which affects the already high cost as well as other rheological and tribological properties to be covered later in this chapter.

2.4 ADDITIVES

Beginning predominantly in the early 1930s [55], [56], additives in oils quickly became essential components of lubricating oils. They are included to improve performance in specific aspects such as wear rate, oxidation resistance or inhibiting corrosion. In general, the same additive technologies that are used in oils are used in greases, although greater concentrations are required due to interaction with the thickener and competition with the thickener for the metal surface [57].

Despite the many benefits offered by additives, their inclusion in grease formulations must be considered carefully due to potential interactions between the polar thickener molecules and the additive themselves, which are often highly polar [58], [59]. This can lead to an undesirable softening of the grease [13].

One of the most important categories of additives are the antioxidants which act to extend the useful life of mineral oils at high temperatures. Oxidation of the oil causes an increase in viscosity and generation of acidic products which may cause corrosion [42]. There are many different types of antioxidants, including phenolics, aromatic amines, sulfides, thiols, phosphites and heterocyclic compounds of sulfur and nitrogen [5], [42]. Many additives are multifunctional such as zinc dialkyldithiophosphate (ZDDP) which is an effective anti-wear additive as well as antioxidant and corrosion inhibitor [56]. The oxidation process will be discussed further in a later section of this review but can be summarised as a propagation of free radicals, leading to high molecular weight products as well as alcohols, esters, acids etc. Antioxidants can be divided into two groups, firstly radical scavengers which react with radicals but form a stable radical, ending the reaction chain. The second group are peroxide decomposers which produce non-radical products after reacting with peroxides [60]. Antioxidants are often used in combination as they have a synergistic effect, improving oxidation resistance beyond their sum contributions [61].

Anti-wear (AW) and extreme pressure (EP) additives are added to some greases in high load and shock load applications. EP additives are chemically reactive species, bonding to the metal surface under the very high flash temperatures under local asperity contact [62], while the AW additive ZDDP has been shown by Zhang et al. to be strongly influenced by shear stress

within the contact, suggesting a mechanochemical contribution to the reaction [63]. The reaction film may contain oxides, phosphides, sulfides, sulfates or carbides depending on the additive and prevent direct contact between the metal surfaces [42]. Though EP/AW additives do improve performance in harsh EP tests, the reactive and polar nature of these additives are likely to disrupt the thickener to some extent (see Lugt [13] and references therein). While solid additives are rarely used for oils, they are considered acceptable in greases, allowing the use of molybdenum disulphide and graphite as anti-wear additives [57], separating the surfaces with laminar sheets with low-friction interfacial sliding [64].

Friction modifiers also act to separate the metal contact surfaces with the primary goal being reduction of friction in boundary lubrication conditions but can do so with or without permanently bonding to the metal. Examples are alcohols, fatty acids, fatty acid salts and amines and amides [65]. It is clear that metal-soap thickeners resemble such additives and are present in large concentrations in greases, as a result even base greases show reduced friction under boundary lubrication conditions [66]. The lubrication mechanisms of greases are discussed in more detail later in this chapter.

Corrosion inhibitors prevent corrosion by creating a physical barrier and blocking the anodic or cathodic (electron releasing or receiving) reactions [60], [61]. For metal-soap greases, a simple and cost-effective method of inhibiting corrosion is to include an excess of the metal hydroxide which will neutralize acidic products of oxidation of the lubricant [42], [59]. Imidazolines, alkenyl succinic acid esters and calcium sulfonates are used in lubricating greases, although the latter is said to modify thickener structure [5], [42].

Polymeric additives common to lubricating oils such as viscosity modifiers are sometimes used in greases, but uniquely, tackifiers and thickener modifiers can be included. Tackifiers are often added to increase adherence to machinery such as gearing as well as aid lubricant transfer between wheel-rail contacts [67]. They consist of long chain of polymers like polyisobutene [5] or isobutylmethacrylate [33]. Thickener modifiers are vaguely defined but act to improve some aspect of grease rheology or structure. Another of Clarence Earle's patents (of lithium grease fame) refers to polymerised esters of methacrylic acid, acting to improve thixotropic effects of his grease [68]. Polymeric structure-modifiers can reduce the

effect of grease hardening in storage [42] and are used to control the formation of the thickener during production, creating a more disperse network and increasing thickener effect [58].

While the inclusion of additives in oils is fairly straightforward, though antagonistic effects must be considered [42], [60], [61], their addition to greases is risky due to the potential interaction with the thickener. Though most additives are likely to affect the thickener in some way, the benefits may outweigh the drawbacks.

2.5 GREASE STRUCTURE

Lubricating greases can be universally described as colloids, as they contain a liquid oil phase with a dispersed, solid, thickener phase. As the liquid phase is usually organic, neglecting silicone-based greases, they may be more specifically described as organogels. As the term gel can describe many things, for example polymeric gels with covalent bonds resisting deformation, it is best to use the more specific term low-molecular-weight gel. Draper provides the following description: “The gels arise from the self-assembly of small molecules into long, anisotropic structures, most commonly fibres. At a sufficiently high concentration, these fibres entangle or otherwise form cross-links, leading to the network that is able to immobilize the solvent through surface tension and capillary forces” [69]. Recent work [70]–[72] on probing the structure of thickener systems in grease has been largely based on molecular dynamics, a computational simulation of the molecules and atoms under study. In general, these have confirmed the earliest theories on grease structure.

A detailed review of early research on the structure of lubricating greases can be found in C. J. Boner’s “Manufacture and Application of Lubricating Greases” [33]. Early optical examination of metal-soap greases revealed a fibrous structure [73]. One of the first descriptions of the modern understanding of the structure and thickening mechanism of metal-soap greases was presented by Arveson [74] in his work on lime-soap greases. It is suggested that interlacing flexible fibres are deformed or separated by shearing, becoming less entangled, but not rupturing, and therefore able to assume their previous form at rest.

The fibrous nature of metal soap greases can also be seen viewed with SEM (scanning electron microscopy) [75]–[77] and AFM (atomic force microscopy) [76]–[79] techniques. To view the fibres with SEM, the base oil must first be removed with a solvent and the soap then dried and gold sputter coated. An example of such images is shown in Figure 2.3a). Given the removal of the base oil, it is possible the soap structure may be disturbed, however AFM measurements which do not require removal of the oil display very similar fibres, seen in Figure 2.3b). The base oil is bound within this fibre matrix by a combination of intermolecular forces, capillary forces and mechanical occlusion [40].

The shape of these fibres is dependent on the thickener composition, manufacturing conditions [80] as well as the type of base oil [53], [81]. Fibre size varies, generally from 1-100 μm in length with a diameter from 0.1-1 μm [75], [82]. The microstructure of the fibres controls grease rheology. The yield stress and consistency increase with the fineness of the fibres [83], as well as their length to diameter ratio [82] due to increased molecular interaction and resulting resistance to shear [53]. Not all metal soap greases form thickener fibres; some, such as some calcium complexes, form a foam-like structure and others form a ‘transition’ structure in between the two [84].

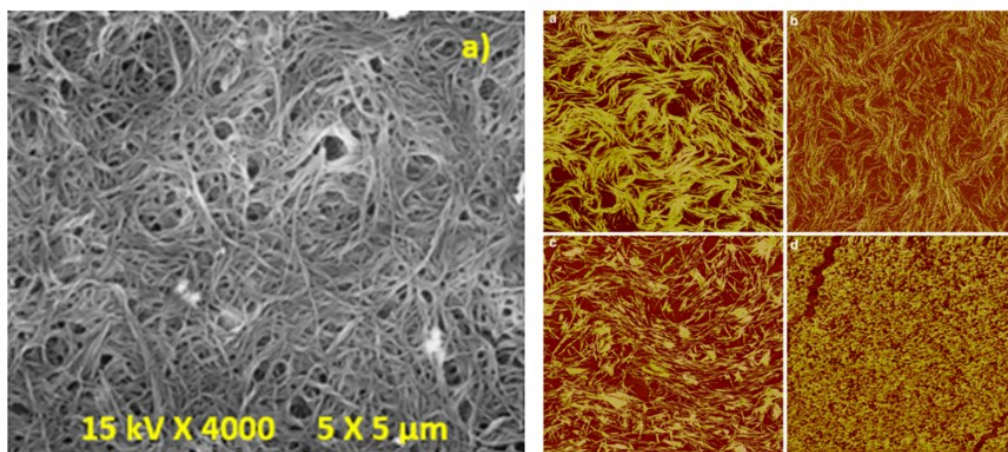


Figure 2.3: a) SEM image of a lithium grease with base oil removed [85]. b) AFM images of lithium greases in the upper two panels, LiX in bottom left and calcium sulfonate in bottom right. Window size 20 μm [78].

Polyurea greases differ from metal-soap greases in terms of structure. The microstructure of polyurea can depend on the composition, with aliphatic amines producing fibres, becoming larger with more urea groups per molecule [44]. Aromatic or alicyclic amines produce fine

needle-shaped crystals [5], though platelet-like polyurea particles were observed by Cyriac et al., using an ester base oil and an unknown polyurea thickener [85].

The structures within the fibres themselves are more difficult to discern. For metal soaps, the thickener molecules associate with one another as the grease mixture is cooled from $>200^{\circ}\text{C}$ during manufacture, precipitating as particles which grow to fibres [84]. The cooling rate is strictly controlled to obtain fibres of an ideal size. Vold, Vold and Hattiangdi [86], [87] conducted investigations into the structure of both pure metal-soaps and soap-oil greases using differential heating and X-Ray diffraction. They concluded that although room-temperature greases are likely to be predominantly crystalline soap dispersed in oil, at higher temperatures of approximately 100°C complex phase transitions occur, leading to the presence of waxy soap containing dissolved oil, and dilute soap solutions in oil [88]. Bondi et al. [89] proposed a structure shown in Figure 2.4(a), featuring alignment of the ionic carboxylate heads, and fatty tails extending outwards towards the base oil. Hydroxyl groups in the soap allow hydrogen bonding between these tails, strengthening the structure. The characteristic helical twist of some grease fibres is believed to be due to the chiral centre at this 12th carbon when a hydroxyl group is introduced [90]. Neighbouring fibres can adhere weakly via their end methyl group, the fibres visible in optical and scanning electron microscopy being composed of many such sub-units. The joints between them are held only by weak interactions of the fatty acid tails end-to-end and are susceptible to delamination.

Modern techniques of molecular dynamics have been applied to organic gelators in organic solvents, analysing self-assembly of carboxylic acids, including 12-hydroxystearic acid [91]. Analysis of carboxylates is, however, lacking. The work of Gordon et al. has found that there are, unsurprisingly, significant differences between the carboxylate and the acid [70], [71]. One novel finding is the suggestion of a ring-like substructure, with the hydroxyl groups forming 5 and 6-membered rings of hydrogen bonds. In a comparison between lithium and sodium 12-hydroxystearate, the suggested structures show more hydrogen bonding and less solvent-exposed polar groups in the lithium salt, going some way to explain its superior dropping point and water-resistance [70]. The lithium aggregate is shown in Figure 2.4(b). It should be noted that such techniques are not without fault and are based on major

assumptions for example that the base oil is pure hexane. Gordon states that “Even though full crystallization is hard to see on MD time scales ... many have been able to work around this problem using different methods” in regard to the techniques used to simplify the problem [71].

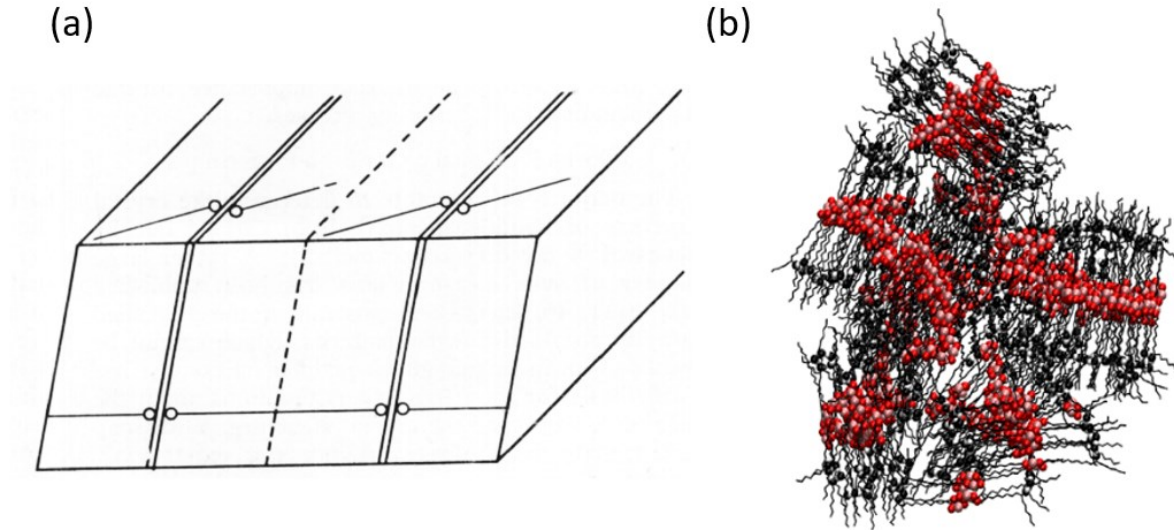


Figure 2.4: (a) Structure of metal soap greases suggested by Bondi et al. [89]. (b) Aggregation of lithium 12-hydroxystearate into 5 and 6-membered rings, making up layers, according to molecular dynamics simulations. Red spheres represent carboxylate oxygens, black spheres the 12-hydroxyl oxygen, white spheres the 12-hydroxyl hydrogens and pink spheres the lithium ion [70].

2.6 GREASE RHEOLOGY

The viscosity of a fluid is its resistance to flow. More specifically, dynamic viscosity is the ratio of shear stress to shear rate. Under the conditions of an EHL contact inlet most lubricating oils can be considered Newtonian, meaning their viscosity is not affected by shear rate or time under shear [92]. The viscosity will, however, be greatly affected by other properties such as temperature or pressure. The dependency on temperature is most commonly characterised by the viscosity index (VI), in essence providing a comparison to the behaviour of two standard oils of VI 0 (high dependency of viscosity on temperature) and VI 100 (low dependency of viscosity on temperature) between the values of 40°C and 100° [93]. Pressure dependence of lubricating oils is often described using a simple exponential relation known as the Barus relation:

$$\eta(p) = \eta_0 e^{\alpha p} \quad (1)$$

where η_0 is viscosity at atmospheric pressure, α is the pressure-viscosity coefficient and p is pressure [94]. This equation has been criticised for inaccuracy at high pressures [95] and a range of other equations have been proposed, reviewed by Spikes et al. [96]. Apart from Roeland's equation [97] these all include more than one lubricant parameter, making them difficult to use in practice.

Greases rheologically differ from oils not only in their non-Newtonian shear thinning, but in their viscoelastic behaviour. Under a shear force they provide a plastic, viscous deformation, but also an elastic deformation that is recoverable, as a solid might. While such materials are often modelled as a combination of spring and dashpot in series or parallel (Maxwell and Kelvin models) [5] they fail to account for the many other variables and behaviours of greases. Time-dependent effects are common in greases which can show a reduction in apparent viscosity with time under shear, termed thixotropy [98].

Greases also display a solid-like 'yield stress', below which they will only deform on long time scales as a creep deformation [99]. Though the term yield stress is used, it is less well defined than in solids. While it is true that any material will deform over long enough time scales, below what is considered their yield stress, the time-scale in which some viscoelastic materials will creep is much closer to engineering practicality [100]. The stress region in which greases show a marked change in behaviour can be very large, Bondi states that the wide distributions of thickener particle sizes, the complex structure and varying bending strengths are likely to lead to successive yielding and so a gradual change in flow curves at low shear stress [99], and some researchers have even identified two distinct yield stresses [101]. Though a range of procedures for measuring yield stress are used [102], the values are only strictly comparable when the same technique is used. Cyriac et al. evaluated a range of techniques and found that by characterising yield stress as the stress at which the response under oscillation becomes non-linear, the value was reproducible and less affected by extraneous parameters [103]. This method has been widely used in recent years [104]–[108].

To engineers, it is important to have a simple measure to assess how solid-like a grease is. For this purpose, the property of 'consistency' is used. It is a measure of how far a weighted cone will penetrate a pre-worked (sheared) sample of the grease and is defined in the ASTM cone

penetration standard D217 [109]. Though it has been widely adopted and gives a useful result, it is not a direct measure of yield stress. Despite being a rather unscientific measure, methods have been proposed to more precisely measure it using rheometers [110].

Apart from consistency, rheological parameters of greases are assessed using rheometers. The standard configuration of these is a conical upper plate rotating above a flat lower disc. When the appropriate gap height is set, the shear rate within the sample is constant. The testing of greases in a rheometer is subject to a number of problematic effects that must be carefully controlled. These include fracture or spillage of the grease, leading to reduced measured viscosity [5] and slipping at the surface of the sample [111]. The latter problem is usually controlled by using rough or hatched plates.

The risk of sample fracture or spillage is greatly reduced performing oscillatory tests rather than continuous flow tests. In an oscillation test, a set stress and frequency of oscillation are applied to the sample and the measured strain is recorded or the reverse, where strain induces a stress. Both follow a sinusoidal pattern, and the response will have a diminished amplitude and phase lag behind the stimulus. The diminished amplitude is the modulus G^* , the ratio of shear stress amplitude to shear strain amplitude, shown in equation 2:

$$G^* = \frac{\tau_A}{\gamma_A} \quad (2)$$

where τ_A is the shear stress amplitude and γ_A is the shear strain amplitude. The phase lag is termed δ and is used to split the modulus into its two constituent parts, G' and G'' , representing the elastic and viscous behaviour of the sample respectively. Equations (3) and (4) describe G' and G'' .

$$G' = G^* \cos \delta \quad (3)$$

$$G'' = G^* \sin \delta \quad (4)$$

these values and their relation to each other describe the behaviour of a grease. For greases G' is greater than G'' [112] at low stresses, meaning the behaviour is mostly elastic. Of particular interest is the stress value at which they are no longer constant or linear, discussed above as being indicative of yield. The value at which they cross over has also been associated with yield stress [113] and consistency [110].

2.7 OIL LUBRICATION

The goal of lubrication is to separate surfaces moving relative to one another and control the friction between them. The Reynolds equation describes how the pressure distribution in a thin fluid gap can support a load [114] but fails to describe how a fluid film can separate systems such as rolling bearings and gears. In the concentrated contacts of machinery, extremely high pressures are created on loading and it is this, and its effect on lubricants, that enables surface separation. As noted above, the viscosity of a lubricant can be modelled as an exponential equation, leading to extremely high viscosities within such a contact, termed elastohydrodynamic (EHD) due to the elastic deformations occurring at the metal surface. It was only when both elastic deformations and piezoviscous effects were included that analytical EHD film thickness solutions could be developed which then lead to the commonly used numerical solution for point contacts, the Hamrock and Dowson equation [115] shown below for central film thickness:

$$h_c = 2.69R'_x\bar{U}^{0.67}\bar{G}^{0.53}\bar{W}^{-0.067}\left(1 - 0.61e^{-0.75\left(\frac{R'_y}{R'_x}\right)^{0.64}}\right) \quad (5)$$

where:

$$\bar{U} = \frac{U\eta_0}{E'R'_x}, \quad \bar{G} = \alpha E', \quad \bar{W} = \frac{W}{E'R_x'^2} \quad (6)$$

Here U is the entrainment velocity, η_0 is the lubricant dynamic viscosity under the conditions of the inlet, E' is the reduced Young's modulus, R'_x and R'_y are the reduced radii of the contact in x and y directions, α is the pressure-viscosity coefficient of the lubricant and W is the contact load.

The implications of this equation can be interpreted by analysing the exponents of each term in equation (5. The largest exponent is attached to the $\bar{U}$ term, meaning such factors as the entrainment speed and lubricant viscosity in the inlet are of greatest importance. The load term $\bar{W}$ has a very small exponent which means load has a weak effect on film thickness, due to the consequent increase in contact pressure and hence lubricant viscosity within the contact.

For oil lubrication the friction of an EHD contact is strongly associated with film thickness and is commonly represented using the ‘Stribeck Curve’, a plot of friction against the product of viscosity and entrainment speed over load [42]. The curve is shown in Figure 2.5, and clearly shows an increase in friction if either viscosity or entrainment speed are too low, or load is too high. This sharp increase is due to contact of the metal surfaces. All real surfaces have a roughness which can be characterised in a number of ways but most often using the mean roughness R_a (also called centre-line average, CLA) or root-mean-square roughness (RMS) R_q [116]. The asperities on either surface will contact if the separating film is too thin and this will cause both friction and wear. In the mixed regime in the diagram below, the surfaces transition from only intermittent contact to frequent contact, leading to a maximum of friction. In the boundary regime the hydrodynamic force from the lubricant is no longer acting in the same way, though the lubricant can still reduce friction and wear significantly if a separating film is able to be maintained [42]. At high values of viscosity or entrainment speed the friction starts to increase. This is due to viscous losses within the contact. Either a highly viscous oil or a high shear rate leads to a high shear stress across the contact area and hence high friction [117]. The minimum friction value is found at the point when the surfaces are barely separated, this is often the goal of modern lubricant selection.

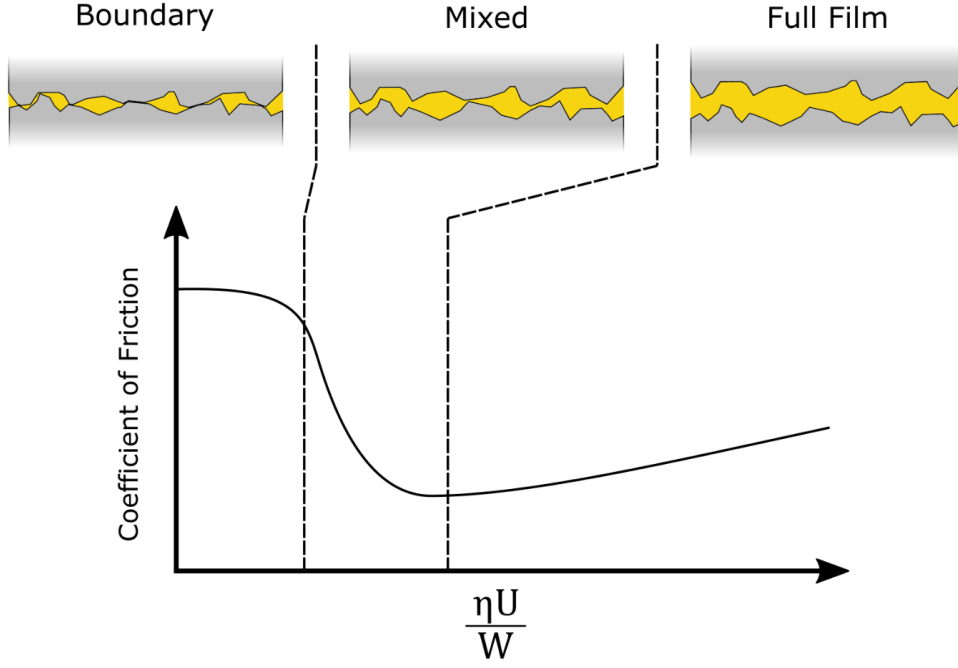


Figure 2.5: The Stribeck curve, showing friction against the product of viscosity and entrainment speed over load.

When considering the friction in an EHD film, surface roughness plays an equally important role. A very rough surface with large asperities will require a very thick film to ensure the surfaces are separated. There is evidence that even when fully separated, a rough surface will display higher friction than expected from the ratio of film thickness to roughness [118]. This ratio is a useful way to compare different lubrication conditions and is termed the Λ ratio, defined as:

$$\Lambda = \frac{h_0}{\sqrt{R_{q1}^2 + R_{q2}^2}} \quad (7)$$

where h_0 is the minimum film thickness and R_{q1} and R_{q2} are RMS roughness values of the surfaces. If the lambda ratio is over 3 the system is considered to be in the full film regime. Despite the utility of this value, it has been criticised when used to describe low lambda conditions when it fails to account for the effects of roughness on film thickness and the flattening of asperities within the contact [119].

2.8 LUBRICATING GREASE – ROLLING ELEMENT BEARINGS

2.8.1 Grease Lubrication Mechanisms in Rolling Element Bearings

Generally, the base oil of a rolling bearing grease will be chosen to have a viscosity high enough to form a lubricant film that will separate the rolling surfaces at all operating speeds. The thickener, therefore, is not explicitly required to contribute to lubrication, and in an ideal case will allow delivery of the oil to the contact inlets until the bearing fails through fatigue. Unfortunately, this is not the case, the grease deteriorates both mechanically and through oxidation, leading to insufficient supply of lubricant and surface contact [120]. This ‘grease life’ usually lasts significantly less than fatigue life of the bearing, requiring re-lubrication [5]. The thickener is also known to contribute to lubrication and the proposed mechanisms for this will be described here.

When a bearing is packed with grease, the first phase of operation is called the churning phase and involves redistribution of this grease in the bearing. Generally, the resistive torque will be high here as bulk grease is sheared. Much of the grease is thrown to the sides where it lubricates the seals of the bearing and physically blocks contaminants from entering the bearing [82]. This grease is relatively unworked, and while it is subject to centrifugal forces and vibrations, it is out of the swept volume of the cage and rolling elements and therefore moves very little. The remaining grease acts as the lubricant and in this phase the contacts are fully flooded as large lumps of grease enter the inlet, providing thick films, though this is highly changeable [121].

Once a steady-state distribution of grease has been achieved, the next phase which Lugt terms the “bleeding phase” begins and it is this phase that continues for the majority of the life of the bearing [5], and in fact, performance in this phase dictates the life of the bearing. In general, there are two proposed mechanisms of lubrication in this phase. Firstly, the name “bleeding phase” is used as some workers conclude that it is oil ‘bled’ from the grease that is acting as the lubricant [122]. Certainly, the ability of a grease to release oil has been shown to correlate with grease life, especially in roller bearings [5]. This bled oil is suggested to be a result of shear degradation of the thickener, leading to reduced ability to contain oil. Other workers suggest that under the high shear rates of an EHD contact, the thickener structure

breaks down and the grease becomes more oil-like, while still containing considerable proportions of thickener [123]. The presence of thickener fibres in the contact was confirmed using Fourier transform infrared spectroscopy (FTIR) by Cann et al. [124]. It is likely that both effects contribute to the formation of the 'active' lubricant that operates for most of the grease life [125].

Scarlett suggested another mechanism: that a significant contribution to the film is provided by a grease film deposited in the early stages of a bearing's life [82]. A deposited film of chemically altered grease was identified by Hurley et al. [126] in both lithium and tetraurea greases using optical interferometry for the film thickness measurements and FTIR for chemical characterisation. The tetraurea showed a much thicker residual film and a greater concentration of thickener in the contact path than the lithium grease. Most likely, both the bled oil (or degraded, mobile grease) model and the deposited layer play a part in the lubrication process, with the deposited layer acting as a boundary lubricant for a short period before it is broken down, being regenerated when lubricant supply increases [125].

In this second phase of bearing life, and therefore most of the life of the bearing, the lubricant supply will be a limiting factor on the film thickness [121]. Unlike oil, grease will not easily flow back into the contact path after being expelled by the passing rolling elements. Contrary to the fully flooded case, in a semi-starved regime, increasing speed will reduce film thickness [127]. Starvation is also worsened by increased viscosity as the lubricant is less able to flow back to the contact path [128].

Since each overrolling will displace some lubricant, some means of reflow must balance this in order to maintain a stable film. If this reflow is insufficient, decay of film thickness with time is observed [129], [130]. The quantity of lubricant that flows back in time for the next rolling element is controlled by factors including bearing speed and hence time between overrollings, the quantity of lubricant adjacent to the track and the rheology of the lubricant [125]. The mobility of the lubricant can be characterised by the time taken for capillary action to draw it into the thin gap between rolling surfaces, and has been correlated with film thickness in the semi-starved regime [131]. Bearing type also influences the reflow ability, with the wide, elliptical contacts of a rolling bearing more susceptible to starvation than the

narrower contacts of a deep groove ball bearing [132]. Apart from reflow by capillary or surface tension forces, centrifugal forces may act to resupply the contact by aiding flow, though the opposite is also possible. Cage design is also known to be vital in resupply. It may either redistribute grease over the surface of the rolling elements or scrape it off depending on the clearance [133].

In addition to shear degradation of grease in and around the contact which breaks down the thickener structure and reduces consistency [134], another mechanism of degradation is oxidation. The base oil will oxidise to form alkyl hydroperoxide radicals and branching reactions which terminate upon the formation of polymerised oils or other molecules such as alcohols, aldehydes, ketones and carboxylic acids [13], [59]. These molecules alter the bulk viscosity, rheology and corrosive behaviour of the lubricant. Interaction between the base oil and thickener will be altered as a result of the solvency of the oil increasing. The thickener itself oxidises, with lithium soaps tending to lose their hydroxyl group leading to reduced shear stability due to reduced intermolecular attraction [53]. The microstructure of the thickener is affected as a combination of the thickener oxidation and altered oil solvency, fibres aggregate and reduce in length [53]. Antioxidants can prevent this process until they are fully consumed, however they can affect the thickener microstructure [135]. While oxidation in oils is universally considered inimical to performance, the same may not necessarily be true in greases. Some effects of oxidation such as reduced shear stability and increased oil bleeding may contribute beneficially to lubrication in a semi-starved regime. At the very least, oxidation of the thin lubricant films is known to occur very soon after or during the running in period and hence the oxidised grease is the main lubricant for the life of the bearing [136].

The lubricating film thickness of fully-flooded rolling contacts has long been modelled to acceptable accuracy by various well-established equations, for example the Hamrock and Dowson equation for point contacts [137]. These equations are only applicable to lubricants that behave in a Newtonian manner in the contact inlet, however, which excludes highly non-Newtonian greases; the shear rate in the inlet varies hugely and hence the grease viscosity varies. The heterogeneous nature of grease and the state of degradation are also variables in

the formation of a film. For these reasons, attempts to model the film thickness of grease rolling contacts have not seen widespread acceptance and will be mentioned only briefly (Lugt reviews film thickness models for greases in detail [5]). By using a rheological model for the behaviour of grease it is possible to produce an equation for film thickness as Jonkisz et al. have done [138]. They used a Herschel-Bulkley model which includes shear thinning and yield stress behaviours. Their analysis still assumed a fully flooded inlet which is not accurate for most of the life of a bearing [120]. Hamrock and Dowson also produced an equation for a starved point contact, but for a Newtonian fluid and requiring accurate knowledge of the inlet meniscus position [139]. Chevalier et al. developed a model that used the amount of lubricant present on the surface instead of meniscus position [140]. Zaretsky developed a very simple empirical model for film thickness under starved conditions, requiring only the material parameter $\bar{G}$ and the speed parameter $\bar{U}$ as inputs, readily available if film thickness was to be calculated [141]. In order to give meaningful results, the degradation of the grease in terms of shear and oxidation must also be taken into account as this will affect ability to resupply. The Chevalier model was coupled with a model for shear degradation of grease by Mérieux et al. to predict film thickness with time for a set of 3 greases [130]. Shear degradation itself has been modelled by Zhou et al. and takes into account accelerated degradation due to increased temperature, but does not account for oxidation of the thickener [105]. The interplay of these effects makes an all-encompassing model extremely challenging to develop and leaves existing models lacking in one area or another.

2.8.2 Traction in Rolling Element Bearings

Together with the life before failure of a rolling bearing, the frictional torque is an important characteristic of bearings, contributing to frictional losses in almost every instance of mechanical work. The abundance of rolling bearings in machinery means small increases in efficiency are worthwhile.

While the dominant contribution to frictional torque of a bearing during the initial phase of operation may be churning of the grease, in the second phase the traction coefficient at each rolling contact will be most important. Ignoring lubrication, there are various sources of friction in rolling contacts outlined by Harris in his comprehensive book on rolling bearings

[21]. There are peripheral sources, for example seal friction, sliding between cage and rolling elements, and viscous drag or churning of the lubricant. There are also sources directly related to the rolling contact. Hysteresis in the elastic deformation of the metal surfaces is a relatively small contribution [47], most of the traction is produced by micro-sliding and micro-slip at the contact surfaces. Most of these sliding effects are inevitable effects of rolling, even in unrealistic situations of perfect alignment of rolling elements. Gyroscopic forces produced by the rotating elements induce motion until they are balanced by resistive forces produced by sliding. While a portion of a rolling contact will be ‘locked’, under the influence of a tangential stress, part of the contact will slip, a phenomenon described by Reynolds [142]. Heathcote described a separate form of slip that is a consequence of rolling in a concave groove. As rolling must occur about a single instantaneous axis of rotation at the contact, a curved contact will only have two points of pure rolling, sliding occurs between these points as well as outside, though in opposing directions [143].

By lubricating the contact, surface-surface sliding can be avoided and traction is then a result of viscous losses in the lubricant. While film thickness of an EHD contact is mainly controlled by the conditions of the inlet, the traction force is controlled by the rheology of the lubricant in contact (though film thickness itself has a large effect on traction). Mathematical models exist for calculating the shear stress in these contacts, considering the extreme pressures, temperatures and shear rates [117], [144]. For the same reasons as discussed for film thickness prediction, these models are not applicable to greases.

2.9 GREASE INDUSTRIAL PRACTICES

When seeking to progress grease technology and produce an enduring and valuable improvement to the tribology of industry, it is important to understand industrial practice as it stands. As a subset of mechanical engineering, tribological research has had an especially strong influence on industry ever since it developed as a field of its own. As a subset of tribology, grease research is the exception. Firstly, there is comparatively little research devoted to grease when compared to oils, with Cousseau finding 1 in every 6 to 9 papers on lubricating oils and greases refers to grease [145]. Secondly, there have not been as many crucial and applicable advancements in grease research as with oils and thirdly, as with many

This method also assumes a constant supply of base oil to the contact which is not valid for greased bearings.

Lubricating oil producers generally provide a wide range of information in their product data sheets. Greases on the other hand inherit all the properties of their base oil in addition to the effects of the thickener but these are rarely specified completely. Usually only the viscosity at 40°C and 100°C, the viscosity index of the base oil and the base oil type are specified, leaving the engineer to make an uninformed selection.

Apart from viscosity, the many other parameters that may dictate lubrication performance such as consistency, corrosion resistance etc. are accounted for by the use of either rules of thumb as in the first case (e.g. bearings should be lubricated with NLGI grade 1-3, higher consistency at higher speed), or standardised test methods to assess suitability as in the second (tests such as the EMCOR water corrosion test).

2.10 STANDARD TEST METHODS

There are many standardised test methods specific to greases, some of which characterise their properties while others assess their performance under particular conditions. An important family of test methods are the full bearing tests, which assess lifetime before failure, noise, and frictional torque.

These tests may be grouped according to the underlying properties being assessed: general physical properties, chemical and tribological.

2.10.1 Physical Properties

Cone Penetration (ASTM D217, IP50, DIN 51804/1-2, ISO 2137)

The cone penetration test was first developed by the NLGI (National Lubricating Grease Institute) and ASTM (American Society for Testing and Materials) International in 1925 [148] and has since been adopted as a joint ASTM-IP (Energy Institute, originally Institute of Petroleum) standard. Many other organisations have their own versions for example DIN and ISO [148].

This test is used to determine consistency of a grease, defined as “The degree of resistance to movement under stress.”[109]. The measured value is influenced by the yield stress of the grease, the viscosity of the base oil and even the density of the grease, which provides an inertial resistance to the impact. The NLGI grade classification ranges from 6, a ‘block’ grease, to 000, a semi-fluid grease. Rolling element bearings usually use a 1-3 grade grease [5].

Yield stress seems to be the salient factor for which consistency is used as a proxy, for example in a high-speed bearing a higher consistency would be recommended to resist centrifugal forces that may starve the contact of lubricant. In this case it is really yield stress that controls this behaviour. Yield stress assessment using more controlled and direct methodology such as a rheometer would improve upon the currently non-specific test. Additional motivations for choosing a higher consistency such as a need for reduced oil bleed would be better answered using other test methods.

Roll Stability Test (ASTM D1831, D8022)

ASTM D1831, cone penetration loss after further working. The grease is sheared by the action of a 5 kg cylindrical bar, rolling inside a cylindrical container. In ASTM D8022, the test is performed with the addition of water. Despite the warning that no accurate correlation can be made between test results and shear-stability in service, the test is used to assess shear-stability of a grease. The test is intended to determine if a grease is likely to stiffen or lose consistency in service [149].

Dropping Point (ASTM D566, D2265, ISO 2176, DIN 51801 and IP 132)

The dropping point of a grease describes the temperature at which it is sufficiently fluid to flow out of a cup, either through release of base oil or complete melt of the thickener. It is described in ASTM D566 and D2265, differing in the method of heating, with D566 describing temperature increase at a steady rate, whereas in D2265 the cup is introduced to a pre-heated chamber. Additional standards for dropping point are ISO 2176, DIN 51801 and IP 132.

As an indicator of performance in a bearing it is very limited as greases are usually far too soft and bleed oil well before their dropping point [150]. As the test is relatively short, sustained temperatures in a hot bearing are not accounted for.

Oil Separation (ASTM D1742, DIN 51817, IP 121)

Oil separation from grease is undesirable in storage, leaving the thickener concentration of the remaining grease higher, resulting in unexpected physical behaviour. DIN 51817, IP121 and ASTM D1742 all assess this behaviour. The percentage mass of oil bled through a wire mesh cone is measured after time under pressure from a weight (DIN, IP) or a pressurised air system (ASTM). The time, temperature and pressure all vary among these tests. The results correlate well with bled oil in storage and hence are valuable for predicting shelf-life [150], however they are not designed for use in predicting oil bleeding under bearing conditions. Nonetheless it is widely used as an indicator for this behaviour, with many researchers correlating bleed-rate with bearing life [151].

Water Resistance (ASTM D1264, D4049, DIN 51807)

The absorption of water by a grease can be assessed with DIN51807, a test in which the amount of water absorbed by a 1 mm layer of grease on a plate in 3 hrs at 90°C is categorised by visual inspection. This is a crude assessment but it is critical to know how much water is absorbed as it can seriously affect the rheological behaviour of grease [104], though absorbing water may be advantageous if it prevents free water corroding the raceway surfaces [5].

The ability to seal against water ingress is ideal but difficult to assess. ASTM D1264 evaluates the “water washout” resistance of a grease in a shielded, unsealed bearing subjected to a stream of water for 1 hour. The mass loss indicates water resistance. This test is unreliable and may not predict bearing performance under presence of water [150]. ASTM D4049 evaluates the resistance of a thin layer of grease on a stainless steel panel to “water spray-off” by directing a water jet at the panel with mass loss indicating resistance. According to ASTM the results correlate well with performance in bearings directly subjected to water such as steel mill roll neck bearings [150].

2.10.2 Chemical Properties

Corrosion (ISO 11007, IP220, DIN51802 and ASTM D6138)

The EMCOR test standard is used to assess the corrosion protection ability of a grease. A number of bearings are partially submerged in water which may be distilled, NaCl solution

or synthetic sea water and run intermittently for 1 week, stopped for many hours. The corrosion of the outer raceways is assessed visually and graded. This can indicate the ability of the grease to protect against condensed water, however the extremely accelerated nature of this test limits its applicability to longer time scales.

Oxidation stability (IP142, ASTM D942, D5483)

The resistance of a grease to oxidation in a pure oxygen environment is assessed using the oxygen bomb methods, IP142 and ASTM D942. ASTM advises caution in interpreting these results, emphasising that the test was originally designed to predict shelf-life of pre-packed bearings and does not correlate with shelf-life of grease in containers let alone in running bearings [150].

Differential scanning calorimetry (DSC) and pressure differential scanning calorimetry (PDSC) are methods more recently being employed to assess oxidation behaviour by detecting the heat released by exothermic oxidation reactions. PDSC test ASTM D5483 can be used to measure the oxidation induction time of a grease, the time until oxidation heat is detected after exposure to oxygen. The test is more reliable than D942 yet similarly has not been correlated with performance in bearings [150].

2.10.3 Tribology

Fretting Resistance (ASTM D4170, D5706, D5707, D3704)

A range of testing standards exist to determine the ability of a grease to protect against fretting, or the more specific term false brinelling. Fretting is the broad term for wear in small-amplitude oscillation while false brinelling is specific to bearings suffering damage when vibrated at standstill [152]. The Fafnir friction oxidation tester (D4170) determines fretting protection from the mass loss of the races of two thrust ball bearings, subjected to 12° rotation at 30 Hz. The relatively large amplitude may limit its applicability to vibration-induced damage.

Other fretting tests exist such as ASTM D5707 which uses a reciprocating ball-on-flat machine called an SRV to determine coefficient of friction and wear scar diameter. Although the standard specifies load, frequency and stroke length, the SRV may be used in various setups,

including the D5706 standard which measures seizure load under otherwise similar conditions. ASTM D3704 employs the Falex block on ring system (similar to the Timken machine) in oscillatory motion to assess in general terms (high, medium, low) the wear protection provided by a grease through measurement of the wear scar diameter.

Timken OK Load (ASTM D2509, IP326)

In the Timken EP test, ASTM D2509, IP 326, the inner race of a bearing is rotated against a stationary hardened steel block lubricated by a pumped supply of grease. The load is then incrementally increased until the lubricant film collapses, a subjective observation. The 'OK' value is the maximum load reached within the 10-minute test, however this test is not indicative of bearing performance for a number of reasons. As a fully flooded, pure sliding contact there is little resemblance to the rolling, partially starved contacts of rolling bearings. It is additionally unclear at what point the film collapses from an external view or how large a wear scar can be considered failure. Timken developed the test machine but stopped producing it in 1972, and state that the original purpose was to identify whether a lubricant contains EP additives, not to assess EP performance [153].

Four Ball Tests (ASTM D2266, D2596, IP 239, ISO 20623 and DIN 51350-4/5)

The Shell four-ball test was developed in the 1940s to assess the anti-wear performance of greases and later oils [148]. In this test, four balls form a tetrahedron, with the top ball loaded against the three stationary balls below and rotated between 1200-1800 rpm. Two ASTM standards relate to greases, D2266 [154] in which the wear scars on the three balls are averaged after 1 hour of running at 1200 rpm, and D2596 [155] in which the top ball rotates at 1770 rpm for 10 seconds, after which the load is incremented and the test continues until welding of the balls occurs. Similar standards are provided by IP, ISO and DIN.

The wear scar and weld load are often used for specifications and provided in grease data sheets as an indication of EP performance in rolling bearings. However the applicability of the test to grease lubrication in bearings is questionable as according to ASTM "results may not correlate with service performance" [148]. The D2266 standard states that "No correlation has been established between the four-ball wear test and field service" [154] which the D2596 standard echoes. ASTM standard D4172, an analogue of D2266 but for oils rather than grease,

also makes clear that “no attempt has been made to correlate this test with balls in rolling contact.”[156]. These tests involve pure sliding contacts, ostensibly fully flooded lubrication and extremely high flash temperatures which all make it a very poor assessment of grease EP in a rolling bearing.

2.10.4 Bearing Tests

Bearing tests are of course vital in grease development and specification. As the geometry is identical to service conditions, they feature all the complex churning, shearing, displacement and reflow mechanisms that occur in a bearing and are extremely challenging to replicate in bench tests. Other conditions such as temperature, load and speed tend to be relatively extreme compared to typical running conditions in order to accelerate bearing failure. Some of the most important bearing tests are outlined in Table 2.1.

Failure, often defined by a maximum temperature or simply by a current limit to the driving motor, is the usual intended outcome. Bearing tests are most often used to validate a grease under certain conditions of bearing type, temperature etc. and to calculate grease life using Weibull statistics. Some have a more specific aim, for example the SKF BeQuiet+ test rig evaluates the noise generated by grease in low noise bearings [157], while the V2F test determines grease leakage under the specific conditions of railway spherical roller bearings [158].

Test Name	Conditions	Use	Standards
R0F	Deep groove ball bearings, 6000, 10000 or 20000 RPM, 70-170°C	Lifetime evaluation for chosen conditions (applicable to electric motors).	-
R0F+	Range of deep groove ball bearings, spherical roller bearings, 5000-25000 RPM, up to 230°C	Lifetime evaluation, higher speeds, temperatures and loads than R0F possible.	-
R2F	1500 or 2500 RPM roller bearing up to 160°C	Weight loss of rolling elements and/or cages used to determine wear prevention in industrial/rail applications.	DIN 51806 (obsolete)
FE8	Axially loaded bearings under wide range of conditions up to 4500 RPM, 200°C	Comparable to R2F, but with axially loaded bearings. Often used to assess wear via weight loss of bearings in mixed regime. Provides friction torque measurement.	DIN 51819
FE9	Angular contact bearings, 6000 RPM, 200°C	Comparable to R0F but slightly slower. Lifetime evaluation	-
V2F	Spherical roller bearing, 500, 1000 RPM	Test for mechanical stability, grease leakage is determined after 72 hours at 500 RPM and 72 hours at 1000 RPM.	SIS 3653, part of railway standard EN 12081
RHF1	Up to 75,000 RPM, 230°C	Very high speed, high temperature life testing.	-
BeQuiet+	Deep groove ball bearings, 1800 RPM	Measurement of bearing noise on addition of grease. Can also measure the effect of contamination of greases on noise.	-
Low temperature torque	Various depending on standard, generally 1 RPM, -18°C to -75°C	Measurement of resistive torque in order to differentiate low-temperature characteristics of greases.	ASTM D1478, D4693, IP 186

Table 2.1: Bearing test conditions and outcomes.

Compared to the bench tests discussed previously, little criticism can be placed on the use of bearing tests which serve their specified purpose, be it lifetime prediction or evaluation of a specific property. In fact, they are, by definition, representative of real-world applications in terms of geometry. Their failing is most often the accelerated nature of the tests, such as unrealistic speeds or temperatures. Differences in these factors may alter the many complex processes occurring in bearings and render the test inaccurate for common applications.

The main difficulty in performing widespread bearing testing of greases lies in the cost of such tests, in particular lifetime tests which, if tested under reasonable conditions, may last well over a thousand hours. At the end of the test, little information is available to indicate how the grease performed or what caused the failure, apart from a similarly time-consuming analysis of the bearings. Additionally, with increasing focus on grease energy efficiency, it is surprising how rarely a test provides friction torque as a data output, the FE8 test being an exception.

Very few of the reviewed methods provide a direct prediction of grease performance in bearings and are difficult to use as criteria for choosing a grease for a particular application. The R0F/R0F+ evaluate grease life under accelerated conditions but do not measure friction/energy over the test life. There is a considerable need for directly applicable test methods, particularly relating to energy efficiency, an area that is particularly lacking in the range of tests that are widely adopted currently, yet has been a driving force in tribology for the past decades.

2.11 SUMMARY

This chapter has reviewed the literature and industrial standards relating to the work of this project. It has aimed to identify the areas that remain to be well understood and highlight areas where existing practice is flawed. Review of the understanding of grease structure has shown that it is far from complete. Theories exist to explain why certain thickener systems behave as they do, but a deeper understanding that would allow design of a thickener to achieve desirable properties is not yet possible. The lubrication mechanisms operating in a running bearing are also only generally understood. It is an extremely complex process in

comparison to that of oil and, as a result, it is potentially impossible to produce a comprehensive analytical model to describe it. It may be only through progressively more powerful numerical models that the process is understood for a range of greases. A generalised description is that it seems to be a combination of multiple processes that conveniently work to maintain film thickness. Research suggests that it is not entirely undesirable for grease to be degraded in the operation of a bearing and that it may in fact contribute to optimal performance.

The increasingly important effect of frictional losses necessitates an understanding of how these processes work, so that improvements can be made to grease formulation with a more informed procedure than is currently possible. Changing economic situations mean that past developments in lithium greases cannot always be relied upon. The current system of testing and analysis in industry has been reviewed and appears insufficient for the purposes of 'enlightened' grease development. Widespread adoption of a technique does not guarantee its validity. In fact, this review has shown that many techniques are used beyond their intended purpose, in direct violation of the standards themselves.

In summary, the understanding of grease lubrication of bearings has progressed greatly in the last century, but is far from complete and, more importantly, is insufficient to enable purposeful grease design and improvement. Grease manufacturers, in general, have strayed from what the author considers the ideal path to improved grease formulation and are not employing suitable tests to distinguish those greases that will perform well in bearings from those that will not. There is more interest in qualifying formulations than in testing to understand the merits of novel formulations.

2.12 RESEARCH STRUCTURE

The literature review has outlined both gaps in understanding of grease lubrication, and flaws in the grease test methods. Work based on the above findings would have the goal of a model grease test that accurately emulates the conditions and geometry of bearings. This would allow results to be applicable to real bearings, while also being much less expensive and time consuming than bearing tests. It would also allow a detailed observation of the lubrication

mechanisms which are not accurately understood, in particular during bearing-like operation which is vital to reproduce the relevant mechanisms in the first place. Bench tests involving ball-on-disc geometry differ greatly from the highly conformal, multi-contact bearings, shown in Figure 2.7. Differences of these kinds can serve to fundamentally change the way lubrication occurs, leading to false conclusions about greased bearing lubrication.

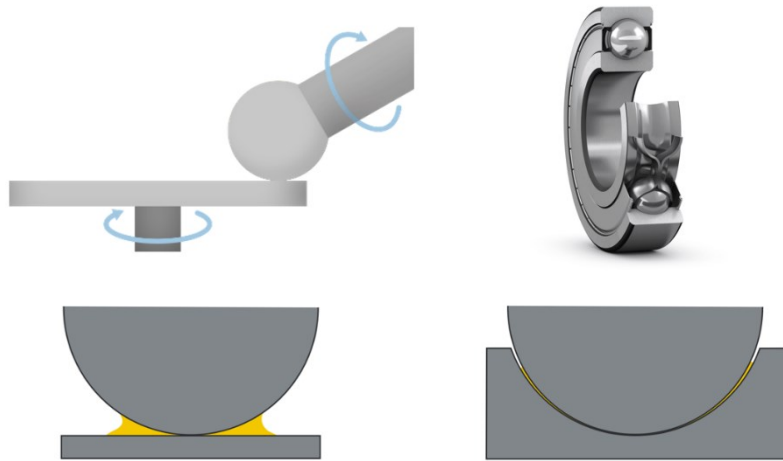


Figure 2.7: Comparison of the contact geometry of a ball-on-disc model test, and the bearings which they must emulate.

Development of such a test device was the ultimate goal of the work undertaken during this PhD. Before doing so, it was first necessary to determine in what ways exactly current model tests fail to replicate bearings. The research programme can be split into three main areas:

- Analysis of bearings during typical running life, observing lubricant distribution, lubricant film composition and state of degradation. This provided an understanding of the condition of the ‘active’ lubricant in bearings. This work is discussed in Chapter 4.
- A battery of model bench tests, measuring both film thickness and friction of a range of greases. The purpose of this work was to assess the effect of grease degradation on these metrics and hence how inaccurate the testing of fresh grease is, in relation to running bearings. Other limitations of these systems were noted. These results are presented in Chapter 5.
- The design, development and testing of a novel film thickness rig, attempting to overcome some of the observed shortcomings of existing test methods. The development of this system is described in Chapter 6, and the results of preliminary testing are presented in Chapter 7.

3 EXPERIMENTAL METHODS AND MATERIALS

This chapter describes the experimental methods and materials used in the project and is intended as a reference for later chapters that report the experimental results. These methods are grouped into three sections: lubrication performance, grease characterisation and grease degradation.

Lubrication performance covers tribological tests from the model bench devices that measure friction and film thickness to the R0F+ bearing component test. These tests aim to help understand the mechanisms of grease lubrication and distinguish formulations that perform well from those that do not in these important metrics of friction and film thickness.

The next section covers grease analysis and characterisation methods. Analytical techniques such as Fourier transform Infrared (FTIR) spectroscopy are used to infer chemical structure. Rheometry is used to characterise the rheological behaviour of greases and these techniques are all used in tandem to understand and interpret tribological results.

The process of greases degradation in bearings has been shown to be of vital importance in the lubrication of bearings in the long term and techniques to replicate the same processes in bench systems are covered in the ‘Benchtop simulation of grease degradation’ section.

All test greases and their relevant properties are displayed in a table near the end of the chapter, and lastly the chapter is summarised.

3.1 LUBRICATION PERFORMANCE: MTM FRICTION

The measurement of grease rolling friction has not been widely studied compared to other performance measures such as grease life, perhaps due to the lack of standardised industry friction tests. A researcher or research and development engineer aiming to evaluate the friction behaviour of a grease in a rolling contact has few options if they wish to use an established system. Versatile ball-on-disc tribometers that are commonly used for a range of tribological tests are often used to emulate the rolling contact of a bearing. These systems remove the influence of bearing geometry and cage, allowing study of grease traction at its simplest level, meaning the effects of formulation can be evaluated exclusively. Removing

such influences on bearing friction has significant effects that must not be ignored and will be discussed in Chapter 6. Examples of these systems are the WAM 11A (Wedeven Associates Inc. [159]) and the MTM2 (PCS Instruments [160]). Many researchers have also developed their own custom machines.

The MTM2 was used for measuring grease and base oil friction in low slide-roll conditions. It is widely used in the measurement of lubricant friction, offering a range of slide-roll-ratios, speeds and loads. This allows a lubricant to be analysed in boundary, mixed and hydrodynamic regimes. Many researchers have previously used this test machine in the study of grease rolling and sliding friction [46], [161]–[166].

3.1.1 MTM Test Rig

In this system, a cantilevered ball specimen is loaded onto a disc specimen and the two roll together, each driven independently. Traction force, produced by the difference in speed as dictated by the slide-roll-ratio and the entrainment speed, is exerted on the cantilevered ball and measured with a force transducer on the ball shaft. The machine alternates between positive and negative slide-to-roll ratio (ratio of sliding speed to mean rolling speed, SRR) i.e. which specimen is moving faster, in order to give an average force measurement. The load is applied via a stepper motor through a load beam onto the ball shaft. A strain gauge on the load beam reports the load value. A stainless steel pot surrounds the disc specimen, which contains the lubricant during the test. A stainless steel lid is placed on the pot and locked in place during the test. In order to achieve an accurate test temperature, PTFE insulation surrounds the pot and lid. Heating is provided by two cartridge heating elements embedded in the pot and a PID control system achieves accurate temperature control based on the readings from two thermocouples, one in the base of the pot and one extending into the lubricant within the pot itself. The second thermocouple indicates the true lubricant temperature. The setup is shown in Figure 3.1.

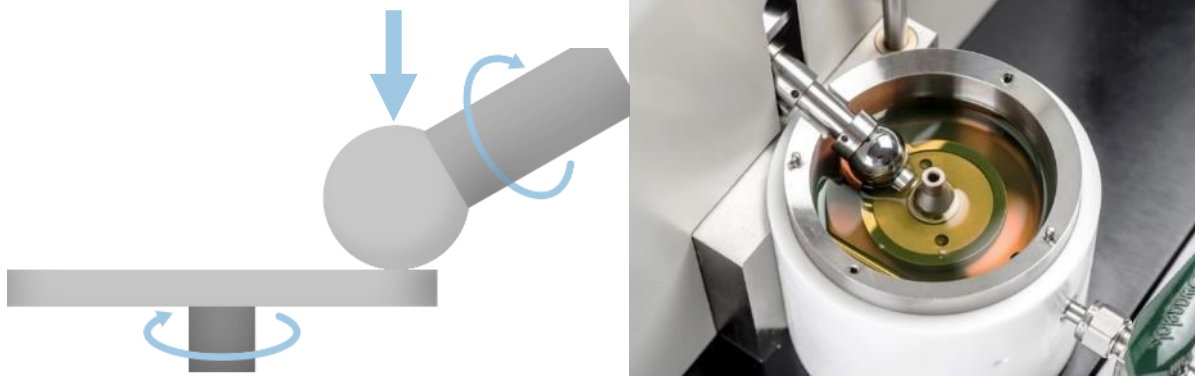


Figure 3.1: a) diagram of the MTM specimen arrangement. b) Image of the MTM pot [167].

A scoop that directs displaced grease back into the contact path was used to ensure a fully flooded inlet when testing the greases and prevent lubricant starvation that might influence measured friction. This consisted of a PTFE block with a V-shaped channel. A locating pin positioned the scoop on the disc specimen contact path so that grease that was displaced by the ball was channelled by the V-groove back into the contact path. A spring on the top of the scoop lightly pressed the block against the disc when the pot lid was in position. This arrangement is shown in Figure 3.2. When testing oils, the disc was instead immersed in a bath of the oil, ensuring complete coverage up to half the height of the ball.



Figure 3.2: a) PCS Instruments grease scoop. b) The grease scoop in position in the MTM, seated on the disc specimen [168].

In addition, a custom, 3D-printed scoop was designed to further ensure no starvation occurred over the course of a long test. This was based on the observation that the existing scoop served to push grease still on the polished contact surface of the disc back into the central contact path, but that grease would also be pushed into the centre of the disc and out over the edge of the disc. Over time this would result in starvation. The body of the new scoop sits

underneath and outside of the disc, preventing accumulation of grease on the edge of the disc. A PTFE strip also sits on the inner surface of the disc, channelling grease outward towards the contact surface. The contact surface itself is not contacted at all by the scoop. As the traction measurement is solely based on the cantilevered ball, the presence of the scoop does not interfere with the traction measurement.

The scoops were printed from PETG in order not to soften excessively at the operating temperature and were considered disposable, but were reused for the same grease. The PTFE strip was reused after cleaning in petroleum ether.

3.1.2 Test Preparation and Cleaning

All the specimens were soaked in toluene for at least 24 hours prior to testing. They were removed from the toluene before use, rinsed in petroleum ether and air dried before assembly.

The MTM oil bath and ball shaft were cleaned after every test. After a complete oil test, the oil was drained and the ball shaft and pot wiped down then cleaned with petroleum ether. The drainage tap was rinsed with petroleum ether also. Retaining bolts were wiped down and cleaned with petroleum ether. On finishing a grease test, as much grease was scraped off as possible, then the surfaces were wiped with paper cloth and rinsed with petroleum ether.

The PCS grease scoop was wiped and cleaned with petroleum ether and the custom grease scoop was disposed of, except for the PTFE strip which was cleaned in the same way and reused.

3.1.3 Test Method

The test conditions are shown in Table 3.1. A reasonably high load was chosen to produce a maximum contact pressure on the order of 1 GPa, similar to contact pressures in a bearing [169]. Similarly, a SRR was selected to approximate the value of a bearing which is generally 3% to 5% [170], however the traction force is directly proportional to this value for a constant value of friction, meaning it must be sufficiently high to produce a measurable signal.

Test Parameter	Value
Load [N]	20
Ball Diameter [mm]	19.05
Specimen Material	AISI 52100
Maximum Contact Pressure [GPa]	0.80
Slide-Roll ratio	5%
Rolling Speed [m/s]	0.01 – 1
Composite Surface Roughness [nm]	~13
Temperature (°C)	40, 60, 80

Table 3.1: MTM test conditions.

A test run is composed of multiple steps, always beginning with a 20-minute step in which the specimen is rotated out of contact at 0.5 m/s, in order to allow the grease to settle in the scoop and reduce the likelihood that starvation would occur during the test. The result of this run-in is shown in Figure 3.3. The standard test used for this work followed this step with 5 successive speed sweeps which were conducted from low to high speed, with a 2 minute ‘recovery’ step after each with no specimen contact, again at low speed. This test scheme allows each speed sweep to reveal any initial shear degradation that occurs within the ~25 minutes of total rolling time and was developed after poor repeatability in trial results.

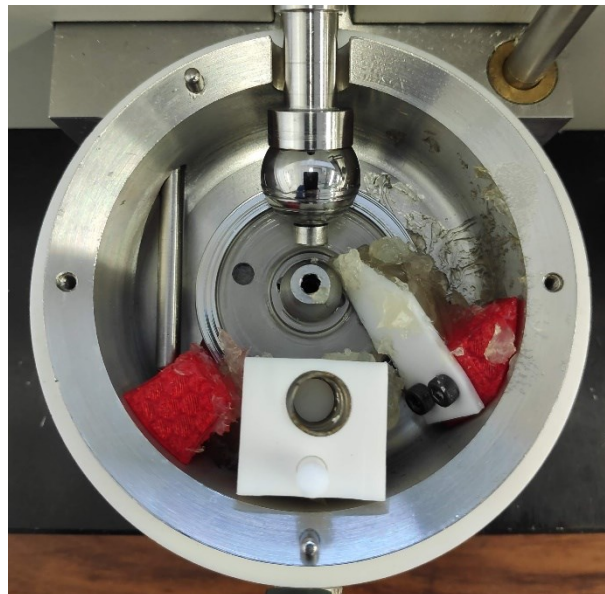


Figure 3.3: Distribution of grease for an MTM test. A large amount of grease is situated in the scoop on the righthand side, creating a thick film on the disc as it rotates.

Longer term tests were also conducted in order to evaluate the degradation that occurred during MTM testing, running the ball and disc at constant speed and SRR for a set time. The MTM discs were kept after testing and used for microscopy imaging as well as FTIR analysis.

3.1.4 Lubricant Supply Conditions

Most testing done with the MTM was ostensibly in the ‘fully flooded’ supply condition and efforts were made to maintain this condition. In reality, it was very difficult to maintain this supply constantly, especially with greases of a higher consistency. Occasionally a speed sweep would begin to starve and the traction coefficient would obviously begin to spike. It was therefore sometimes necessary to complete one sweep manually resupplying grease with a spatula to provide a baseline measurement, any deviation from which would indicate starvation in subsequent tests. Tests were repeated until at least three uninterrupted sweeps were obtained which were then averaged to provide the final data for those conditions.

A small number of starvation tests were conducted in which only the PCS grease scoop was initially used during the run-in and then removed for the main test. The traction coefficient after that point was largely dependent on the ability of the grease to resupply the contact.

3.2 LUBRICATION PERFORMANCE: EHD – FILM THICKNESS

Film thickness measurements of rolling contacts are of value to researchers or engineers as they indicate whether a sufficiently thick elastohydrodynamic film is developed under the test conditions to separate the rolling surfaces and prevent high friction, wear and resulting failure. It is possible to measure film thickness in a bearing system, but these techniques have several downsides. Capacitive and electrical resistance measurement necessarily include all of the bearing contacts. Additionally, they are only applicable at high film thicknesses (hydrodynamic regime or $\Lambda > 3$) or low (mixed regime or $\Lambda < 3$) respectively and the techniques must be combined to cover the whole range of interest [171]. Optical interferometry measurements necessitate modification of the bearing in order to achieve a transparent contact surface. Bench top single-contact optical interferometry tests have been widely used to study the behaviour of grease in a rolling contact and draw conclusions about

performance in a bearing, with many groups making use of the technique [51], [85], [124], [172]–[174].

The original model EHD rig produced by PCS Instruments was used in this project. This system, and its successor have been used for decades to understand lubricant behaviour under EHD conditions, differing only in terms of software and electronics. By attaching a camera to the microscope, images of the rolling contact can be obtained which are extremely valuable, especially with an inhomogeneous lubricant like grease.

3.2.1 EHD Test Rig

A ball on disc rig like the MTM, the EHD rig uses a transparent BK7 glass disc through which a microscope can focus on the rolling contact. An AISI 52100 steel ball is loaded against this disc, sitting on top of a carriage of deep groove ball bearings, allowing it to rotate with very little friction, driven by the motion of the disc and the traction between them. A stainless steel pot contains the test lubricant. A PTFE insulating lid is placed on the pot during the test, with a hole through which the microscope can observe the contact.



Figure 3.4: a) Disc specimen in pot, with microscope in position [175]. b) Diagram of EHD function.

The heating system is similar to the MTM, with cartridge heating elements embedded in the pot and thermocouples in the pot and projecting into the lubricant.

3.2.2 Optical Interferometry Film Thickness Measurement

Ultra-Thin Film Measurement

A thin-film interference film thickness measurement method is used, first applied to elastohydrodynamic contacts by Gohar and Cameron in 1963 [176]. Since this first use, many developments have been made, perhaps most significantly the use of a spacer layer to allow very thin films (<100 nm) to be measured and a spectrometer to determine accurately the wavelength of peak constructive interference [177]. This allowed sub-nanometre resolution film thickness to be measured down to zero film and ± 1 nm resolution [175].

The underside of the glass disc is coated with a thin, semi-reflective chromium layer. A silica spacer layer of ~450 nm thickness is then sputtered on top of this. In use, a light source reflects off a beam-splitter and is directed through the microscope objective to illuminate the contact. At the chromium layer, some of the light is reflected back and some continues through the lubricant film and is reflected off the ball. These two beams interfere with one another, assuming normal incidence of the beams, constructively [177]:

$$h = \frac{(N - \phi)\lambda}{2n} \quad N = 1, 2, 3 \quad (8)$$

where h is the thickness of the lubricant film, N is the fringe order, ϕ is the net phase change on reflection, λ is the wavelength of light and n is the refractive index of the fluid. By illuminating the contact with broad-band white light from an incandescent bulb and passing the reflected light (having interfered with the incident light) through a diffraction grating, the light diverges based upon its wavelength. This light is directed at a CCD sensor, producing an image where brightness of each pixel column corresponds to light intensity at a given wavelength. This provides information about light intensity across the width of the contact, where each row relates to a single point across the contact width. It is important to restrict the measurement to only the contact centre, by taking only the central rows of the image to average into a single spectrum. The system is calibrated first by normalising the imperfect white light emission of the incandescent bulb, and then using the known emission spectra of a mercury-vapour arc-discharge lamp to provide a relationship between image column and wavelength. Once the system is calibrated, determination of the wavelength of maximum

interference is made by measuring the column of highest intensity and, along with knowledge of the current fringe order, this can then be used to calculate film thickness.

3.2.3 Optical Imaging

With a simple reconfiguration of the microscope setup, a camera can be used to capture images of the contact. In this work two different cameras were used, a high-resolution Ximea MQ022CG-CM and a 3CCD JAI CV-M9CL that displays high colour accuracy due to the individual colour channel CCDs. It was then possible to image the contact while running.

This method allowed observation of the fundamental differences between oil and grease lubrication: the lumps of thickener which entered the contact inhomogeneously and raised the film thickness at low speeds, and the starvation that could begin to occur at higher speeds. Starvation would begin with an advancing inlet meniscus, eventually nearing or entering the contact, leading to film thickness collapse. The coated discs that allow film thickness measurement provide a colourful view of the contact, allowing inference of film thickness

3.2.4 Test Cleaning

As with the MTM, the pot was wiped with paper towels after testing and rinsed with petroleum ether. The disc specimens were cleaned similarly, and reused only on areas of the disc that were not worn, scratched or flaking due to previous overrolling. This was possible due to the ability to choose test radius during test setup.

The grease scoop was wiped down and rinsed with petroleum ether. The ball specimen was cleaned similarly and reused as long as it was not showing signs of wear. It runs on a seat of three bearings, with very small sliding at these contacts so wear does occur, but very minimally. The ball carriage with its bearings became covered with grease and it was necessary to dismantle the carriage, wipe off the grease, soak in toluene and leave in an ultrasonic bath for 10 minutes to completely clean them. A separate carriage was used when testing oils to ensure no dried thickener was able to contaminate the oil.

3.2.5 Test Procedure

The rig was set to achieve temperature and left for at least two hours at the highest temperature to sufficiently equilibrate. The zero-speed film thickness measurement was taken

under load in order to calibrate to zero film thickness. The machine was then set to trigger film thickness measurements only at this point, to eliminate variations in the thickness of the spacer layer from the measurement. The speed was then increased by a set percentage successively, with three film thickness measurements taken at each speed. Once maximum speed was reached, a measurement was taken at the trigger point at zero speed in order to measure any residual film that resisted dissipation. The disc was then removed, cleaned at the trigger point and repositioned so that the trigger point remained in place. The ball was either replaced or cleaned and grease was resupplied to the grease scoop. A further two speed sweeps were then taken.

Test Parameter	Value
Load [N]	20
Ball Diameter [mm]	19.05
Specimen Material	AISI 52100
Maximum Contact Pressure [GPa]	0.50
Slide-to-Roll ratio (nominal)	0%
Rolling Speed [m/s]	0.1 – 1
Composite Surface Roughness [nm]	~13
Temperature (°C)	40, 60, 80

Table 3.2: Test conditions of the EHD film thickness testing.

3.2.6 Supply Conditions

The PCS grease scoop was used during standard tests to resupply the contact and as such all testing was ostensibly fully flooded but, as with the MTM, testing was subject to intermittent starvation. This would be apparent at higher speeds as a sudden drop or plateauing of film thickness, accompanied by much more fluctuation than would be typical at such speeds. Additionally, a live cross-sectional image of the contact would often clearly show starvation. This meant the assumption of fully-flooded inlet was quite reliable.

As with the MTM, a small number of tests were conducted in a ‘starved’ supply condition after fully flooded testing, where the grease scoop was removed. This allowed a long ‘run-in’ to enable the development of an active lubricant.

3.3 LUBRICATION PERFORMANCE: R0F+ - BEARING TEST

3.3.1 R0F+ Test Rig

The R0F+ test rig is a grease qualification tool developed by SKF, designed to assess the time to failure of greases in standard bearings at high temperatures and speeds [178]. It is an improvement upon the older R0F test, able to run at higher speeds and loads and is able to record temperature and energy consumption of the motors and heating elements. These tests are used to calculate the expected lubrication intervals as well as grease life, for example the L10 life, the time that 90% of bearings can be expected to run without failure. In this work it served to provide bearings tested under realistic operating conditions, ready to be analysed in a variety of methods in order to understand the condition of grease during bearing operation. The work was carried out during a secondment at Shell Technology Centre Hamburg, using their R0F+ rig. The technical specifications of the machine are as follows, taken from the SKF-published datasheet [179]:

R0F+ Specifications	
Spindle speed	5000 – 25000 RPM
Test temperature	Up to 230°C
Radial load	50 – 900 N/bearing
Axial load	100 – 1100 N/bearing
Drive	3 phase motor, 0.525 kW, 25000 RPM, KAISER
Power supply/Air supply	3 x 400 V/50 Hz/7.5 kVA
	Or
	3 x 480V/60 Hz/7.5 A
	Pneumatic system: min. 6 bar/87 psi
Bearing type	6204 2Z/C3 S2 VM104
	6203 2Z/C3 S2 VM104
	6202 2Z/C3 S2 VM104
	608 2Z/C3 S2 VM104

Table 3.3: R0F+ test specifications.

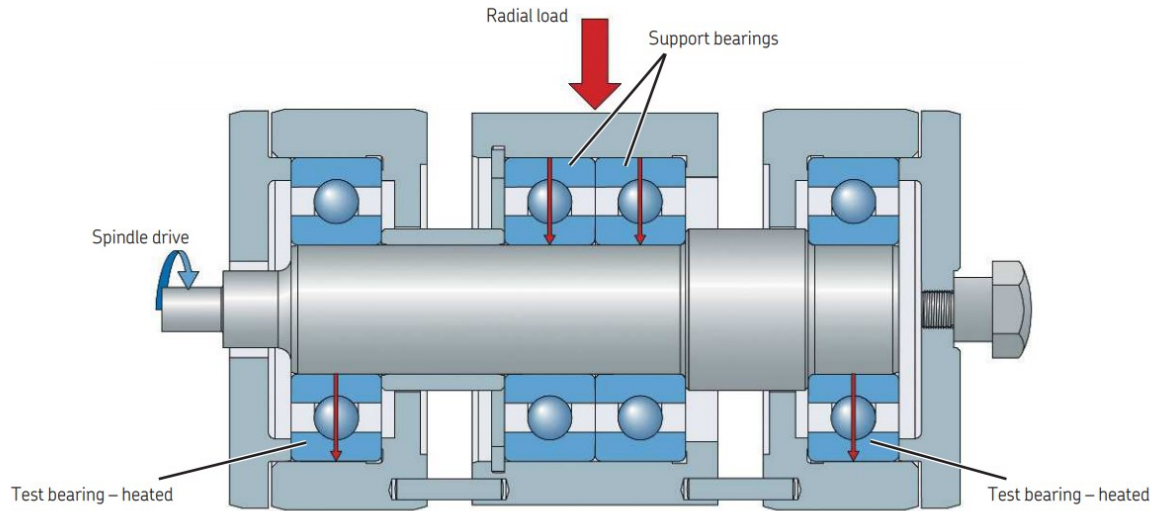


Figure 3.5: Radial load transfer in the R0F+ rig. All four bearings, including the support bearings, experience the same radial load. Image taken from [179].

The R0F+ rig consists of five separate test units, each with its own motor and bearing shaft. A diagram of the unit is shown in Figure 3.5. There are four bearings on the shaft, though two are support bearings, through which radial load is applied. The two test bearings at the ends of the shaft are seated in the cast iron housing and adjacent to heating elements which allow temperature control. Feedback is provided by temperature probes which are inserted to contact the outer races of the test bearings. The support bearings are primarily surrounded by air and are not directly heated. A single temperature probe measures the temperature of both support bearings.

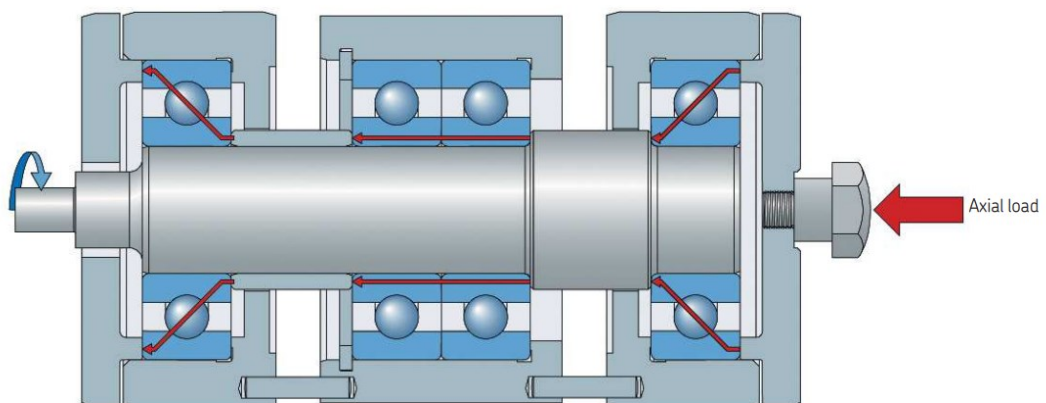


Figure 3.6: Axial load transfer in the R0F+ rig. Only the test bearings experience the axial load, it is passed through the inner races of the support bearings. Image taken from [179].

As Figure 3.6 shows, axial load is transferred through the inner races of the support bearings and therefore not through the concentrated contacts of the rolling elements. This, as well as the option of cooling air supply over the support bearings, is intended to create failure solely in the test bearings. The same grease is always used in the support bearings and test bearings and they are identical apart from their loading and temperature conditions. Usually, all five test units would use the same grease in order to gather multiple data points for a statistical analysis of estimated time to failure. In this case, as failure was not the explicit goal, each test unit was used to test different greases, though all ran under the same test procedure.

3.3.2 Test Cleaning and Procedure

All 20 bearings for a single R0F+ run were prepared together using the Shell standard procedure. They were soaked in petroleum ether to remove anti-corrosion oil and then dried in an oven at 56°C.

Five syringes were prepared, each containing a small amount of the test greases. Digital scales were used to add a controlled mass (1.4 – 1.44 g) of the test grease to each bearing with the syringe. The grease was distributed around the bearing and primarily applied to the outer and inner races, where it would be displaced by the rolling elements. Figure 3.7a) shows a bearing prepared in this way.

Once the grease had been applied, a hydraulic press was used with a specially formed tool to press the shields on tightly.

Rig Assembly

The bearings were inserted into the three housings and pressed onto the driveshaft. This assembly was located into the main housing and a coupling was fixed between the test shaft and the motor. Figure 3.7b) shows the component bearing housings prior to fitting on to the drive shaft. The temperature probes and hydraulic actuators were then put into position.



Figure 3.7: a) A bearing prepared with ~1.4 g of grease. b) The three assembled bearing housings making up a single test unit ready for assembly onto the drive shaft.

Rig and Bearing Disassembly

The bearings were pressed or pulled off the shaft using custom jigs that applied force only on the inner race in order not to damage them or apply force through the rolling elements. Any oil on the outside of the shields was wiped off and they were labelled.

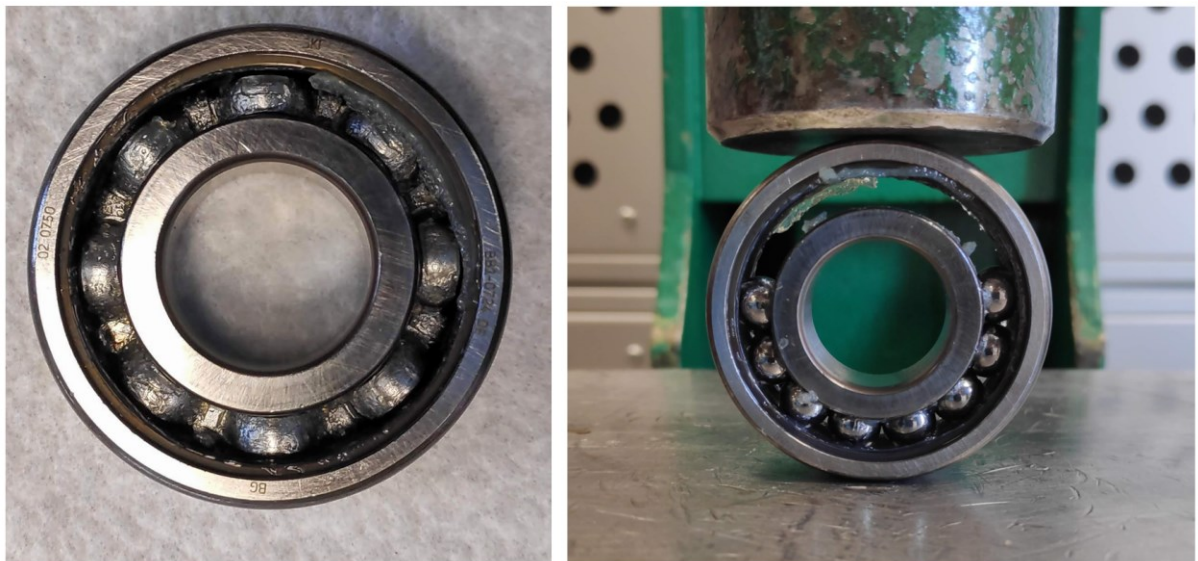


Figure 3.8: a) A bearing after removal from the R0F+ rig and removal of the shields. b) A bearing after the cage has been removed, ready to be deformed by a hydraulic press, allowing the inner race to be lifted past the balls and individual balls to be extracted, freeing up space for the inner race to be removed itself.

When dismantling a bearing, a fine pair of pliers was used to pry the shields off without denting them and transferring grease from the shields to the cage. Figure 3.8a) shows a bearing at this point of the dismantling process. The pliers were then used to fold open the tabs of the cage until the two halves of the cage could separate. All the balls were moved to

one side. As it was still not possible to release the inner race at this point, a hydraulic press was used to deform the outer race slightly, allowing a pair of pliers to extract individual balls until there was enough space to pull out the inner race. This point of the process is shown in Figure 3.8b). Care was taken throughout this process not to contaminate one region of the bearing with grease from another. It was not possible to ensure this completely, and occasional small lumps of grease would fall onto the inner race but were easily identifiable when it came to later analysis and avoided.

3.4 CHARACTERISATION OF GREASE PROPERTIES: FTIR CHEMICAL ANALYSIS

Fourier-transform infrared (FTIR) spectroscopy is a standard analytical technique which is used mainly to identify the composition of organic materials. It was performed on the test lubricants and on the thin films coating the races of the R0F+ test bearings and MTM discs after testing. Such work has previously been performed by researchers on R0F [136] and R2F [180] bearings, as well as MTM [126], [181] and EHD [182] ball-on-disc tests. IR spectroscopy can identify chemical bonds by passing broadband infrared light through the sample, and measuring the wavelengths that are absorbed. The chemical bonds within the sample vibrate in several resonant modes upon absorption of light with the corresponding energy. With knowledge of which wavelengths correspond to which bond vibrations, the absorption spectrum of a sample provides useful information about its composition. The Fourier-transform infrared spectroscopy technique utilises a Michelson interferometer to systematically create interference in the infrared light that passes through the sample and the resulting interference intensity is recorded as a function of optical path difference. The Fourier transform is then employed in processing the recorded interferogram to transform it into the wavenumber domain for analysis.

A Perkin Elmer Spectrum One FTIR was used for transmission measurements and an attached Perkin Elmer Multiscope IR microscope, shown in Figure 3.9a), was used to analyse small areas of surface films. Figure 3.9b) shows a bearing inner raceway, with the small sample area indicated.

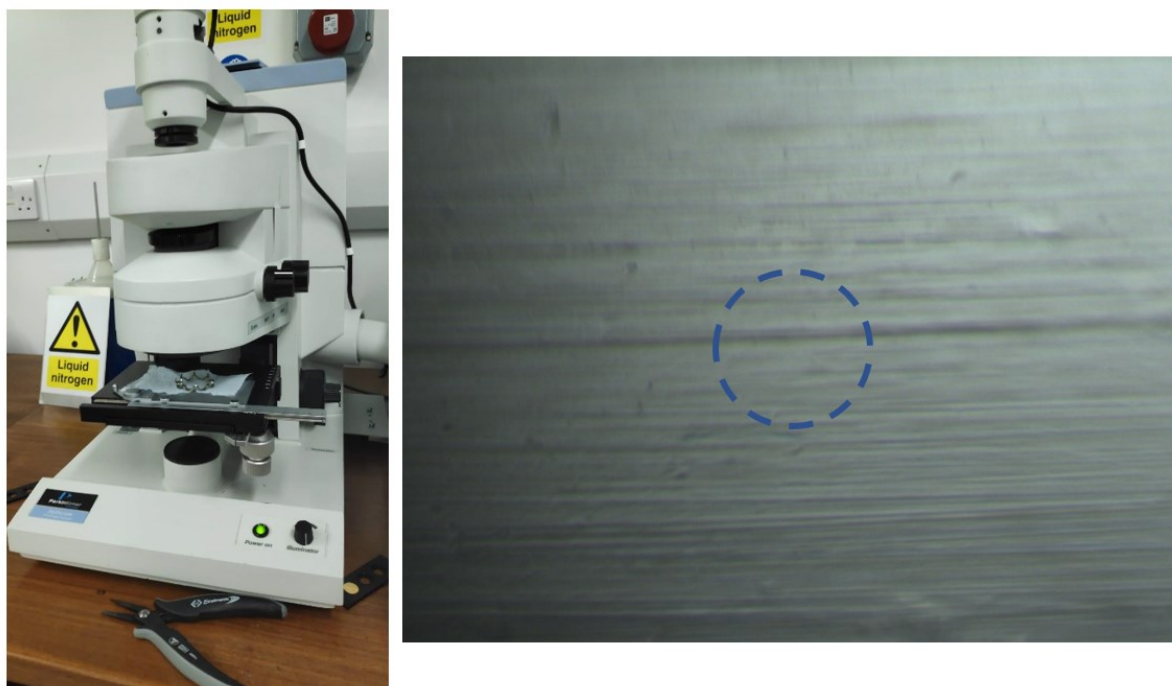


Figure 3.9: a) The Perkin Elmer Multiscope in use measuring the reflected FTIR spectrum of a bearing cage pocket. b) An image of a bearing inner raceway directly from the IR microscope, with the region from which the sample is taken indicated by the dashed circle.

With regard to lubricating greases, as the base oil and thickener generally have several unique bond vibrations, it is possible to detect changes in the relative proportions of each, compared to another sample. This technique can provide evidence of oxidation or compositional changes in both bulk and thin film samples [136], [181], for example the deposition of thickener-rich films on rolling surfaces [181]. More subtle changes such as a shift in the wavenumber of a peak or band broadening can be associated with a change in the chemical interactions of a mixture of molecules [183].

3.4.1 Sampling Methods: Transmission Measurements

The standard method for low-volatility, high viscosity liquids and pastes is transmission measurements. The spectra may be plotted either in transmittance or absorbance units. By applying a thin film of lubricant to an infrared-transparent potassium bromide (KBr) disc and passing an infrared beam through the sample, it is easy to produce a well-resolved spectrum. Figure 3.10 shows the general principle of operation in this mode. The thickness of the film must not be too great, or some absorbance bands become saturated, where nearly all the light of that wavelength is absorbed. Accuracy at and near this wavelength suffers, making it

impossible to determine the intensity of this band relative to others reliably. The thickness at which this effect becomes prevalent depends on the strength of the individual absorbance bands. Similarly, too thin a film will show very small absorbance and the signal-to-noise ratio may be a limit accuracy of the measurement.

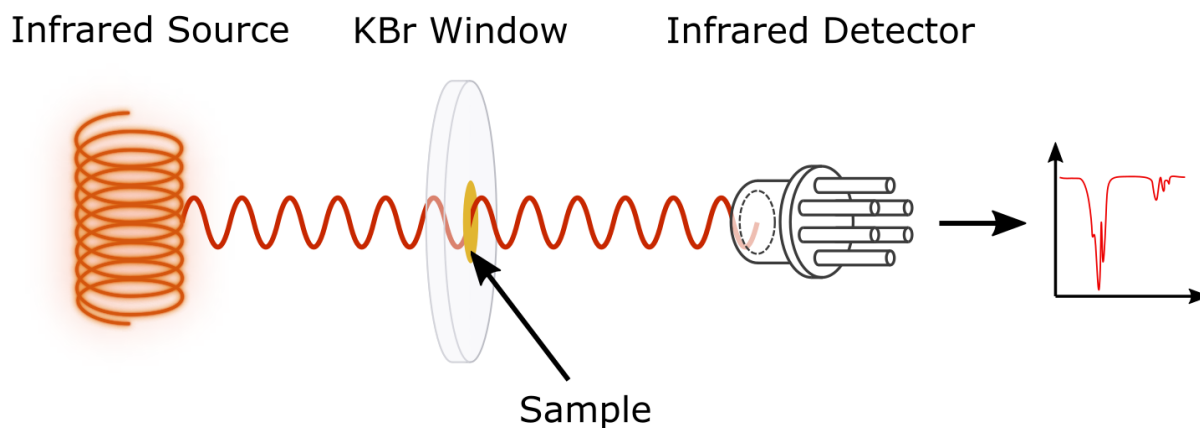


Figure 3.10: Diagram showing the principle of transmission infrared spectroscopy. Broadband infrared light is shone through the sample and the resulting spectrum recorded, showing decreased transmission at the absorbance bands.

The KBr disc is cleaned prior to the test, ensuring a non-aqueous solvent is used as KBr is water-soluble. The clean disc is then placed in the machine and a background spectrum is run. This is subtracted from later measurements, allowing extraneous absorbances such as from water vapour in the air to be neglected.

A thin drop of oil, or film of grease is applied to the disc and a measurement is taken. Care must be taken with grease to not influence the relative proportions of thickener and oil by physical manipulation. Scraping an extremely thin film will produce a result that differs from bulk.

While transmission values are the standard output of infrared spectrometers, the value is not directly proportional to concentration of the absorbing material. It is more practical to use an alternative value, absorbance, which directly relates to concentration. In other terms, a halving of sample concentration would cause a halving of absorbance, but not a doubling of transmission. The relationship between transmission and absorbance is given in equation 9:

$$A = -\log_{10} T \quad (9)$$

Where A is absorbance and T is transmission, as a decimal fraction. In general, an absorbance greater than ~0.4 would indicate a sample may be beginning to saturate, however, in this work the absorbance values were typically normalised to a specific band, making the absolute value arbitrary.

3.4.2 Micro-IRRAS measurements

Micro infrared reflection absorption spectroscopy (Micro-IRRAS) can be used to take infrared spectra of thin films deposited on reflective surfaces. In this mode, the microscope is used to focus the broadband infrared beam onto the surface using gold-coated Cassegrain mirrors. Figure 3.11 shows this arrangement. A 100 μm aperture is used to limit the analysis region. The reflection is then delivered to a highly sensitive liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector and processed in the same way as in transmission spectroscopy. It has been used in this work to take infrared spectra from the inner races, cages and rolling elements of bearings, and from the rolled tracks of MTM discs.

Prior to taking the infrared spectrum the same microscope system is used in the visible spectrum to locate and position areas of interest to be analysed. A moving mirror is used to switch between the two modes.

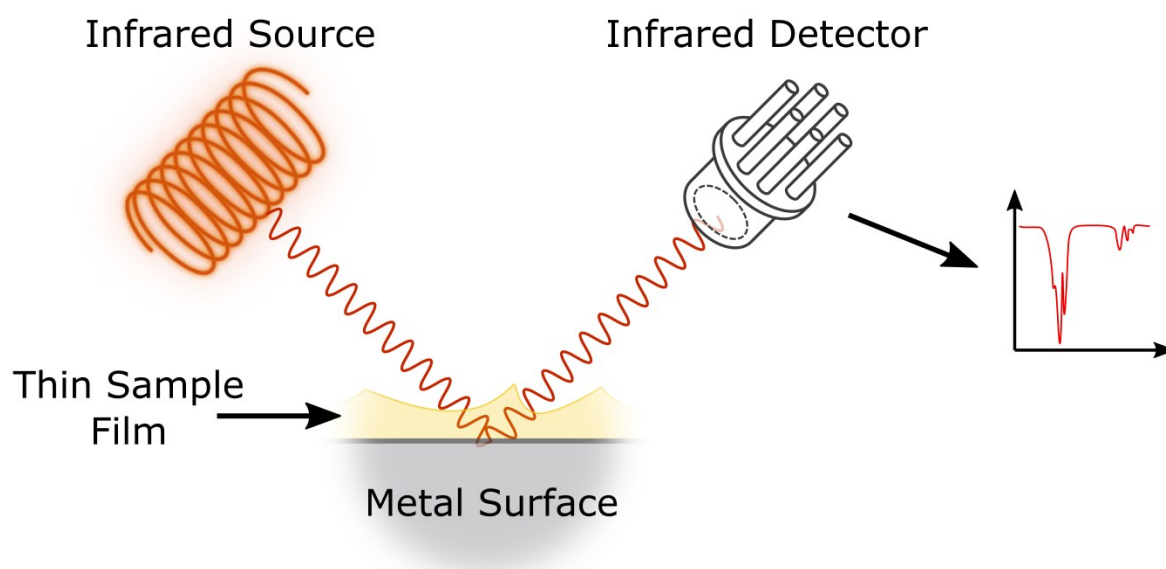


Figure 3.11: Diagram showing the principle of Micro-IRRAS. The broadband infrared light is focused onto a thin film of the sample on a reflective surface. The reflected infrared spectrum is then recorded.

In order to background-correct this technique, ideally exactly the same surface as holds the film to be measured will be used. Fortunately, this was possible in all cases, as unused bearings could be dismantled and cleaned, and new MTM specimens used. Once the background spectrum had been taken, the specimen could be analysed. For each sample, several measurements were taken aiming to represent the entire area. For extremely thin films of <200 nm the signal to noise ratio was unacceptable, and for very thick films the peak saturation meant reliable analysis could not be performed. This occasionally limited possible measurements when the entire film fell into one of these categories.

3.4.3 Data Processing

The recorded spectral data was processed in order to simplify analysis and ensure they were comparable across different measurement techniques. All spectra were background-corrected upon measurement. It was often necessary to baseline-correct the spectra, especially those collected using micro-IRRAS as the reflectivity of the metal surface varied by location, often leading to apparent low peak absorbance across the spectral range. This procedure was performed using spline fitting, provided by the Spectragryph spectroscopy software[184]. Normalisation of the absorbance values to a specific band, for example one provided solely by the base oil, was performed for all samples. This allowed direct comparison, in this case enabling thickener content to be quantitatively assessed. Extremely thin reflection samples showed considerable noise and in an effort to reduce this multiple samples from similar locations were averaged.

3.5 CHARACTERISATION OF GREASE PROPERTIES: RHEOLOGY

A Discovery HR-1 (TA Instruments [185]) stress-controlled rheometer was used to characterise the rheology of the test greases. Cross-hatched stainless steel parallel plates of 40 mm diameter were used at a gap height of 1 mm. All testing was preceded by a conditioning step in which the grease was continuously sheared at 50 s^{-1} for 60 s at the test temperature. This was based on the DIN standard 51810-1 in which a pre-shear of 100 s^{-1} for 60 s at 25°C is specified [186]. A reduced shear rate was used in order to prevent the problematic edge effect of spilling or tearing which occurred at higher shear rates with stiffer greases.

A similar procedure to that described by Zhou [187] was used during this pre-shear step to minimise edge effects, which consisted of applying an excess of grease to the lower plate, lowering the upper plate to the specified gap height and starting the pre-shear once test temperature was reached. At the end of the pre-shear step, all excess grease was trimmed with a spatula, leaving a vertical edge for the remaining test. The grease was allowed to relax for 15 minutes before the testing step began.

Frequency and amplitude oscillation tests were performed primarily, in order to prevent the above-mentioned edge effects. G' and G'' , the storage and loss modulus respectively were evaluated to characterise the elastic and viscous behaviour of the sample. In an oscillation test, a set stress and frequency of oscillation are applied to the sample and the measured strain is recorded. Both follow a sinusoidal pattern and the response will have a diminished amplitude and phase lag behind the stimulus. The diminished amplitude is the modulus G^* , the ratio of shear stress amplitude to shear strain amplitude, shown in equation 10:

$$G^* = \frac{\tau_A}{\gamma_A} \quad (10)$$

where τ_A is the shear stress amplitude and γ_A is the shear strain amplitude. The phase lag is termed δ and is used to split the modulus into its two constituent parts, G' and G'' , representing the elastic and viscous behaviour of the sample respectively. Equations 11 and 12 describe G' and G'' .

$$G' = G^* \cos \delta \quad (11)$$

$$G'' = G^* \sin \delta \quad (12)$$

3.6 BENCHTOP SIMULATION OF GREASE DEGRADATION IN BEARINGS

In Chapter 4 the extent of thermal and shear degradation in bearings is analysed, and these findings are used to develop methods of benchtop simulation of these two processes, in order to assess their effect on tribological performance.

3.6.1 Thermal Aging

Long and short-term thermal aging of the lubricant samples was performed in order to examine the chemical and structural changes that occurred and how this affected lubrication

performance. It was also possible to correlate these changes with those occurring in the greases used in the R0F+ tests.

A bench top oven was used and set to 100°C, a balance between the accelerated aging at high temperatures which can initiate reaction pathways that are not applicable to lower temperatures, and realistic operating temperatures which would be too long to be practical, perhaps 60-70°C for electric motor bearings [188]. For the long-term tests, the greases were aged for 35 days. For these tests, 4g of grease was applied to a glass petri dish and manually smoothed with a spatula, leaving a film of ~5 mm.

For the short-term tests, a thinner film of ~400 µm was applied to polished stainless steel plates. This was performed by punching holes into a silicone sheet of that thickness and applying it to the steel. The grease was applied to the hole and smoothed level. On removing the silicone, a disc of grease remained with a reasonably consistent thickness. These were run for 72 hours.

The thermally aged samples were analysed using FTIR and also used in tribological testing, using the MTM and EHD rigs, as well as the bearing rig developed in this work.

3.6.2 Shear Degradation: Ball Mill

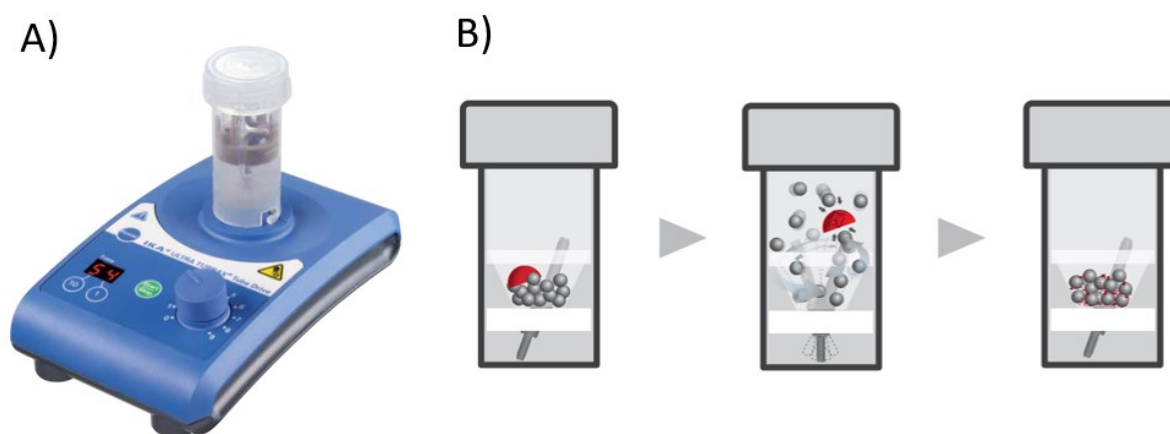


Figure 3.12: A) Ball homogeniser. B) Homogenising process. Images taken from [189].

An IKA ULTRA-TURRAX ball homogeniser was used to subject a small amount of grease to intense shear rates and high pressures. A small sample was placed inside the polypropylene test tube with ~20 AISI 304 stainless steel balls and sealed. A small rod then precessed at high

speed, agitating the balls and causing collisions between them. The device and method are shown in Figure 3.12. This was left operating for 1-3 hours. The samples ran unheated in room temperature air but were subject to a small degree of self-heating. The pressures and shear rates that the grease is subjected to when two steel balls collide are difficult to approximate but are extreme, and likely similar to that in the contacts of a bearing. The volume of grease sheared in each collision is very low but with many collisions occurring per second and hour-long run times a bulk change in properties is achievable.

3.6.3 Shear Degradation: Roll Stability Test

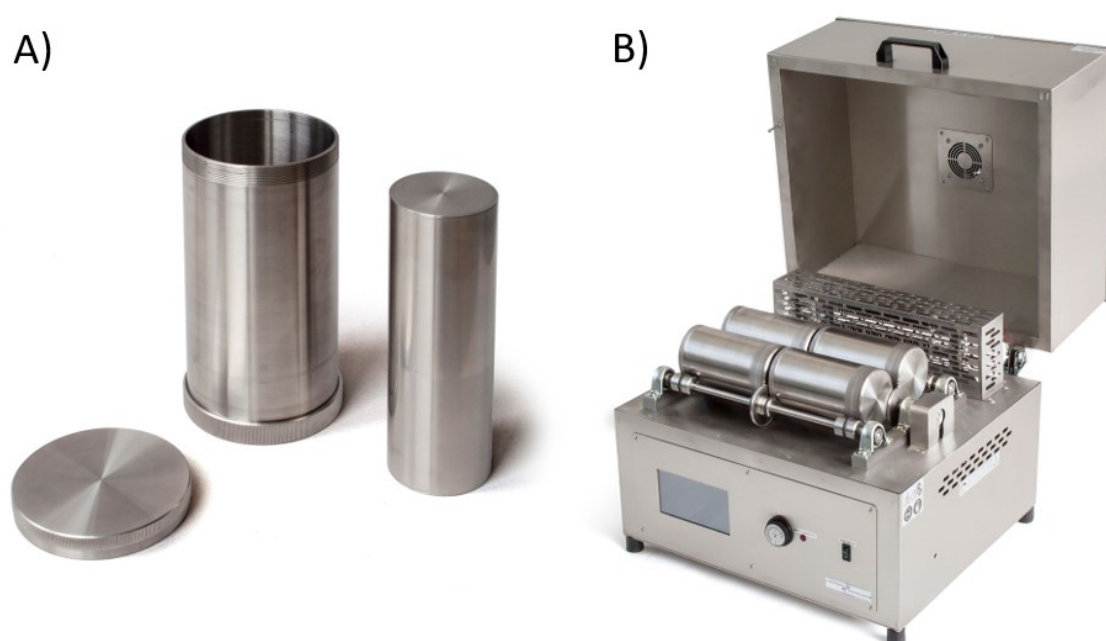


Figure 3.13: A) Cylinder and inner roller. B) Roll stability tester. Images taken from [190].

A selection of greases were shear degraded in a roll stability test machine, used for standards ASTM D1831 and D8022 [149], [191]. An example machine and test chamber are shown in Figure 3.13. The machine consists of a large cylinder containing a 5kg stainless steel roller. A sample of 50 g of grease was placed in the machine and rolled at 165 RPM for 168 hours with no heating except that generated by churning of the grease. The pressure and shear rate in this test are far lower than those of a tribological contact but the test is able to approximate shear degradation in other parts of a bearing such as between rollers and shield, or beside the contact itself. This processing was kindly performed by the grease team at the Shell Technology Centre Hamburg.

3.7 TEST GREASES

A range of greases was used throughout this project, shown below in Table 3.4. These greases represent some of the most ubiquitous thickener types, and base oil viscosities that are typical for a wide range of rolling bearing applications. Not all of these greases were used in every stage of this work due to limitations on testing, particularly for the R0F+ tests, but they were chosen to provide representative performance of greases in general. The downside of such an approach is that the effect of one single variable such as thickener type, additives or oil viscosity cannot be reliably explored, but it allows an assessment of grease performance in general, and the identification of common characteristics.

Abbreviation	Thickener	Base Oil Viscosity at 40°C [cSt]	Additised	R0F+ Tested	MTM and EHD Tested
Li 100	Lithium 12-Hydroxystearate	100	Yes	Yes	Yes
LiB 100	Lithium 12-Hydroxystearate	100	No	No	Yes
CaXB 100	Calcium complex	100	No	Yes	Yes
CaX 100	Calcium complex	100	Yes	No	Yes
PU 220	MDI diurea	220	Yes	Yes	Yes
LiXB 220	Lithium complex	220	No	Yes	Yes

Table 3.4: Properties of the test greases.

3.8 CONCLUSION

This chapter has described in full the greases used in this work and the methods used in their tribological evaluation, specifically friction and film thickness testing under a range of conditions. A wide range of characterisation techniques were utilised to assess the greases in terms of chemical and physical structure as well as rheological properties. The importance of grease aging in the life and function of rolling bearings was emphasised in the literature review chapter and the methods used to reproduce this have been presented, separating the thermal and shear effects in order to understand how each affects lubrication.

4 THERMAL AND SHEAR DEGRADATION IN BEARINGS

This chapter outlines the existing evidence that shear and thermal degradation in bearings is integral and possibly beneficial to lubrication performance and presents the findings of analysis of R0F+ test bearings. The degradation is characterised using FTIR measurement of grease within these bearings. Methods which emulate this degradation are described for use in bench-top tribological testing.

4.1 INTRODUCTION

Shear and thermal degradation of grease in a bearing are two processes that both influence the typical performance of the bearing and dictate the ultimate life. While oxidation has long been known to lead to increased viscosity of oils which can result in failure [60], the effects on greases may be more complex.

Gonçalves et al. studied the rheological changes in polymer and LiX greases after thermal aging and found that while the LiX grease increased in consistency after aging, the polymer greases showed reduced consistency [48]. Huang et al. measured apparent viscosity of lithium and polyurea base greases and found that both greases showed a reduction in apparent viscosity upon thermal aging [165]. Their conclusion was that there was both a beneficial effect of increased oil bleeding and lowering of apparent viscosity of the grease which enabled greater replenishment to resist starvation, but also a negative effect of reducing lubricity which they theorise may be due to competition between the thickener and polar oxidation products for surface adsorption. Salomonsson observed fibre aggregation and breakage in a lithium grease upon severe oxidation [53], explaining the finding as a result of altered interactions between the oxidised soap and oil molecules. This structural change goes some way to explain bulk changes in rheology of thermally aged greases. Hurley investigated lubrication of artificially thermally aged greases under starved conditions with a ball-on-disc setup [192] and found that while moderate aging increased film thickness, heavy aging reduced it below that of the fresh grease. They observed that the rate of reflow, as assessed by reformation of the meniscus after stopping motion, correlated well with starved film thickness, and that the initial reflow lubricant was mainly base oil [192]. This supports the

idea that a small amount of thermal degradation is beneficial to starved lubrication by increasing the rate of oil loss from the bulk grease.

It is perhaps more intuitively understandable that shear degradation might improve resistance to starvation for a grease. As is known from testing cone penetration after working a grease in the 'roll stability test' machine [149], the penetration generally increases on working [81], [193], implying a reduction in yield stress and greater ability to flow. For some greases, a short time of shearing in the roll stability tester can reduce cone penetration, which is attributed to a stage of further homogenisation [194] and is unlikely to continue far into the life of a bearing. These changes are accompanied by a reduction in fibre length due to breakage [80], [89], [108], [134], [193], [195] which is also observed in grease-lubricated bearings [36], [195], [196].

Attempts have been made to simplify the modelling of shear degradation of grease by analysing it in terms of entropy [113], [197], which would allow a wide range of shear conditions to be accounted for. Zhou et al. developed an equation using this idea to describe the changes of the rheological properties of a lithium grease with the generation of entropy [134]. They further extended this equation to cover a range of temperatures [105], finding that high temperatures increased the rate of mechanical shear degradation. While a simplification of these complex phenomena is attractive and probably necessary to develop a usable model of grease degradation, it has been noted that shear degradation under various conditions such as grease workers or bearings result in different residual grease structures and the manner of the shearing is of great importance [195]. It is also clear that different parts of a bearing will experience different shear rates and it is difficult to model these cases as a whole.

Shear degradation of greases has been observed to reduce initial film thickness under constant speed conditions [80], [173] in ostensibly starved grease supply (no attempt made to redirect grease into the contact path). This effect is also observed by Cen et al. at low entrainment speeds, when the V-shaped 'thickener effect' is in action, but not at the highest speeds [52]. The authors suggest this is directly caused by a reduction in particle size after mechanical degradation which reduces the contribution of the thickener at these speeds [52]. An analysis

of the starved lubrication of a ball-on-disc setup linked the observed film thickness recovery after many overrollings to a progressive shear degradation, which causes a loss of yield stress and increased release of 'free' lubricant [130].

An analysis of grease film thickness in a bearing at room temperature using the capacitance method showed that the film thickness is starvation-dominated and that film thickness was increased by artificially aging the grease which increased the rate of oil bleed and reduced the yield stress [14]. The authors found that shear degradation of grease reduced starvation in three ways: "higher grease bleeding, more migration and the formation of smaller thickener particles which can enter the contact easier."

A study of the distribution and chemical composition of the grease around bearings in conditions of high temperature and relatively low speed was conducted by Cann et al. [180], using FTIR spectroscopy to analyse lubricant films post-test after 50 to 300 hours of operation. The lubricant in the raceway was observed to be heavily shear degraded and consisted mainly of base oil, with the thickener concentration decreasing with test temperature and running time. It appeared that this oil was primarily the paraffinic constituent of the base oil, rather than the naphthenic which was present in roughly equal proportion, suggesting it is preferentially released from the bulk grease. The thickener concentration of the grease around the bearing varied, with grease on the bearing seals containing more, depending on location. Small areas of higher thickener concentration were observed in the raceway and imply that there is a continued supply of small amounts of grease from the seals to the raceway. Oxidation was not observed in these tests [180].

A similar investigation analysing bearings that operated at a similar temperature but a much higher nDm value studied bearing lubrication under demanding conditions that led to L_{50} lives generally less than 2500 hours [136]. A different lubrication mechanism was observed, with the 'active' lubricant on the raceway and cage pockets consisting of oxidised material containing a significant fraction of the original thickener content. The grease on the shields was observed to oxidise, but only the oil component and not the thickener which may be a result of cooler temperatures or lack of metal debris which can accelerate thickener oxidation. The failure mechanism of bearings that do not fail quickly is suggested to be a result of the

lubricant reaching its oxidation limit, reducing mobility. The fact that oxidation of the active lubricant was observed early in the life of test conditions that showed relatively long L_{50} lives suggests that grease-lubricated bearings can operate for many hours with shear and thermal degradation [136].

Chatra and Lugt studied the temperature profiles of bearings at a range of speeds while analysing the structural changes of the thickener and attribute 'good' channelling performance to those greases that largely remain in their displaced position outside the raceway and undergo a short churning period [36]. Their findings suggest that a grease that is too shear-unstable will not channel effectively and this leads to excessive temperatures during churning as well as longer churning times [108]. The positive effect of shear degradation of a grease must therefore be controlled in order to not cause bearing failure through means other than starvation.

The implication of these results is that, despite the negative connotations of the word 'degradation', oxidation and shearing of grease may play a role in effective lubrication and the production of the 'active' lubricant which is located on the raceway, rolling elements and cage pockets. This is an important idea to explore, as the extent of degradation could potentially be tuned to optimise life, minimise friction and reduce churning losses at the start of use.

4.2 ANALYSIS OF THE CAUSES OF DEGRADATION IN BEARINGS

The extent of shear and thermal degradation processes in bearings is dependent on the shear rates and temperatures present. To understand these processes, we must understand in detail the conditions the grease is subjected to.

The grease within the contact is subjected to a shear rate dependent on the slide-roll-ratio, the entrainment speed and the film thickness. For a deep-groove ball bearing (DGBB) of outer diameter 100 mm, rotating at 3000 RPM the entrainment speed will be approximately 6 m/s. The slide-roll-ratio can be assumed to be 4%, a typical value for bearings, and the film thickness 400 nm, a value taken from capacitance measurements in bearings running under realistic conditions [15]. The grease within the contact is then subjected to a shear rate of

$\sim 6 \times 10^5 \text{ s}^{-1}$, falling in line with the 10^5 - 10^7 s^{-1} within tribological contacts estimated by Spikes et al. [96]. The volume of grease sheared within the contact per second is fairly small due to the extremely thin gap but, for context, it would take roughly an hour and a half to shear the entire grease volume of the bearing, assuming no recirculation.

In reality, there will be significant recirculation and a relatively small volume of the total grease will be continuously sheared. Additionally, shearing will occur at a lower rate in the much larger volume surrounding the contact which may be a larger contributor to shear degradation. A simple analysis was conducted to estimate the Couette shear rate between a rolling ball and raceway within a ball bearing. Figure 4.1 shows the decay of shear rate beside such a ball bearing contact with geometry representative of common bearings (the conformity or ratio of race radius to ball diameter taken as 0.52, a value used in ISO 16281:2008 [198]). The plot shows that most of the raceway is subjected to shear rates of more than 10^4 s^{-1} as the ball passes, a significant value. Grease homogenisation performed as a final step in manufacture typically utilises shear rates greater than 10^5 s^{-1} and causes significant change to thickener structure, often performed in a single pass [58]. It is reasonable to suggest that, even at the very edge of the raceway, thickener destruction is occurring over the many hours of bearing life. At higher loads, speeds, or more conformal bearing geometry, these values would be even higher. This simple analysis neglects the many other forms of shearing present in a bearing: shearing between the balls and cage, balls or cage and shields, as well as the potentially very high shear rates at the contact inlet as grease is displaced rapidly.

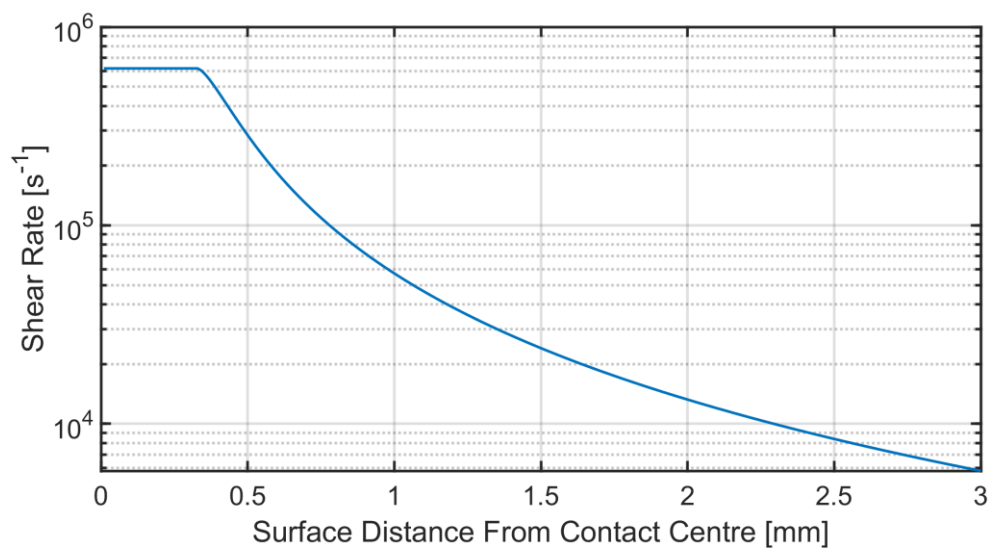


Figure 4.1: Plot showing the shear rate inside and in the vicinity of a typical ball bearing contact.

These effects have implications beyond those of shear degradation. The shear thinning that grease in the vicinity of the contacts experience will likely aid reflow as the apparent viscosity reduces. The time between overrollings may be insufficient to allow any relaxation at all. At 10,000 RPM, there is likely to be less than 1 millisecond between overrollings. A loss of viscosity will also allow this lubricant to preferentially reflow under the influences of capillary and centrifugal forces, further establishing a small volume of ‘active’ lubricant.

The temperature of bearings in use can vary widely, dependent on the environment as much as on heat dissipated due to friction within the bearing. Those operating in electric motors are known to endure high ambient temperatures, the motor coils reaching up to 180°C for ‘many seconds’ [24], while those operating in exposed, cold environments such as wind turbine bearings will not experience significant temperatures unless flash heating raises the temperature of small volumes of lubricant. As discussed in the next section, R0F+ bearing tests operating at realistic conditions in a room temperature environment reached temperatures of up to 90°C during churning and 50°C post-churning, purely from heat generation within the bearing itself.

4.3 R0F+ TESTS TO EXAMINE GREASE DEGRADATION

A series of bearing tests were conducted using the R0F+ test rig, aiming to test a variety of greases under demanding, yet realistic conditions. The system and conditions are described in full in Chapter 3 but a summary is presented here. The system consists of five independent test units. Each containing a shaft on which two ‘support’ bearings and two ‘test’ bearings are mounted, differing in two ways: loading condition, with the support bearings having zero axial force, and vicinity to the heaters, which are situated around the test bearings only. All four bearings are lubricated with the test grease.

The intention was to avoid accelerated aging which may result in alterations to lubrication mechanisms. These would prevent the results having relevance to real bearings. Post-test analysis of the grease within the bearings would indicate the extent of shear degradation and oxidation of typical greases at a functional stage of their life. To ensure that the tests were stopped at a mid-phase of life, it was first necessary to establish the duration of the churning

phase, and whether the bearings were likely to be close to failure. To achieve this, a range of greases were run at the standard test conditions and bearing temperatures were monitored. A spike at the beginning is indicative of grease churning and will fall to a more constant level. A spike in temperature after this stage can indicate incipient starvation which may resolve quickly, or a large lump of grease entering the track and causing an additional, shorter, temperature rise due to churning. A severe temperature spike usually indicates severe starvation and is likely to lead to runaway temperature rise as lubricant oxidation reduces lubricating ability.

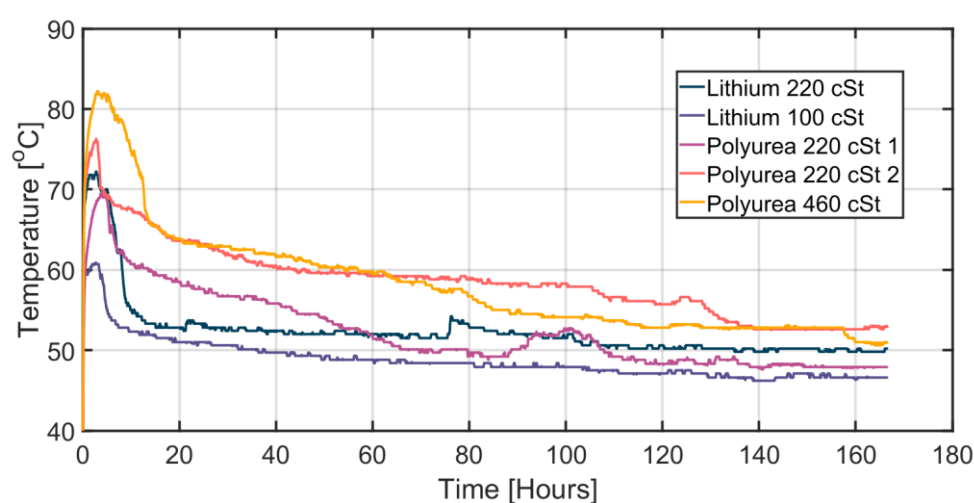


Figure 4.2: R0F+ trial run bearing temperatures for a range of greases.

Figure 4.2 shows the results of this test. Two lithium thickener greases were used with base oil viscosities of 220 and 100 cSt at 40°C, and two polyurea greases were used with base oil viscosities of 220 and 460 cSt at 40°C. The first of these polyurea greases was included in two test units, as a simple indicator of repeatability. This test of repeatability shows that there is significant variation in both churning and plateau temperatures even for the same grease under the same conditions of speed and temperature. The second unit testing this grease, shown in pink in Figure 4.2, reaches a much higher churning temperature and final temperature than the first. The difference can only be attributed to a difference in the initial churning, with the first able to displace the majority of the grease while the second was unable to do so as quickly. Apart from this bearing, the final plateau temperatures are in order of base oil viscosity. The churning temperatures are also ordered this way, with the 460 cSt

polyurea producing the highest temperatures. These temperature differences are simply the result of increased viscous losses, dissipating as heat within the sheared grease.

This test was run for 167 hours at 5,000 RPM, at which point it was clear the churning phase had ended, typically lasting around 10 hours. Bearing temperatures had begun to plateau, with the largest temperature difference between 100 and 167 hours being 5°C. No significant temperature rises had been observed, suggesting bearing failure was not likely. These results suggested that a test time of 100 hours would be sufficient to pass the churning phase completely, while reducing total test time. Rather than allow a steady-state temperature to be reached which may result in some greases reaching high temperatures and oxidising while others did not oxidise simply because they did not reach such high temperatures, the R0F+ tests were conducted at a temperature of 80°C. Test speeds of 5,000 and 10,000 RPM were used in this work, which equate to nDm values of 170,000 and 340,000, considered medium and high speeds respectively for a ball bearing by SKF [199].

Table 4.1 provides the properties of the four greases used for the full testing, which will be referred to by their abbreviation, indicating thickener type, additisation (B standing for base), and base oil viscosity.

Abbreviation	Thickener	Base Oil Viscosity at 40°C [cSt]	Additised
Li 100	Lithium 12-Hydroxystearate	100	Yes
CaXB 100	Calcium complex	100	No
PU 220	MDI diurea	220	Yes
LiXB 220	Lithium complex	220	No

Table 4.1: Properties of the test greases

These greases clearly differ in many ways, from base oil viscosity to thickener type, with no controlled change of one variable. The results are therefore not intended to test the effect of a change in one variable but are an exploratory attempt to examine grease degradation in realistic bearings and determine if the findings are common to many grease types.

In a later chapter of this thesis, the CaX base grease, CaXB 100, is examined in more detail. The grease is blended with a range of base oil types and these blends are compared with one another. In the current chapter only the greases shown in Table 4.1 are discussed.

4.4 FTIR ANALYSIS OF BEARING FILMS - GREASE CHARACTERISATION

By applying Fourier-transform infrared (FTIR) analysis to the lubricant films remaining in the bearing raceways it is possible to infer important information about the ‘active’ lubricant as done by Cann et al. [136], [180]. FTIR can be used to assess relative proportions of chemical constituents in a sample and, as will be shown in this chapter, can reveal changes in the intermolecular forces between thickener molecules. Unless specified, wavenumbers for bond vibrations are taken from “The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules” by Lin-Vien et al. [200].

Before analysing the bearing films, it was first necessary to measure the IR spectra of the fresh greases. This allowed a direct comparison with the bearing films, enabling detection of subtle changes to the absorbance peaks. This data was taken using the transmission technique to provide the highest quality data, with minimal noise. The absorbance spectra of the Li 100 grease and its components are shown in Figure 4.3. The spectral range has been limited to only show a region in which absorbance bands corresponding to thickener and oil are present and of similar strength, meaning they can all be resolved optimally in a single measurement. The base oil was provided by Shell along with the grease, and the thickener was separated from the oil by rinsing with heptane multiple times, dissolving the oil and leaving the thickener behind.

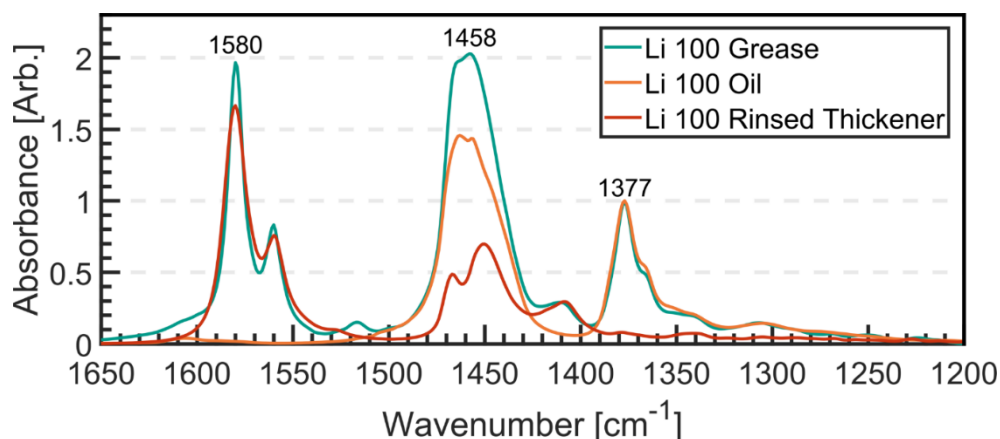


Figure 4.3: Transmission FTIR spectra of the Li 100 grease and its constituent oil and rinsed thickener.

As all the spectra in this work are taken with an uncontrolled film thickness it is not possible to directly compare their absorbances unless they have first been normalised to a known common peak. The grease and oil in Figure 4.3 have been normalised to the peak at 1377 cm^{-1} which is due to symmetric bending of the CH_3 methyl group, also called the ‘umbrella’ mode due to the similarity of the vibration with an umbrella opening and closing. The thickener has only one of such groups per molecule, while the base oil will have many more due to the branching nature of mineral oil hydrocarbons. This means it is a good peak to normalise against as any difference in the results will be almost entirely due to the presence of thickener. If the thickener content of the grease were to change, it would be apparent as a relative increase in the thickener-associated peaks. As stated, the thickener, shown in red, does not have a significant absorption at this value and so is approximately normalised for this plot against the $1550\text{--}1600\text{ cm}^{-1}$ peaks to provide comparison.

Another group of peaks around 1450 cm^{-1} is present in all three samples and is also due to vibration of the C-H bond. In this case it is two peaks that overlap, one around 1465 cm^{-1} which is due to asymmetric bending of the CH_3 (rather than the symmetric ‘umbrella’ mode) and one at a slightly lower wavenumber due to symmetric bending of the CH_2 methylene group (the hydrocarbon back-bone). In the three samples the positions of these two peaks vary slightly, with a clear distinction in the rinsed thickener while for the grease they appear largely as a single peak.

The doublet, in the region of $1550\text{--}1600\text{ cm}^{-1}$, is only present in the thickener and grease because they are due to the carboxylate group at the end of the Li-12HSA molecule. These

are attributed to asymmetric stretching of the COO^- ‘bond-and-a-half’ bonds present in the carboxylate ion. Symmetric stretching of these bonds produces the peak around 1410 cm^{-1} . The reason the asymmetric stretching produces a doublet, rather than the expected single peak, is not clear, however it has been theorised to be due to two coordination modes of the carboxylate ionic bond or coupling of neighbouring carboxylate groups, among other reasons [201].

It is clear that the grease spectrum is simply a superposition of the thickener and oil spectra. Any other minor peaks present in the grease are due to additives that were rinsed away with the base oil, and not present in the base oil sample.

The other grease types are characterised below, differing mainly in the carboxylate region due to the different thickener systems. The LiXB 220 grease is shown in Figure 4.4. As a complex, there are at least two fatty acids present, potentially providing slightly different carboxylate resonances or altering any crystal structure which may also influence these absorbances. In fact, the carboxylate region from $1550\text{--}1600\text{ cm}^{-1}$ is remarkably similar to the Li 100 grease. One change is the intensities of these peaks which are increased compared to the Li 100 grease. This suggests a higher concentration of thickener, which is likely as the two greases both have an NLGI grade of 2 despite complexes generally having a reduced thickening effect [40], necessitating a greater percentage composition. Other minor differences in small peaks are likely due to additives present in the Li 100 grease.

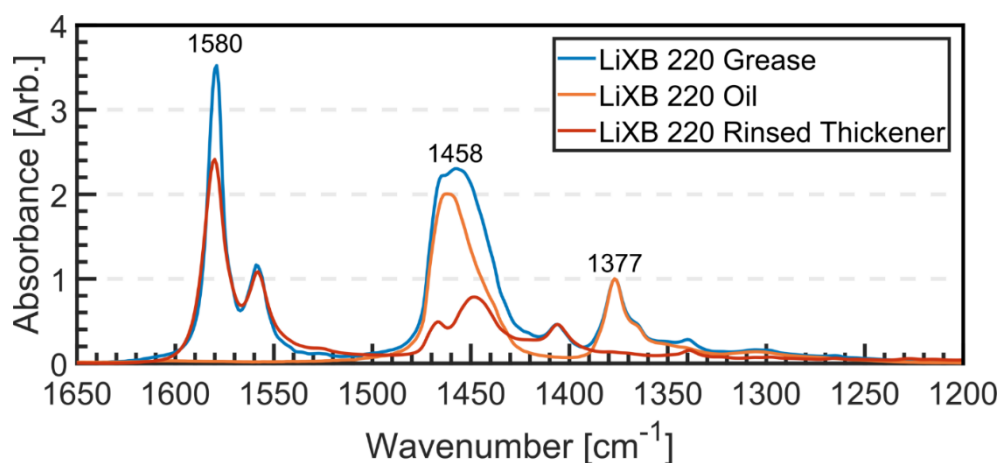


Figure 4.4: Transmission spectra of the LiXB 220 grease and its constituent oil and rinsed thickener.

Figure 4.5 shows spectra of the CaXB 100 grease, thickener, and base oil. While the oil is almost identical to the previous two samples, here there are major differences between the thickeners. The carboxylate region contains many more peaks, giving the appearance of a single, wide band. It also covers a much wider region than the lithium greases. As calcium complexes typically contain acetic acid, this may be a factor in producing some of these higher frequency peaks as the lack of a long carbon chain may influence the vibration frequencies of the COO^- bonds. Other complexing agents such as aromatic acids like benzoic acid, or even inorganic acids like phosphoric or boric acid will also have different absorbances. Considering the influence of intermolecular forces, these and other complexing agents like dicarboxylic acids will strongly influence the thickener structure, preventing the formation of a uniform crystalline structure which will affect the carboxylate absorbances. An additional consideration is that hydrogen bonding of a functional group tends to broaden the absorbance peak, as a wider range of energies can excite the bond, since it is subject to varying extents of hydrogen bonding within the sample.

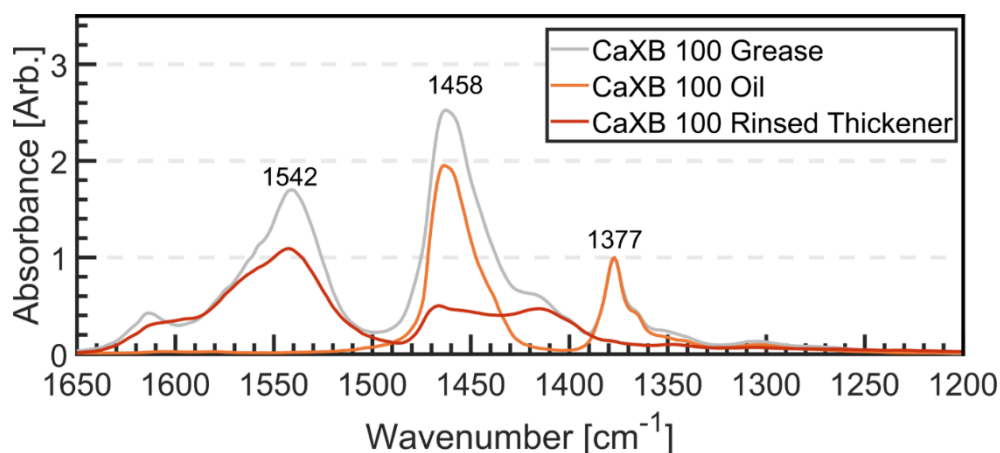


Figure 4.5: Transmission spectra of the CaXB 100 grease and its constituent oil and rinsed thickener.

Figure 4.6 shows spectra for polyurea grease PU 220. These spectra differ the most from the lithium grease shown originally as several new bonds are introduced in the thickener. This grease is a diurea, formed from the MDI precursor, and as such contains aromatic rings as well as the NH and CN bonds of the urea group. The two peaks either side of 1600 cm^{-1} and the peak at 1517 cm^{-1} are likely to be ring modes of the benzene ring which can vary in number and position depending on the neighbouring groups, or in-plane vibrations of the CH bond surrounding the benzene ring. The carbonyl bond is also present in carboxylates, however in

this case the stretch band appears at 1633 cm^{-1} as it is no longer in a ‘bond-and-a-half’ arrangement. The NH bond has a peak at 1566 cm^{-1} due to in-plane bending [202]. The latter two bonds readily form hydrogen bonds which are likely to influence the position or strength of their absorbances. In fact, the act of rinsing the oil away from the grease appears to have changed the 1566 cm^{-1} peak subtly.

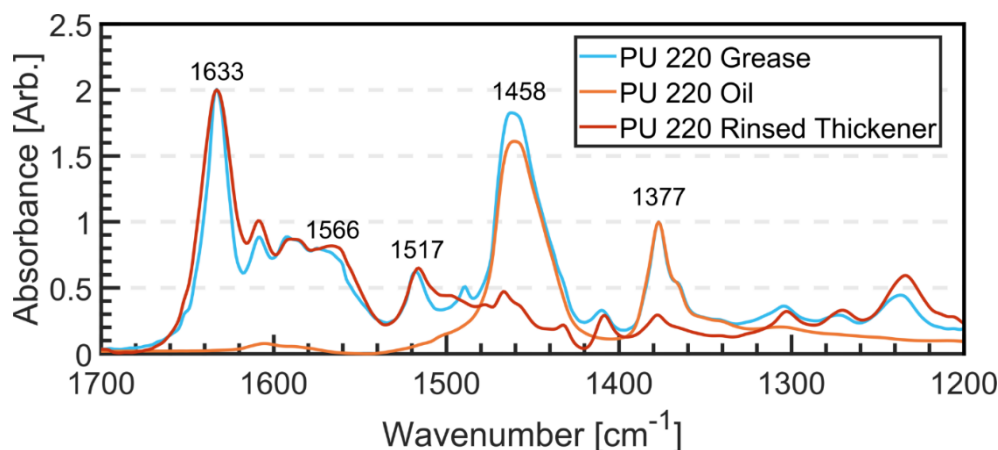


Figure 4.6: Transmission spectra of the PU 220 grease and its constituent oil and rinsed thickener.

4.5 R0F+ BEARING ANALYSIS – 5,000 RPM

The R0F+ bearings were analysed using the infrared micro reflection-absorption spectroscopy (IRRAS) technique to obtain infrared spectra of the thin lubricant films in the bearing raceways and other locations in the bearing. The locations of these measurements are shown in Figure 4.7. All raceway spectra were taken from the inner race, geometry precluding measurement on the outer race. At least three measurements were taken at the cage pockets and shields, and at least four were taken at the inner race, with all spectra shown being representative of the group. In cases where the inner race samples showed variation between measurements, many more samples were taken. These numbers include only samples that were deemed to be of sufficient quality, excluding the many that were over-saturated or of insufficient signal-to-noise ratio. In general, there were large differences between spectra taken from different locations within the bearing, however measurements within a location, for example the raceway, were fairly consistent. This is discussed in more detail for each individual grease.

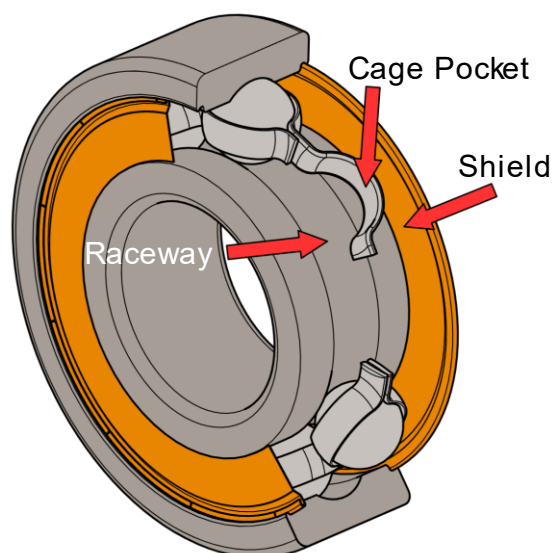


Figure 4.7: Diagram indicating the three locations from which IR measurements were taken. IRRAS was used to measure thin films in the inner raceway and cage pocket, and samples from the shield were taken to measure using transmission IR. CAD files adapted from [203].

Samples described as being from the shield were not taken with IRRAS due to the films being far thicker than could be measured with this technique. Instead, a small sample of grease was extracted and measured using the transmission technique, as with the fresh greases.

4.5.1 Grease Distribution

Figure 4.8A) shows part of a dismantled bearing from the churning test, with the inner race removed to view the outer race, shields, cage and balls. This dismantling process involved cutting the outer race in half, which produced a lot of debris and prevented analysis of the bearing using IR. As such, this was not performed for any of the bearings in the main test programme. The distribution of grease around the bearings followed the pattern well-described in the literature [13], [36], [136], [180] of the majority of the grease being found on the shields/seals, and relatively little on the balls and raceways. The shields were generally coated in a layer of grease, though it was not always evenly distributed around the circumference of the shield. The grease that remained on the cage was often visibly drier, showing a rough surface indicative of a higher thickener content than fresh grease. The grease on the outer race beside the track was visibly wet with oil, shown in Figure 4.8B).

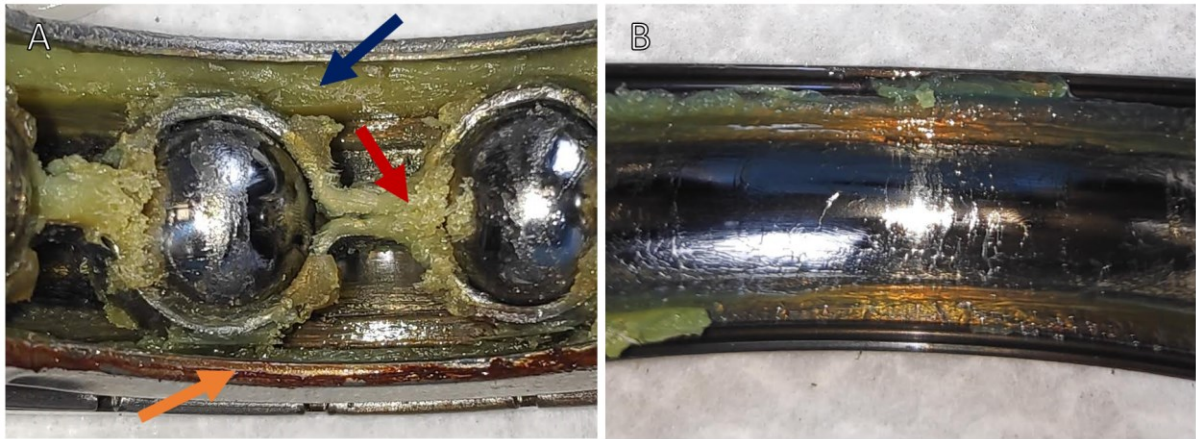


Figure 4.8: A) Image of a bearing from the churning test containing the PU 220 grease that has been split in half, and the inner race removed. This provides a view into the remainder of the bearing. Relatively unsheared grease sits on the shields, marked by the blue arrow. Hard, thickener-rich grease is located on parts of the cage, marked by the red arrow. A small region of dark, oxidised lubricant sits on the innermost edge of one of the shields, marked by the orange arrow. B) Outer race alone, showing mostly thin films in the raceway and apparently oil-rich grease beside the track. The apparently dark colour of the grease is a result of the lighting in this case.

The PU 220 grease was a slight exception in that the balls, cage pockets and raceway were covered in lubricant that retained solid behaviour, in contrast to other greases that formed films that were smoothed by surface tension, appearing to contain a lot of base oil or containing highly shear-degraded thickener. The CaXB 100 grease is an example of this. Figure 4.9 shows a partially dismantled bearing from the main test programme, showing the visible difference in lubricant consistency between the cage pocket and the rest of the cage in A). Figure 4.9B) shows how the distribution of grease around the shield sometimes varied, and the relative lack of grease elsewhere in the bearing. Figure 4.9C) shows the inner race, with thin films within the raceway itself, and bulk grease beside it on the shoulders of the race.



Figure 4.9: A partially dismantled bearing run at 5,000 RPM, lubricated with CaXB 100 grease. A) one half of the cage, showing oil-rich semi-fluid lubricant within the cage pockets, and grease that appears much 'drier' on the other parts of the cage. B) Bearing after removal of the shields, showing variability in the distribution of grease on the shields, both circumferentially and between the two sides. C) The inner race, showing very thin, fluid, films within the raceway.

A bearing lubricated with Li 100 is shown in Figure 4.10, to illustrate the visible difference in grease morphology even within the shield. The orange arrow in B) shows grease that appears rough and like fresh grease, presumably not being sheared once settled in the corner away from the moving elements of the bearing. The blue arrows show smoother grease that appears to be more fluid, with surface tension smoothing the surface. This may be through prolonged shearing breaking down the thickener structure, or an increased base oil content. The right shield in Figure 4.10B) appears to be coated in the sheared lubricant, while only the innermost edge of the left shield is coated in this lubricant. This suggests the development of this sheared lubricant is chaotic and most likely dependent on the way the bearing was filled with grease.

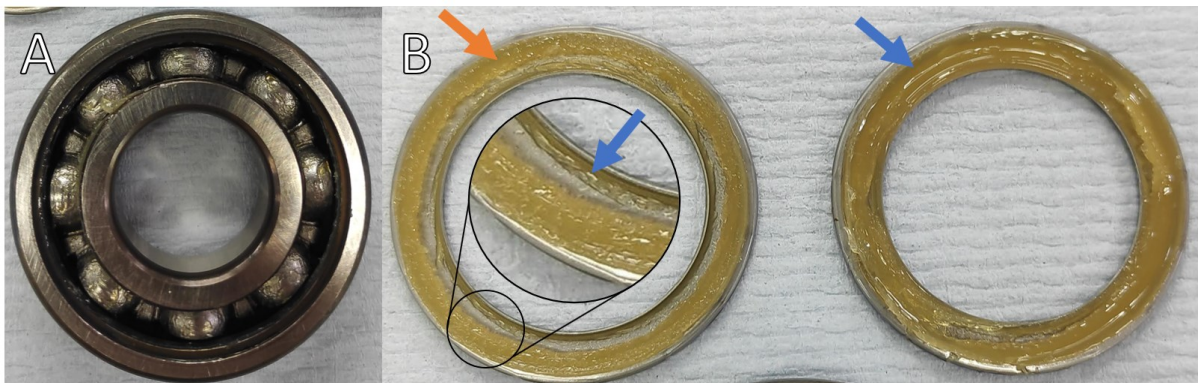


Figure 4.10: A partially dismantled bearing run at 5,000 RPM, lubricated with Li 100 grease. A) the bearing after removing shields. B) the shields, showing slightly different morphology on either side, with the left shield largely

showing grease with a rough surface, appearing mostly unsheared. This is shown by the orange arrow. At the centre-edge of the left shield a thin strip of smoother grease suggests a more intense shear history, indicated by the blue arrow. On the right shield, most of the grease is similarly smooth and appears to have been sheared.

In summary, the majority of the grease in the bearings was distributed on the shields and shoulders of the raceways, with a small amount of dry grease attached to the cage. The cage and balls were typically coated in a thin film of relatively fluid lubricant, with a smooth appearance. The bulk grease at the shields varied in appearance, with some areas appearing to have been sheared to a greater extent, producing a surface smoothed by surface tension, in contrast to fresher grease which retains the ability to resist smoothing by surface tension.

4.5.2 Li 100 – 5,000 RPM Bearing

FTIR spectra from the Li 100 R0F+ bearing are shown in Figure 4.11, normalised to 1377 cm^{-1} . The large reduction in absorption at 1580 cm^{-1} in the inner raceway measurement demonstrates a corresponding significant reduction in thickener content. The opposite is seen in the sample from the shield. This suggests that the lubricant in the raceway contains more oil, and the grease on the shield less oil, which aligns with the theory of oil bleeding from shear-degraded grease on the shields contributing to lubrication [122]. Equally, the loss of base oil from the shields could be leakage out of the bearing, or volatile loss over the test time.

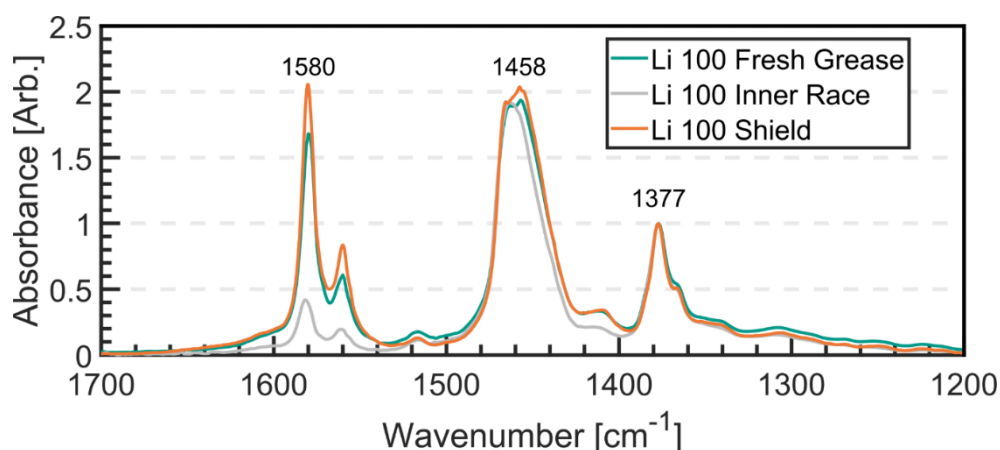


Figure 4.11: FTIR spectra of the fresh Li 100 grease compared to measurements from the bearing raceway and shield.

Figure 4.12 shows a magnified view of the 1580 cm^{-1} carboxylate region for the same spectra, in this case the highest peak in this region has been normalised to 1. Compared to fresh, the grease in the raceway shows a significant peak shift to higher wavenumber, suggesting some change in the -COO^- group that produces this band. This shift is very small in the sample

from the shield. A large increase in the intensity of the 1560 cm^{-1} peak is also observed in the raceway film, as well as a shift of this peak to higher wavenumber. This peak may in fact be an unresolved doublet, with the constituent peaks shifting apart.

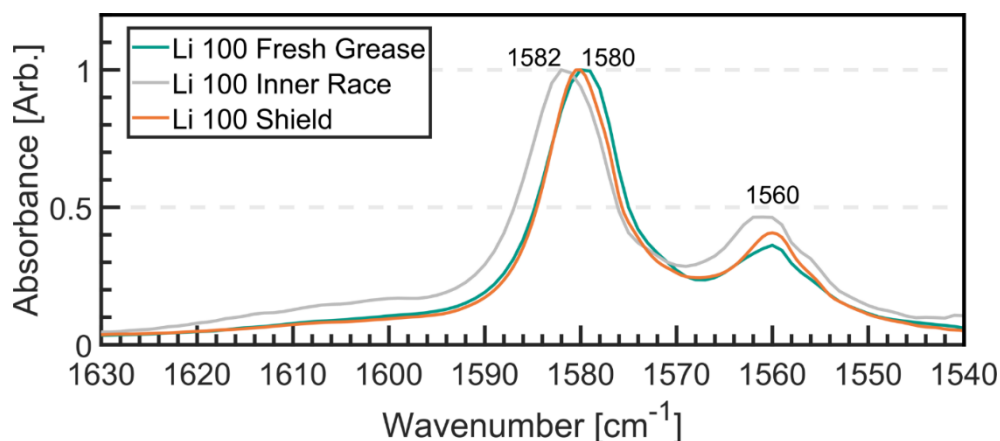


Figure 4.12: Magnified carboxylate region of the Li 100 fresh grease and bearing films, showing a shift in the position of the 1580 cm^{-1} peak.

Figure 4.13 shows two images of the Li 100 bearing raceway. The ground surface of the raceway is covered in a thin lubricant layer, visible only where it distorts the view and also from interferometric colours. Here the film is seen to be fairly uniform, with some regions having collected only slightly more lubricant than thinner regions. In the thinner regions interferometric colour can be seen, suggesting film thickness less than approximately 5 microns. There are no areas that appear to have films less than ~ 2 microns, however. This appearance corresponds to the inner race spectrum in Figure 4.11, with a reduced thickener content leading to a more fluid lubricant.

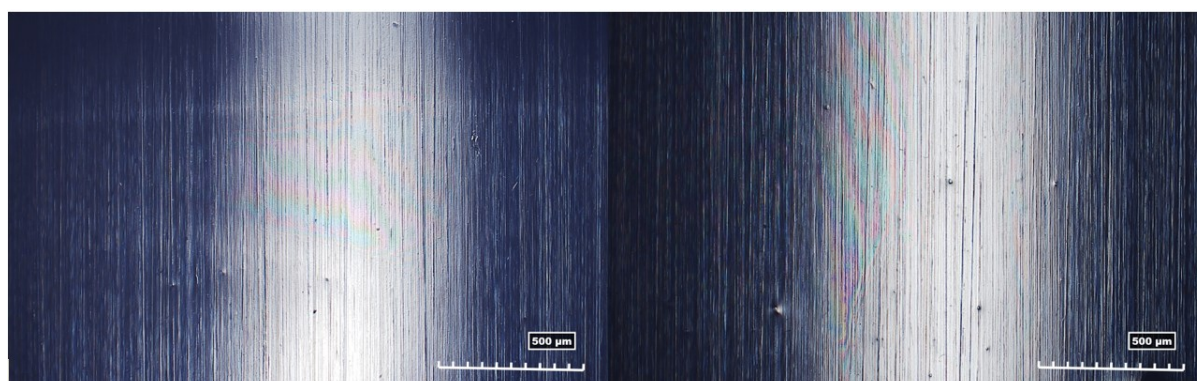


Figure 4.13: Images of the Li 100 raceway, showing a relatively uniform film thickness, with some regions thin enough to display interferometric colours.

4.5.3 CaXB 100 – 5,000 RPM Bearing

Figure 4.14 shows the IR results for the CaXB 100 grease bearing, this time with a slightly extended range to include a group of peaks between 1800 and 1700 cm^{-1} . The shape of the carboxylate group of peaks is very different in both samples from the bearing when compared to fresh. A peak at 1575 cm^{-1} has become much more pronounced and the peak at 1542 cm^{-1} is also increased in intensity but is much narrower than in the fresh grease too. The peak around 1605 cm^{-1} is no longer distinguishable. These changes are all suggestive of drastic alterations to the carboxylate bonding conditions.

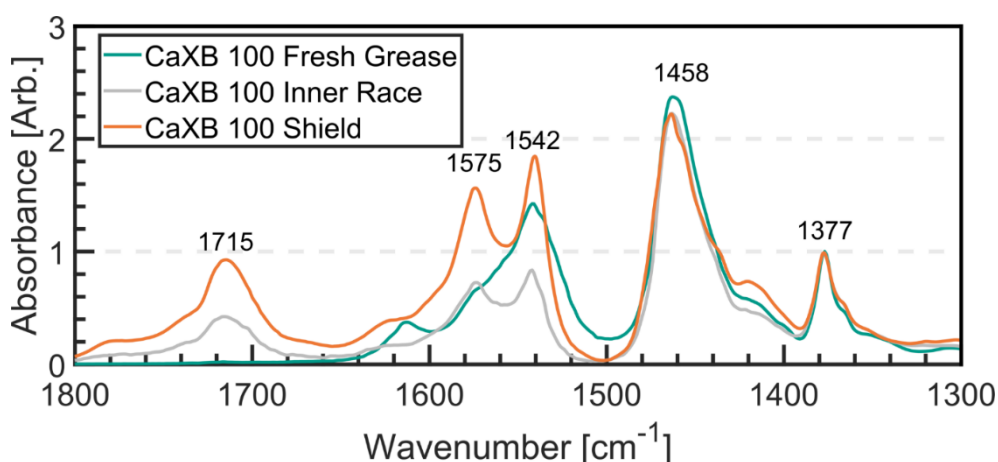


Figure 4.14: FTIR spectra from the CaXB 100 bearing raceway and shield, compared to fresh.

With the introduction of complexing agents, the thickener structure must be considered in terms of multi-component molecular crystals. These include cocrystals, where properties are discontinuous between regions of uniform, single-molecule crystals and solid solutions where different molecules mix in a homogeneous structure, being analogous to liquid solutions [204]. Sada et al. analysed the solid solutions of aliphatic carboxylates of different chain lengths, forming a salt with amines [205]. They found that complementary chain lengths matched to create a consistent spacing between the hydrophilic carboxylate ends, forming a homogenous solid solution. A grease is even more complex in that the thickener is surrounded by the oil which has some solvent ability and will influence the thickener structure. In his review of molecular solid solutions when discussing their synthesis, Lusi states: “A small (catalytic) amount of liquid (i.e. liquid-assisted grinding or kneading) can ease the speed (kinetic) as well as the extent (thermodynamic) of the reaction” [204]. The intense shearing of the oil-surrounded thickener in a bearing can be considered an example of these conditions,

implying these conditions are capable of producing such structural changes. In another paper by Lusi he states that the mechanochemical grinding action of anthracene and two other similar molecular crystals was essential in the formation of a solid solution of these molecules [206]. He also suggests that the mixture of three, rather than two, molecules was important in enabling their solution. This can be applied to grease thickeners, suggesting that the more complexing agents used, the more integration there will be between them as they assist one another in dissolution. These results probably only describe a part of the grease thickener interactions and should not be assumed to be accurate until more specific analyses are performed. They are useful, however, in revealing the complexity of the changes that are possible in such mixtures and imply that complex greases are likely to provide the largest changes in the carboxylate IR region due to structural change.

With all this in mind, the changes seen in Figure 4.14 can be explained as a significant structural change, possibly due to an alternative solid solution or increasing extent of solid solution vs cocrystal. The change in the 1542 cm^{-1} peak specifically suggest a reduction in hydrogen bonding as the peak has become narrower. Looking at the carboxylate region more generally, the same findings as with the Li 100 grease are present in this grease too, with a reduction of thickener content in the raceway, compared to fresh, and an increase in the shields. In this case the effect is not so significant, with the raceway sample still containing a significant amount of thickener.

In contrast to the Li 100 grease, the sample from the shield shows the carboxylate changes as seen in the raceway. The changes must therefore either be induced by relatively little shearing, as was experienced by the shield grease in the churning phase, or is actually an oxidation effect that would be experienced by the bearing as a whole.

The new group of peaks around 1715 cm^{-1} indicates oxidation, with a number of oxidation products such as ketones and acids having carbonyl bond absorptions in this area. A base grease subjected to 80°C for 100 hours oxidising is not particularly surprising, however, the differing intensity of this peak in the shield and inner race sample is unexpected. Given the different concentrations of thickener in these two samples, it suggests that the oxidation is predominantly occurring in the thickener, or that oxidised oil molecules are preferentially

retained with the thickener at the shields. The former appears more likely. The oxidation of the thickener is another reason why the carboxylate region may change so significantly. Whether this change is due to oxidation or shear is investigated in a later section of this chapter.

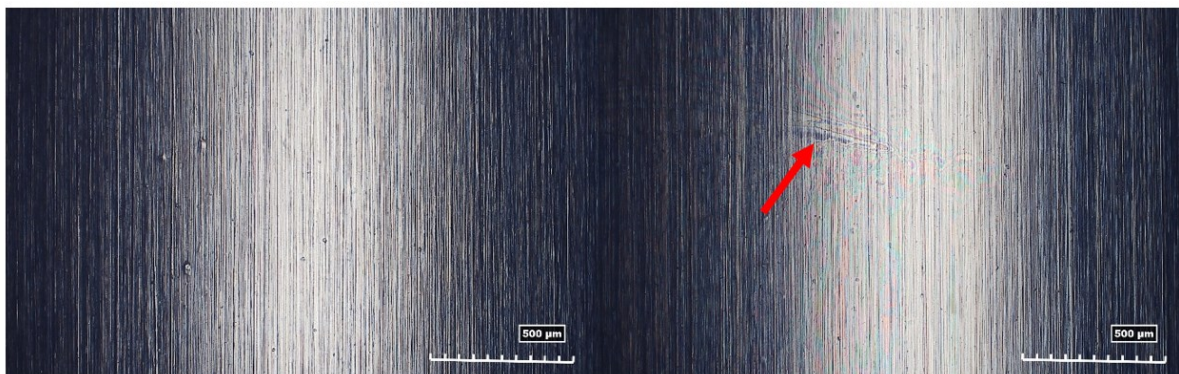


Figure 4.15: Images of the CaXB 100 bearing raceway. The second image features a small region of very low film thickness (<100 nm), marked by the arrow.

Images of the CaXB 100 raceway are shown in Figure 4.15, appearing quite similar to the Li 100 grease in that the films are fairly uniform in thickness. In the second image a small area, marked by the arrow, is covered by only ~ 100 nm of lubricant, as estimated from the interferometric colour. See Figure 6.7 in Section 6.2.1 on page 212 for simulated interferometric colours as a function of film thickness. The majority of the raceway, however, is covered with >5 microns of lubricant.

4.5.4 LiXB 220 – 5,000 RPM Bearing

The raceway of the LiXB 220 bearing is shown in Figure 4.16. The films are very similar to the previous two bearings, with very uniform thickness. Here they appear to be slightly thicker, with just a small region of the second image showing a slight tint due to thin-film interference.

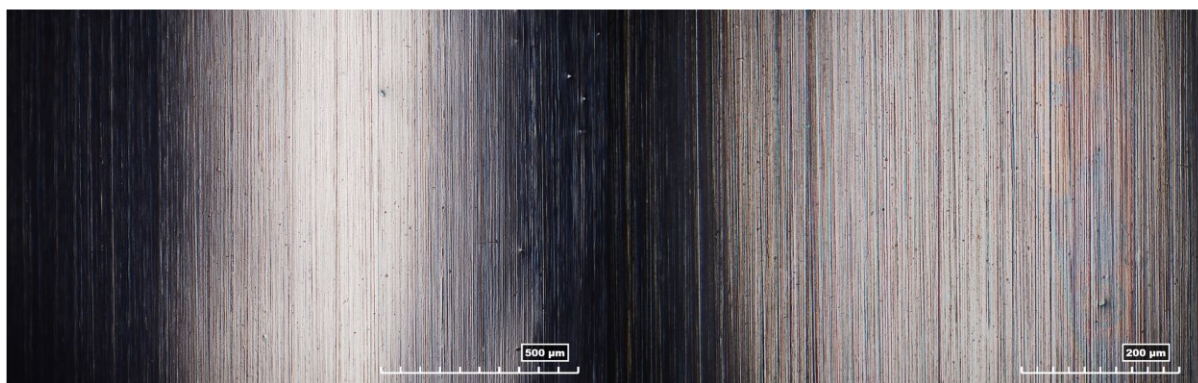


Figure 4.16: Images of the inner race of the LiXB 220 bearing.

Figure 4.17 shows the infrared spectra of LiXB 220 bearing samples. The inner race and shield samples are compared to fresh, along with an additional sample taken of a lump of grease resting on the cage, not in a cage pocket. For a more detailed analysis of the distribution and properties of grease on the cage, see section 4.7 later in this chapter, on page 132. Except for the inner race sample, these were transmission measurements. The inner race spectrum shows a slight reduction in thickener content, but not to the extent seen in the Li 100 bearing. The shield sample actually appears to show a slight decrease in thickener content compared to fresh, but the difference is so small that we cannot reliably conclude that there is less thickener, considering the various changes these peaks may have undergone. Regardless, it is clear that we do not see the same loss of oil as in the Li 100 and CaXB 100 bearings. The sample from the cage lump on the other hand does show a more significant increase in thickener content. This is likely due to the centrifugal forces any grease on the cage is subject to, which will increase oil bleeding. This is a known phenomenon assessed by the ASTM standard D4425 [207], in which the volume of oil released from bulk grease after centrifuging is measured. This observation is also discussed in further detail in section 4.7. The grease at the shields (for a centre-rotating bearing like those in the R0F+ test) is not subjected to this force and therefore will bleed at a slower rate.

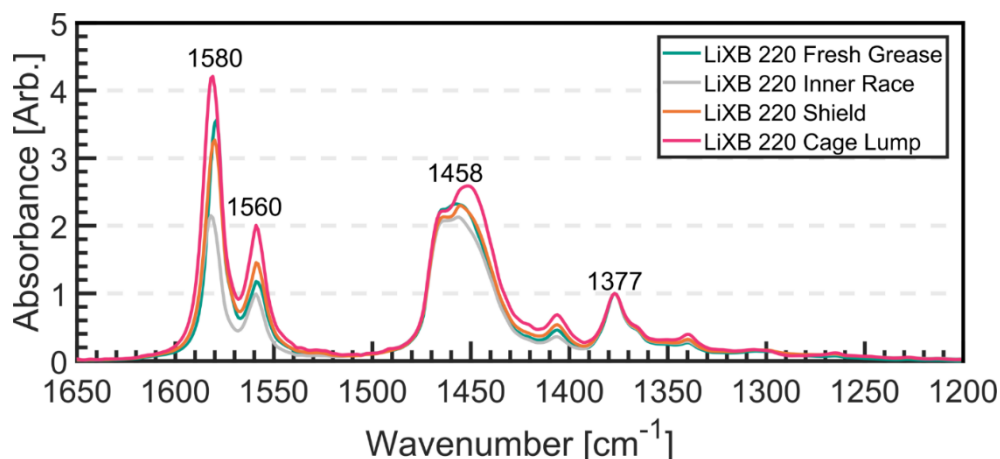


Figure 4.17: FTIR spectra of the LiXB 220 bearing samples, compared to fresh.

Figure 4.18 shows the same spectra but in a magnified view of the carboxylate region, with all the spectra normalised to the peak around 1580 cm^{-1} . The same changes as seen in the Li 100 grease are seen here, a shift of the 1580 cm^{-1} peak. In fact, the peak shift is slightly larger in this case, as the original peak is at 1579 cm^{-1} , yet the final position is still 1582 cm^{-1} . The samples around the bearing differ in the extent to which they display this shift. The shield sample peak has increased in wavenumber by $\sim 1 \text{ cm}^{-1}$, while the cage lump and inner race samples have a much greater increase of $\sim 3 \text{ cm}^{-1}$, the latter being the largest of all. This aligns with the expectation of the extent of shearing, with the shield sample experiencing the least shearing and the inner race sample experiencing the most. The 1560 cm^{-1} peak has increased in intensity and shifted to higher wavenumber, as with the Li 100 bearing, with less change observed between the different samples here.

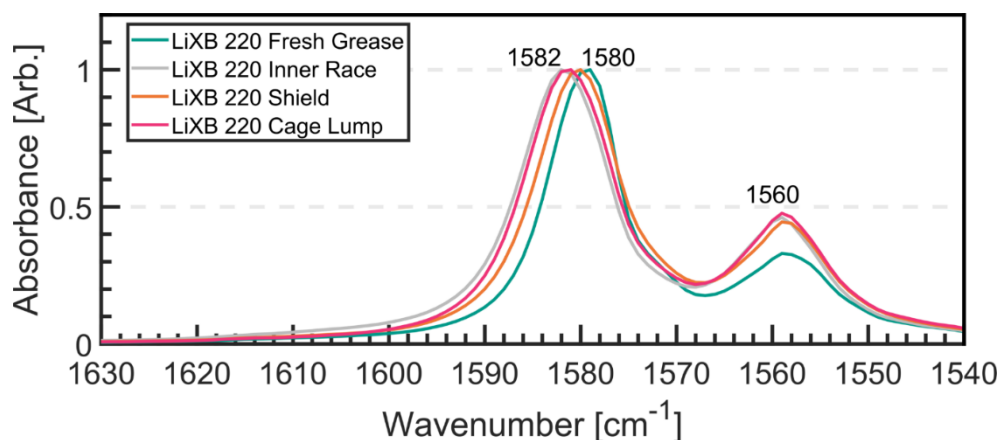


Figure 4.18: Magnified carboxylate region of the LiXB 220 bearing samples, all spectra normalised to the $\sim 1580 \text{ cm}^{-1}$ peak.

4.5.5 PU 220 – 5,000 RPM Bearing



Figure 4.19: Images of the PU 220 bearing raceway.

The grease films in the PU 220 bearing were observed to be inhomogeneous, shown in Figure 4.19, with areas of very thick films that appeared to contain a lot of thickener due to their uneven surface. The middle of the race where the contact would pass appears to be relatively free of these thickener lumps, while the edges are coated in lumps that tend to grow larger away from the contact. The film at the centre of the race clearly retains solid-like rheology, forming small, sharp fingers behind the ball contact. In general, the films are thick and only show interference fringes in small areas, therefore having a thickness greater than $\sim 5 \mu\text{m}$. The second image in Figure 4.19 shows the point where a ball came to rest, annotated with blue arrows, and only small areas of this point have films thin enough to produce interference colours. The film in this area appears to have the uneven surface characteristic of very thickener-rich lubricant.

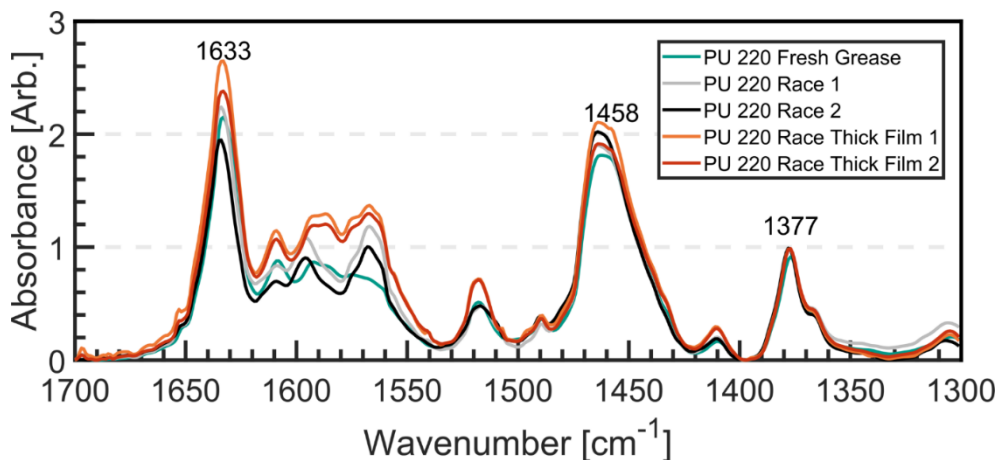


Figure 4.20: FTIR spectra of the PU 220 bearing raceway films, compared to fresh.

Measurements were taken from both the thick and thinner regions. Figure 4.20 shows two spectra from each of these regions, compared to fresh, while Figure 4.21 shows the areas at which these spectra were taken. The spectra from the thicker regions do show increased thickener content as the peaks from 1650-1550 cm^{-1} are all increased in intensity above that of the fresh grease and the lubricant in the thinner regions. It is more difficult to say whether the grease in the thinner regions has more or less thickener than the fresh grease as there have been significant changes in the peaks of that region. They generally appear to have a similar thickener content to fresh grease.

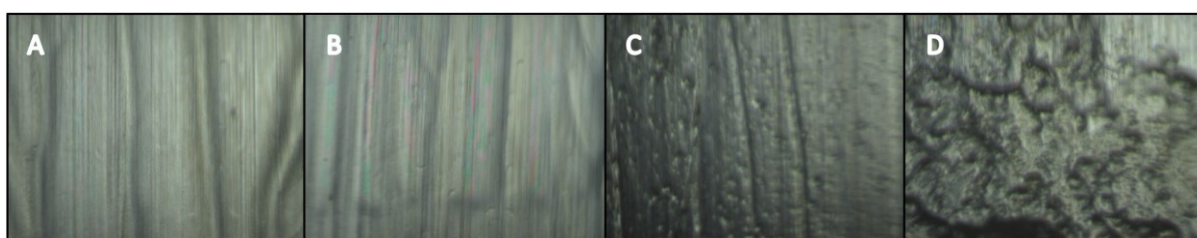


Figure 4.21: Images of the PU 220 raceway, the first two images showing the thinner regions (lighter colour and showing interferometric colours), C and D showing the thicker regions.

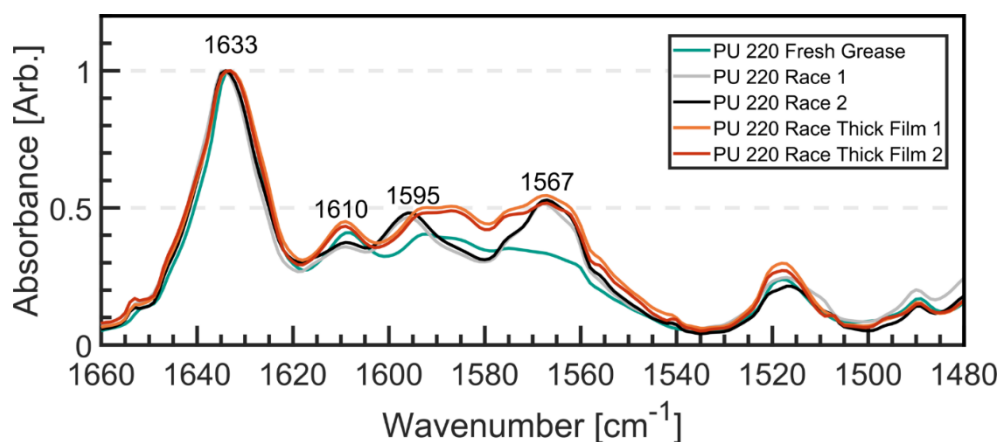


Figure 4.22: Magnified view of the urea region of the PU 220 grease. All spectra normalised to the 1633 cm^{-1} peak.

Figure 4.22 shows the 1600 cm^{-1} region of the PU 220 bearing spectra, normalised to the 1633 cm^{-1} to better compare peak changes. There are many changes in all the raceway samples compared to fresh grease, the largest being the increase of the 1567 cm^{-1} peak which has increased in all samples compared to fresh, in which it is not distinct among the group of peaks. There is a very small but consistent shift of the 1633 cm^{-1} peak in all raceway samples, but the remaining changes are not uniform across the raceway samples. In fact, the measurements from the thinner region are similar to one another but have important

differences to the measurements from the thick region. The 1610 cm^{-1} peak appears to increase in the thick region but decrease in the thinner region. The peaks around 1590 cm^{-1} increase in intensity in the thick region but in the thinner region there is a different change. It seems that there are two peaks at slightly different wavenumbers and in the thinner region the peak at lower wavenumber decreases in intensity, shifting the apparent peak to higher wavenumber. These changes suggest that not only are there significant changes to the intermolecular forces between the urea thickener molecules when lubricating a bearing, but that different locations in the bearing produce different changes. The thicker regions are presumably less sheared than the thinner regions as we would expect thickener lumps to break up on shearing. The mechanism may then be that, as the structure starts to break down, the peaks from $1560\text{--}1620\text{ cm}^{-1}$ begin to increase in intensity generally, but, as a more complete breakdown occurs, the more subtle changes seen in the 1610 and 1595 cm^{-1} peaks begin.

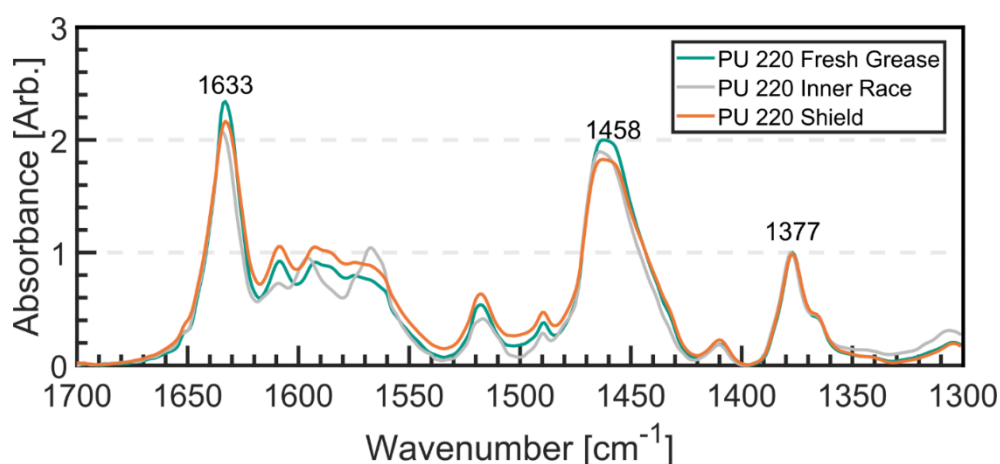


Figure 4.23: PU 220 inner race and shield sample spectra, compared to fresh.

Figure 4.23 shows the PU 220 inner race sample spectrum (PU 220 Race 2 in Figure 4.20) compared to those of the fresh grease and a sample taken from the shield. As with the previous greases, the extent of degradation, as measured by IR changes, is reduced in the shield sample, here showing no change compared to fresh. The thickener content has appeared to increase slightly, however, implying a small loss of oil.

4.6 R0F+ BEARING ANALYSIS – 10,000 RPM

A second round of R0F+ testing was performed under conditions that were kept the same except for rotation speed. Rather than 5,000 RPM as used in round one, 10,000 RPM was used in round two. This was done as no bearings had failed in the first round, and it was deemed useful to bring the bearings closer to failure to observe if that changed the findings.

In this round, some bearings did fail. To understand exactly what this meant, it is necessary to understand the geometry of the R0F+ test units. Figure 4.24 shows a cross-section of one unit. There are four bearings in each unit, two on the ends of the shaft which are the ‘test’ bearings, and two in the middle which are the ‘support’ bearings. All the bearings are greased with the test grease according to the R0F+ procedure. There are two differences between the test and support bearings:

- Loading: the test bearings experience a small additional axial load. This was kept at the minimum allowable value of 100 N, in comparison to the radial load of 500 N.
- Thermal conditions: each test bearing is surrounded by a heating element used to maintain a temperature of 80°C. A large cast-iron support surrounds each test bearing, potentially acting as a significant heatsink. The support bearings do not have a heating element but are placed adjacent to one another and do not have a significant mass supporting them. This allows them to reach significantly higher temperatures than the test bearings in some situations.

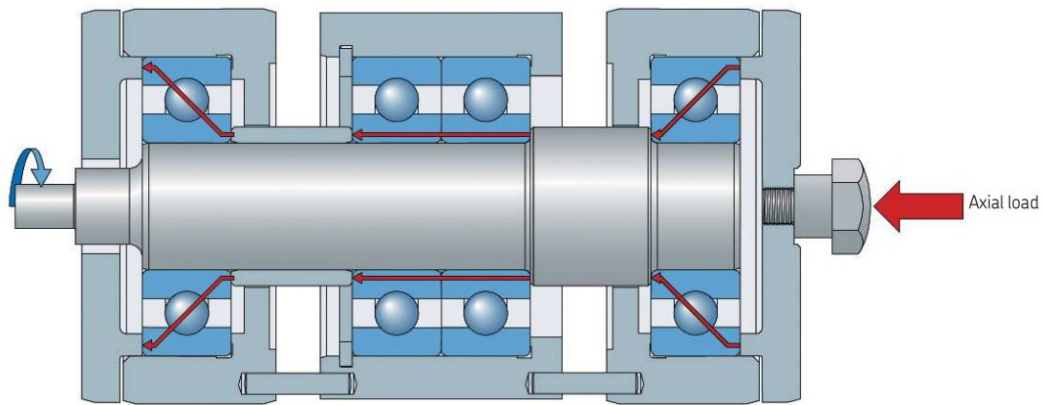


Figure 4.24: Cross-section of a single R0F+ test unit, showing the path of axial load, bypassing the support bearings. Radial load is applied on the support bearings and shared by all four bearings.

As might be expected, the additised greases survived the test and it was one of the base greases that failed. The LiXB survived the 100-hour test, however the CaXB 100 grease unit failed after 49.9 hours.

The temperatures of the support and test bearings are shown in Figure 4.25. The test bearings both maintain 80°C throughout the test, with no apparent temperature rise due to churning (note the 100 cSt grease shown in Figure 4.2 reaches a maximum churning temperature of only 60°C). The support bearings on the other hand spike in temperature during churning despite conditions being almost identical. In fact, due to the slightly lower total load, heat dissipation within each support bearing will theoretically be lower than in the test bearings. Despite this, their proximity to one another and the lack of a large cast iron mass to dissipate heat results in higher temperature spikes. For ~35 hours the support bearings ran at almost exactly 80°C like the test bearings, but then began an extreme temperature spike to 120°C, over the course of around 5 hours. These temperatures will accelerate oxidation to far higher levels than might be seen in the test bearings. For a brief period, the support bearings appear to recover but a second temperature spike causes friction to rise to such a degree that the test is halted due to overcurrent of the motor. Despite the severe temperature spike at 40 hours, the motor current at this time barely rose above previous levels and fell to previous levels after the temperature spike finished. This falls in line with the thermal runaway explanation of bearing failure, in which excessive temperatures cause lubricant oxidation, an increase in

friction, and contribute to even higher temperatures [192]. Eventually, lubricating ability is limited to such a degree that gross metal to metal contact occurs, and a failure like this one arises.

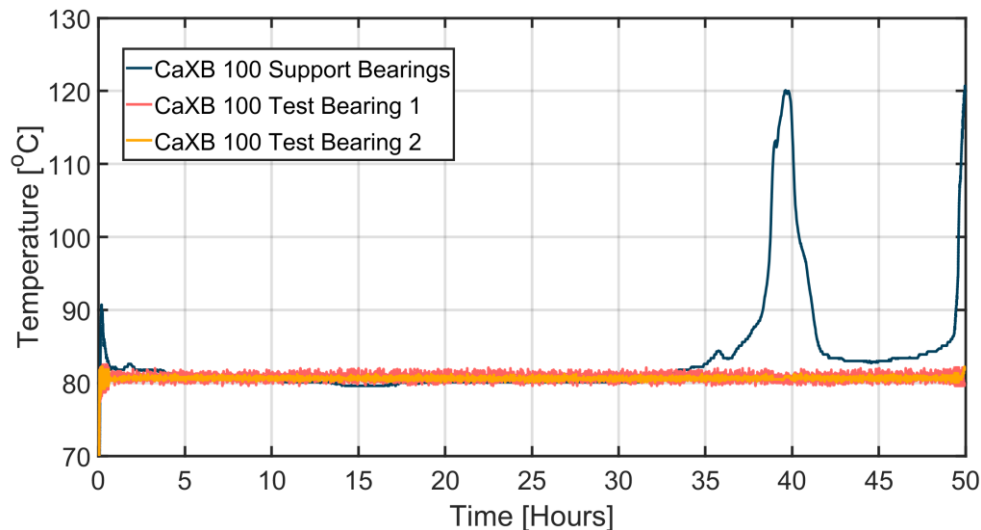


Figure 4.25: Bearing temperatures during the 10,000 RPM test of the CaXB 100 grease.

Dismantling the support bearings revealed that the lubricant had oxidised almost completely, appearing as a carbon dust on the surfaces. No liquid film was present on the inner race, balls or cage pockets and no IR signal was attainable. As the failure has occurred in one or both support bearings, the test bearings are not subject to this thermal runaway. Due to the similarity of test conditions between support and test bearings we can conclude that, while they have not experienced the demanding thermal conditions of the support bearings, the test bearings are stopped at a point reasonably close to failure. This makes the analysis of the CaXB 100 bearing useful, but subject to a more nuanced analysis due to the shorter test time compared to the other greases.

4.6.1 CaXB – 10,000 RPM Bearing

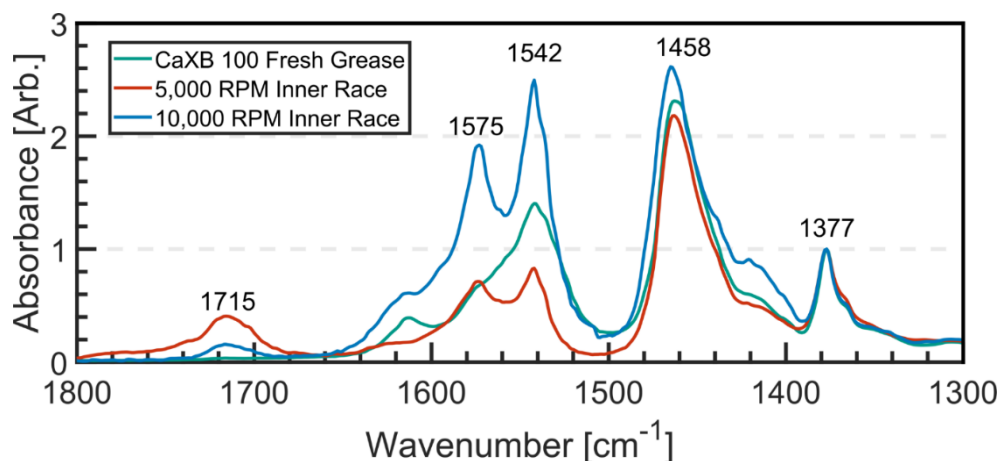


Figure 4.26: FTIR spectra of the 5,000 and 10,000 RPM CaXB 100 bearing inner races, compared to fresh grease.

The IR spectrum of the 10,000 RPM CaXB 100 inner race is shown in Figure 4.26, alongside the 5,000 RPM inner race, and the fresh grease spectra. Two major differences are observed between the different speeds. The higher speed spectrum has significantly more thickener present, clear from the increased intensities across the carboxylate region, more than the fresh grease in fact. The other difference is that the oxidation peak at 1715 cm⁻¹ is not as high as in the 5,000 RPM bearing. The carboxylate region shows exactly the same peak changes as observed in the 5,000 RPM bearing, but are simply at a higher intensity.

The fact that the same peak changes in the carboxylate region are observed is not surprising as the grease has been subjected to more extreme shear conditions than the 5,000 RPM bearing, if for a shorter time. As the test time has been halved and the speed has been doubled, the total shear work is theoretically very similar. The sample from the 5,000 RPM shield, shown in Figure 4.14, has already suggested that the effect occurs with only small shearing or is an oxidation effect. Given the oxidation here is reduced but the carboxylate changes are at least as drastic, this begins to imply that the carboxylate changes are indeed shear-caused. The 1715 cm⁻¹ peak reduction suggests that the observed oxidation is mainly time-based. Any higher flash-temperatures induced by the increased speed have not compensated for the halving of the test time.

As the carboxylate region appears to be a complex superposition of many peaks it is difficult to analyse the changes in detail. If the ratio of the 1575 and 1542 cm⁻¹ peaks is indicative of

extent of degradation, the order of CaXB samples goes: fresh, 10,000 RPM, shield and 5,000 RPM. This would suggest a reduced test time and hence oxidation in the 10,000 RPM sample is a strong influence on the carboxylate changes.

The greater thickener content in the 10,000 RPM race is surprising. The images of the raceway shown in Figure 4.27 display thick films, clearly having a greater solid-like rheology as a result of the greater thickener content than the 5,000 RPM bearing race in Figure 4.15 on page 115. They are not the thin films that might be expected of a bearing close to failure. There is little evidence of oxidation in this bearing, despite the failed support bearings evidently failing due to thermal runaway. This means that the final oxidative failure process has not been initiated in this bearing, but it is possible that the current lubricating state is on the same path to failure. It could be that an oil-rich lubricating state akin to the 5,000 RPM bearing was in operation for the most part of the test, but as time went on this thickener-rich lubricating state developed. Alternatively, this state could have developed from the start of the test.



Figure 4.27: Images of the CaXB 100, 10,000 RPM bearing raceway.

Centrifugal force increases with the square of rotation speed, meaning the centrifugal forces on the grease in this bearing are four times that of the 5,000 RPM bearing. If the grease on the bearing shields was unable to resist this force, there could be bulk flow of grease within the bearing, preventing the formation of an oil-rich active lubricant. This would not explain how a thickener content greater than the fresh grease could be observed, however, these forces will act to squeeze bled oil out of the bearing, through the small gaps at the shields. A greater quantity of oil was observed coating these bearings upon disassembly of the R0F+ test unit than in the 5,000 RPM tests.

These findings suggest that it was not necessarily the lack of antioxidant additives that caused the support bearings to fail, but the increase in test speed. Loss of oil from the bearing and potentially bulk, churning, flow of the thickener-rich grease within the bearing prevented the formation of a small quantity of oil-rich lubricant in the races which would provide low-friction lubrication. Instead, a thickener-rich lubricant was sheared in greater volumes. This may then have led to increased heat dissipation and ultimately failure in the support bearings. Chatra et al. describe this in terms of failure to channel or clear, leading to excessive temperatures, and ultimately failure to lubricate due to oxidation [36].

4.6.2 Li 100 – 10,000 RPM Bearing

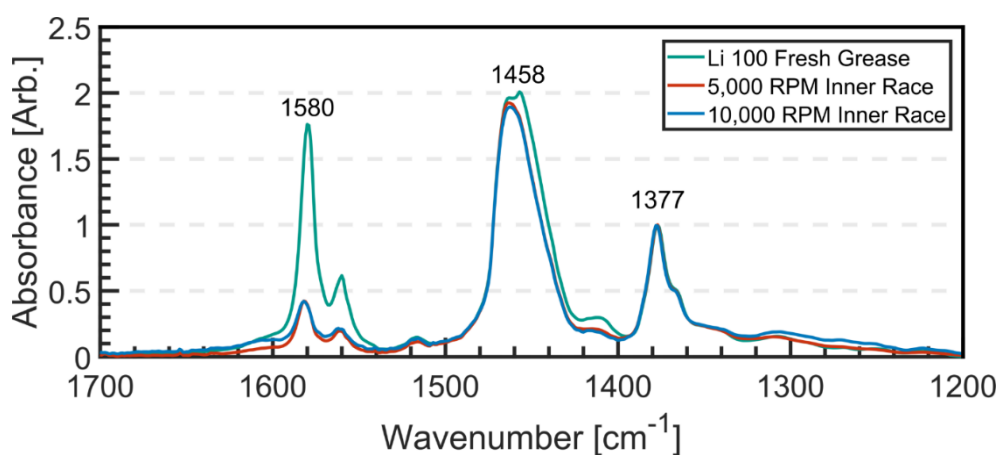


Figure 4.28: FTIR spectra of the 5,000 and 10,000 RPM Li 100 bearing inner races, compared to fresh.

The IR spectra of the 10,000 RPM Li 100 bearing is shown in Figure 4.28 and compared to the 5,000 RPM and fresh spectra. Very little difference is observed between the two bearing spectra, the variation between samples in different locations on the same raceway being larger than the difference between the two bearings. A small increase in a shoulder peak around 1605 cm^{-1} is the only difference, shown in more detail in Figure 4.29. This is not oxidation, which would present as a group of peaks around 1710 cm^{-1} and is not observed in either sample. Previous changes to the carboxylate region in other greases has been suggested as a change in proportion of two or more cases of an existing bond's vibration, however here the change is occurring to a peak that is almost non-existent initially. It may simply be the result of an inaccurate background correction process, however, one possibility is that it is a new carboxylate formed from reaction with an additive, or even iron or chromium released via wear debris. While not typically energetically favourable to substitute a lithium ion for

either of these metals, substitution of metals in organometallic systems, ‘transmetalation’, can occur in reverse due to mass action [208]. The specifics of the new structure will also dictate the reactivity once formed.

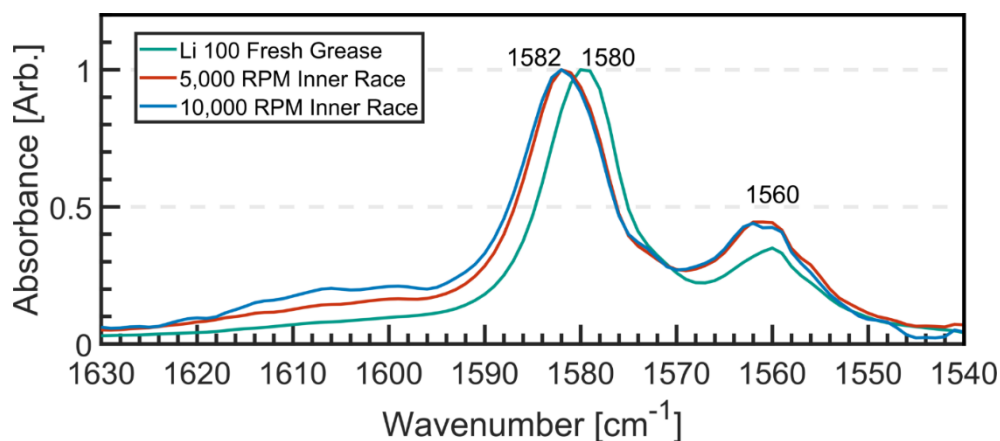


Figure 4.29: Magnified carboxylate region of the Li 100 bearings compared to fresh grease.

The spectra normalised to the carboxylate peak around 1580 cm^{-1} , shown in Figure 4.29, have almost exactly the same peak shift of the larger peak, and increase in intensity of the smaller peak. The higher speed spectrum has a potentially larger shift, though the difference is small. The increase of the shoulder around 1605 cm^{-1} calls into question the validity of the peak shift, as it is possible the shoulder itself, when superposed with the carboxylate peak, causes a shift. This would not require any change of the carboxylate bonds due to shear or thermal degradation. This question influenced the design of later tests to establish the origin of these peak changes.

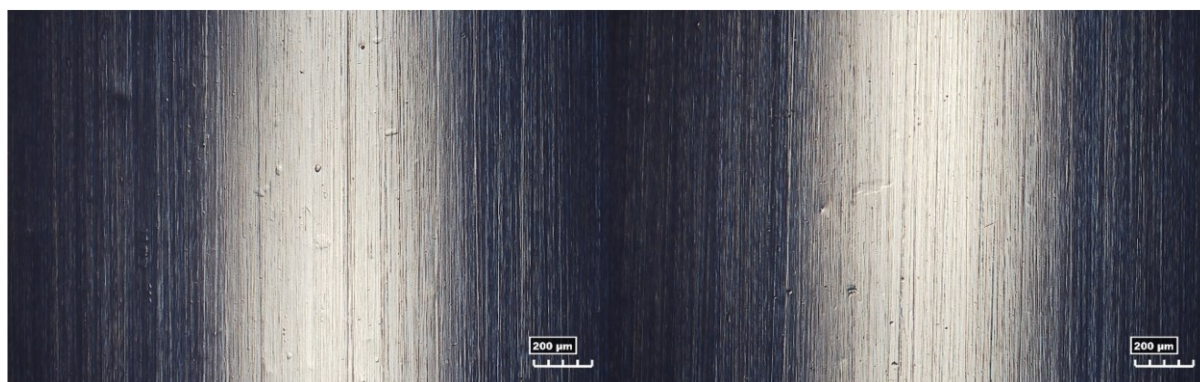


Figure 4.30: Images of the Li 100 10,000 RPM bearing raceway.

Figure 4.30 shows inner race of the Li 100 10,000 RPM bearing, appearing very similar to the lower speed bearings in Figure 4.13. This supports the IR finding that there is little change in

thickener content of the lubricant in the raceway. Unlike the CaXB 100 grease, the Li 100 IR spectra suggest very little change to the lubrication mechanism at play due to an increase in speed. This further supports the idea that the altered lubricant in the CaXB 100 10,000 RPM raceway was a symptom or cause of its failure.

4.6.3 LiXB 220 – 10,000 RPM Bearing

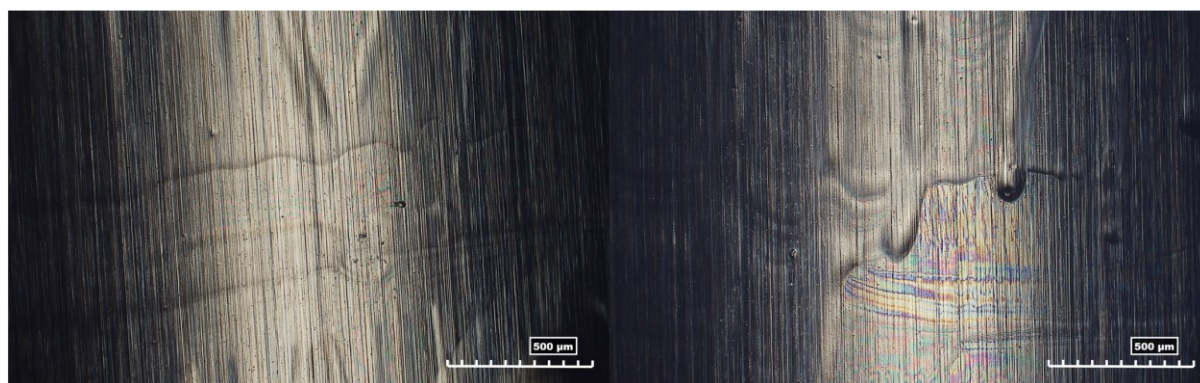


Figure 4.31: Images of the LIXB 220 bearing inner raceway. Here there are regions where the solid-like behaviour of the grease has allowed thicker regions to be preserved.

Figure 4.30 shows the raceway films in the LiXB 220 10,000 RPM bearing. In contrast to the 5,000 RPM bearing the films are much less uniform, displaying some solid-like rheology, with sufficient yield stress to retain the morphology produced by the contact outlet. Other areas have much reduced film thickness where the lubricant has not flowed back to coat it.

Figure 4.32 shows IR spectra from the LiXB 220 bearings, with three spectra from the 10,000 RPM inner raceway: the mean of five measurements at the inner raceway, the spectrum with the lowest thickener content and the spectrum with the highest thickener content. While the lower speed had quite a homogeneous lubricant in the raceway, this bearing displayed regions that contained significantly higher thickener concentrations, though all measurements showed a lower thickener concentration than the fresh grease. Some areas had less thickener than the 5,000 RPM raceway lubricant. The mean of all these measurements suggests a slightly higher thickener concentration than the 5,000 RPM bearing, which does align with the observation of more structured films, though the difference between the images in Figure 4.16 and Figure 4.31 might imply a greater difference in thickener content. Despite being an unadditised grease, there were no signs of oxidation.

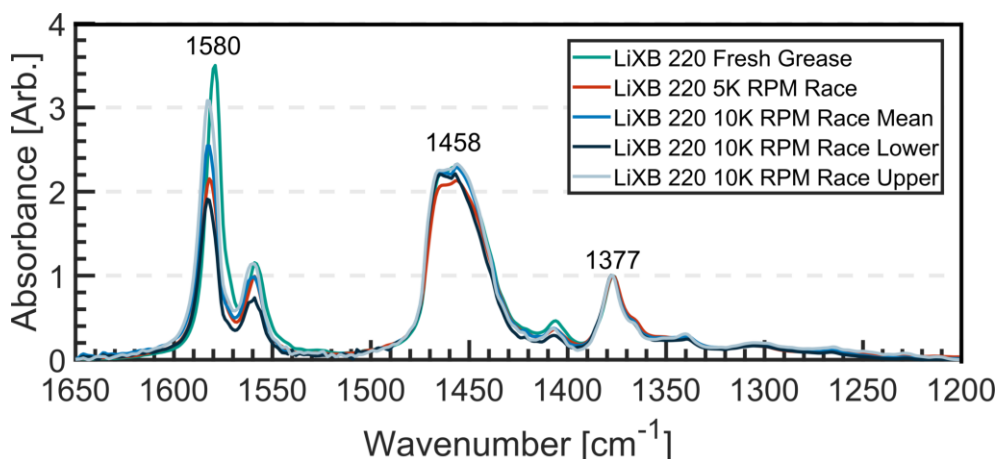


Figure 4.32: FTIR spectra from the LiXB 220 10,000 RPM bearing raceway, compared to the 5,000 RPM bearing and fresh.

The $\sim 1580\text{ cm}^{-1}$ peak of the 10,000 RPM bearing, shown in Figure 4.33, has shifted even further to higher wavenumber, presumably due to the greater extent of shear degradation in the higher speed bearing. The total shift is of 4 cm^{-1} , greater than the shift of 2 cm^{-1} in the Li 100 grease. Interestingly, the 1560 cm^{-1} peak is not as intense as in the lower speed sample, though it has shifted more. While this may be an artifact of different thickener concentrations, it could also signify a different structure or mechanism of shear degradation. This is a complex grease and, as previously mentioned, the potential for shear-induced change to IR spectra is likely to be greater in complexes.

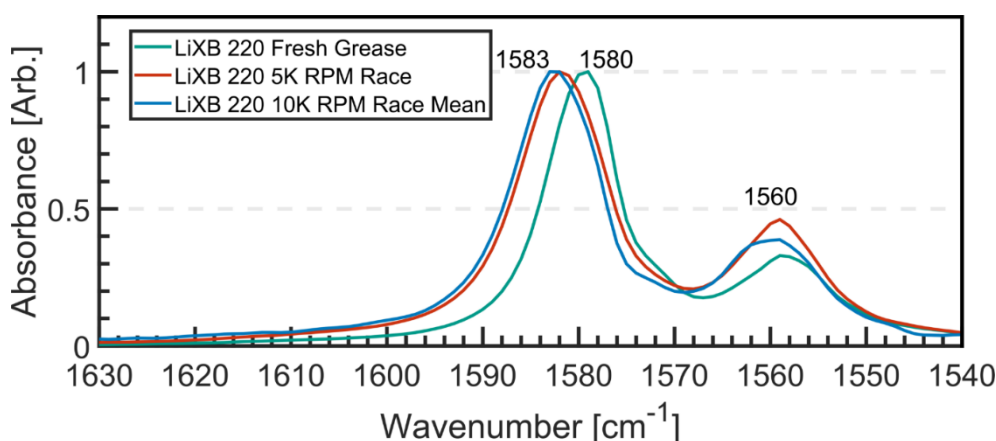


Figure 4.33: Magnified carboxylate region of the LiXB 220 bearing spectra, compared to fresh.

The suggestion from these results is that a slightly different lubrication mechanism was operating in the 10,000 RPM bearing compared to the 5,000 RPM bearing. While the lower speed ‘active’ lubricant contained roughly 60% of the original thickener content, the higher speed bearing contained, on average, around 70% of the original thickener content. The same

cause as suggested for the CaXB 100 grease, a greater introduction of bulk grease to the ‘active’ lubricant due to increased centrifugal forces, could explain the greater thickener content. The inhomogeneous lubricant in the track may be due to incomplete mixing of fresher and degraded grease. The unusual change in the 1560 cm^{-1} peak is difficult to explain and likely requires greater understanding of the specific structures present in lithium complex greases.

4.6.4 PU 220 – 10,000 RPM Bearing

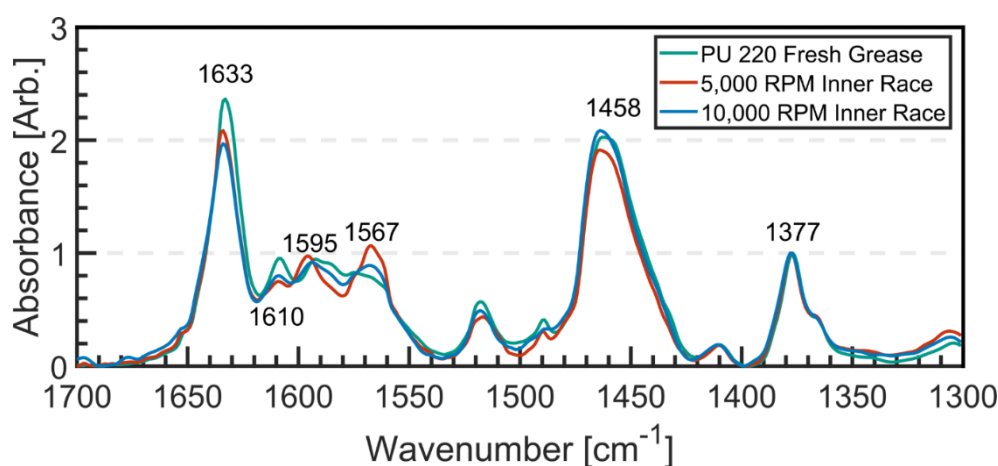


Figure 4.34: FTIR spectra from the PU 220 10,000 RPM bearing raceway, compared to the 5,000 bearing and fresh.

The 10,000 RPM raceway spectrum of the PU 220 grease, shown in Figure 4.34, displays roughly the same thickener content as the 5,000 RPM raceway and the fresh grease. In contrast to expectation, the higher speed bearing films showed smaller changes to the bands around 1600 cm^{-1} compared to the lower speed. The same reduction in the 1610 cm^{-1} peak is observed, however the 1567 cm^{-1} peak does not increase to the same extent, and the changes observed near the 1595 cm^{-1} peak at 5,000 RPM are not observed here. Apart from the reduction in the 1610 cm^{-1} peak, the 10,000 RPM raceway film appears similar to the 5,000 RPM ‘thick film’ sample that consisted of larger thickener lumps.

Assuming that these changes monotonically increase with shear degradation it would be expected that the higher speed would display greater changes. This was seen in the LiXB 220 grease, and to a lesser extent in the Li 100 and CaXB 100 greases. This assumption may not be valid, however, as little is understood about the specifics of what is happening to the thickener molecules upon shear degradation. It may be that different stages of degradation

create different environments around these polar thickener bonds that readily hydrogen bond which causes them to have different IR profiles. Equally, this difference could be due to altered ‘active’ lubricant composition. It has been suggested previously that the higher centrifugal forces in the 10,000 RPM bearings could facilitate greater transfer of fresher grease into the raceway, limiting the extent of degradation.

All measurements shown previously have been of films in the estimated range of 1~20 microns, thin films are possible to assess via interferometric colours, and we can conclude that any films producing unsaturated IR spectra are thinner than ~20 microns, based on prior experience. The ability to measure thin films is limited by the reducing signal-to-noise ratio and a tendency for the baselines to slope, which makes it difficult to reliably baseline-correct such measurements and provide a fair comparison. All previous bearings have not shown any difference between these very thin films and other measurements and so they have been excluded in place of higher quality measurements. The exception is the PU 220 10,000 RPM bearing in which these very thin films appeared to contain significantly more thickener than thicker films, significantly more than even the fresh grease.

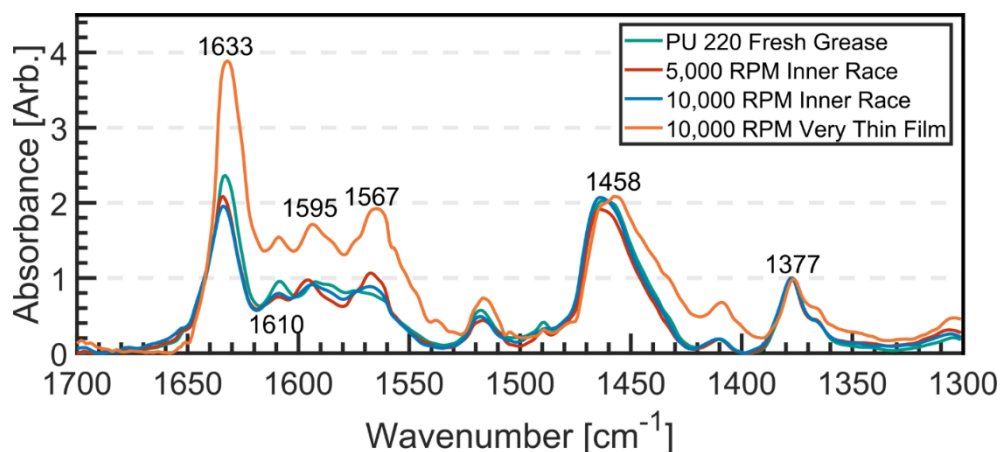


Figure 4.35: FTIR spectra of the PU 220 grease at both speeds, including a very thin film measurement at 10,000 RPM.

Figure 4.35 shows the previous spectra, now compared to a spectrum from a very thin-film region. Note that the poorer quality of the thin-film sample, in orange, has led to an unusual line shape around some areas of the spectrum. Even considering these sources of error, the large increase in intensity of the 1600 cm^{-1} thickener peaks clearly suggests greater thickener content. The location of this measurement is shown in the first image of Figure 4.36, along

with a comparison of the location of another typical measurement. This spectrum is the highest quality of a range of samples taken in these thin areas, all showing significantly increased thickener content. The 1567 cm^{-1} peak of the very thin sample also shows a large increase compared to fresh, greater than the 5,000 or 10,000 RPM race samples, implying significant structural change.

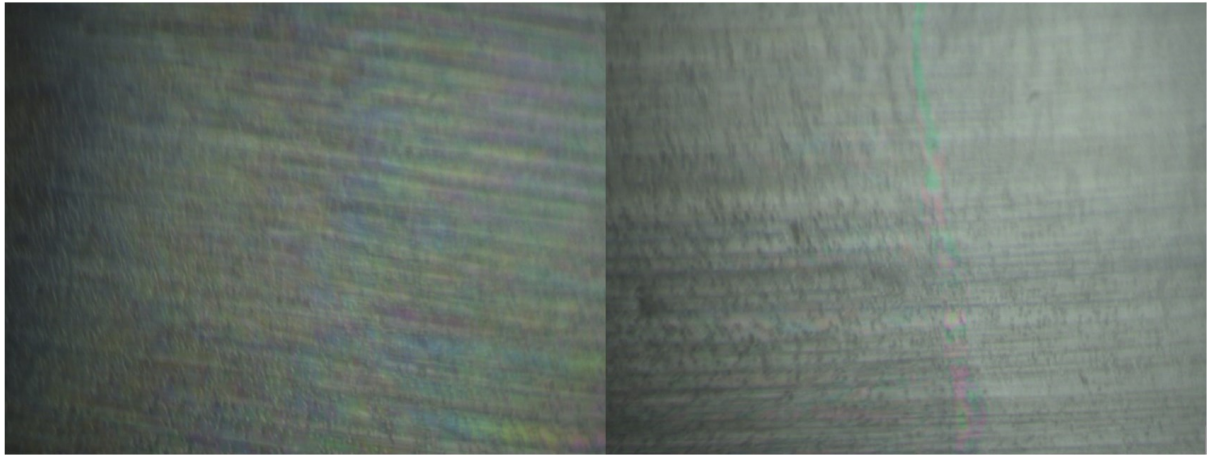


Figure 4.36: Left: Very thin-film region. Right: Typical film thickness for standard measurements in the raceway.

These thin-film measurements imply a thickener-rich film is deposited as a thin layer. The thicker samples which show approximately the same thickener content as fresh grease then suggest that on top of this deposited thickener-rich layer lies an oil-rich layer. The total spectrum of these layers in combination yields a thickener content that averages to that of the fresh grease. The deposition of a thickener-rich layer in polyurea greases has been observed both in ball-on-disc tests [126] and, as reported by Cann [209] in the difficult-to-access NLGI Spokesman [210], in bearings also. While the entrainment, crushing, and deposition of thickener particles in a fully-flooded ball-on-disc test is not particularly surprising, if this layer is still being formed or has endured hours into a real bearing's life, the benefits of surface protection when starvation causes film collapse may still survive. Ito et al. found that polyurea greases displayed superior seizure life compared to other greases [211], which might be explained by this type of thickener-rich film.

4.7 CAGE POCKET ANALYSIS

Here the opportunity is taken to describe the grease distribution at the bearing cages, which was observed during disassembly of the bearings to be common to all tested greases. Figure

4.37A) is an image of one of the cage pockets from a LiXB 220 bearing, showing the hemispherical pocket that retains the ball in place, B) shows the pocket of a Li 100 bearing, showing a similarly thick film of lubricant. Grease in this pocket is heavily sheared between the cage and ball, while outside this area large lumps of grease are observed attached at points of the cage where they are not disturbed by the rotation of the bearing. They have been shown to be very thickener-rich as oil is removed by the high centrifugal forces induced by rotation. Assuming the grease is sufficiently supported, and the cage moves at half the bearing speed, they will experience immense accelerations of 120 and 475 g at 5,000 and 10,000 RPM. For comparison, 500 g is a typical acceleration used to fractionate blood over 10 minutes [212]. Over the long test time this is likely to aid oil bleeding and reduce the oil content significantly.

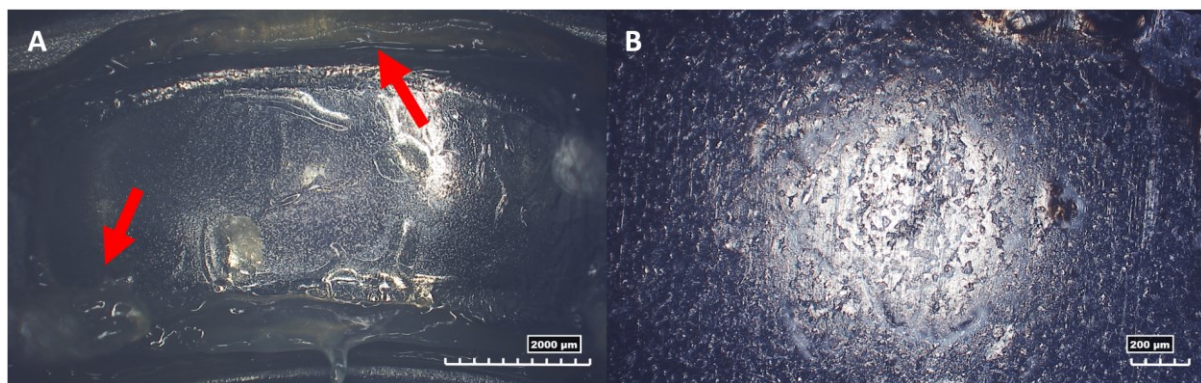


Figure 4.37: a) View of the hemispherical cage pocket from a bearing containing LiXB 220, with arrows indicating lumps of relatively unsheared grease. b) View of the bottom of the cage pocket from a bearing containing Li 100.

Figure 4.38A) shows a zoomed-in area of the lip of one of these pockets, showing wear at the point of contact with the ball. These wear scars were observed on all the bearings, including those containing additised greases, as in a Li 100-containing bearing, shown in B). While the presence of the cage can be expected to aid resistance to starvation through the action of scraping and redistributing the grease as well as providing a means of shear degrading the grease as found by Damiens et al. [133], the authors also warn that the scraping action may dominate and result in removal of lubricant from the contact path. The wear scars are evidence of extremely thin contact films and therefore are likely to be removing grease, however the spherical zone of the balls that contacts the raceways on each rotation is generally far from this point of the cage pocket, which is quite near the spin-axis of the balls. The direct effect on starvation at the race-ball contact is probably limited as a result. Contact

between the ball and the lip of one of these pockets will, however, produce wear debris that may potentially be entrained and cause surface indentation that could go on to cause surface-initiated fatigue failure of the bearing over long lifetimes [11].

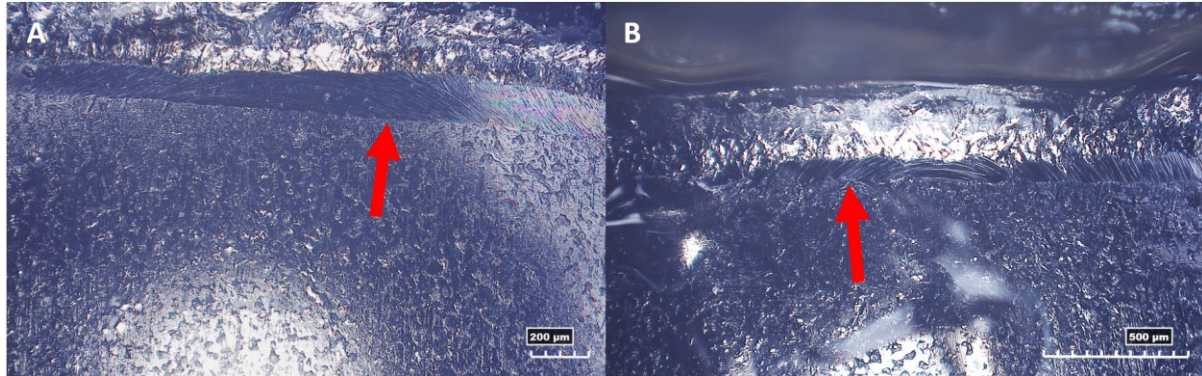


Figure 4.38: A) Rim of the cage pocket from a LiXB 220 bearing, showing wear at the rim, marked by the red arrow. B) Wear at the rim of a Li 100 bearing.

The IR measurement of the thin films in the cage pockets was more difficult than measurements on the inner raceways for two reasons. The tightly curved surface meant that it was only possible to measure a small area at the bottom of the pocket without losing measurement signal. Additionally, the quantity of lubricant in the pockets was typically larger than on the race, where large areas were of an optimum film thickness to provide good signal without saturating IR absorbances. As a result, it was difficult to take unsaturated measurements of the cage pocket films.

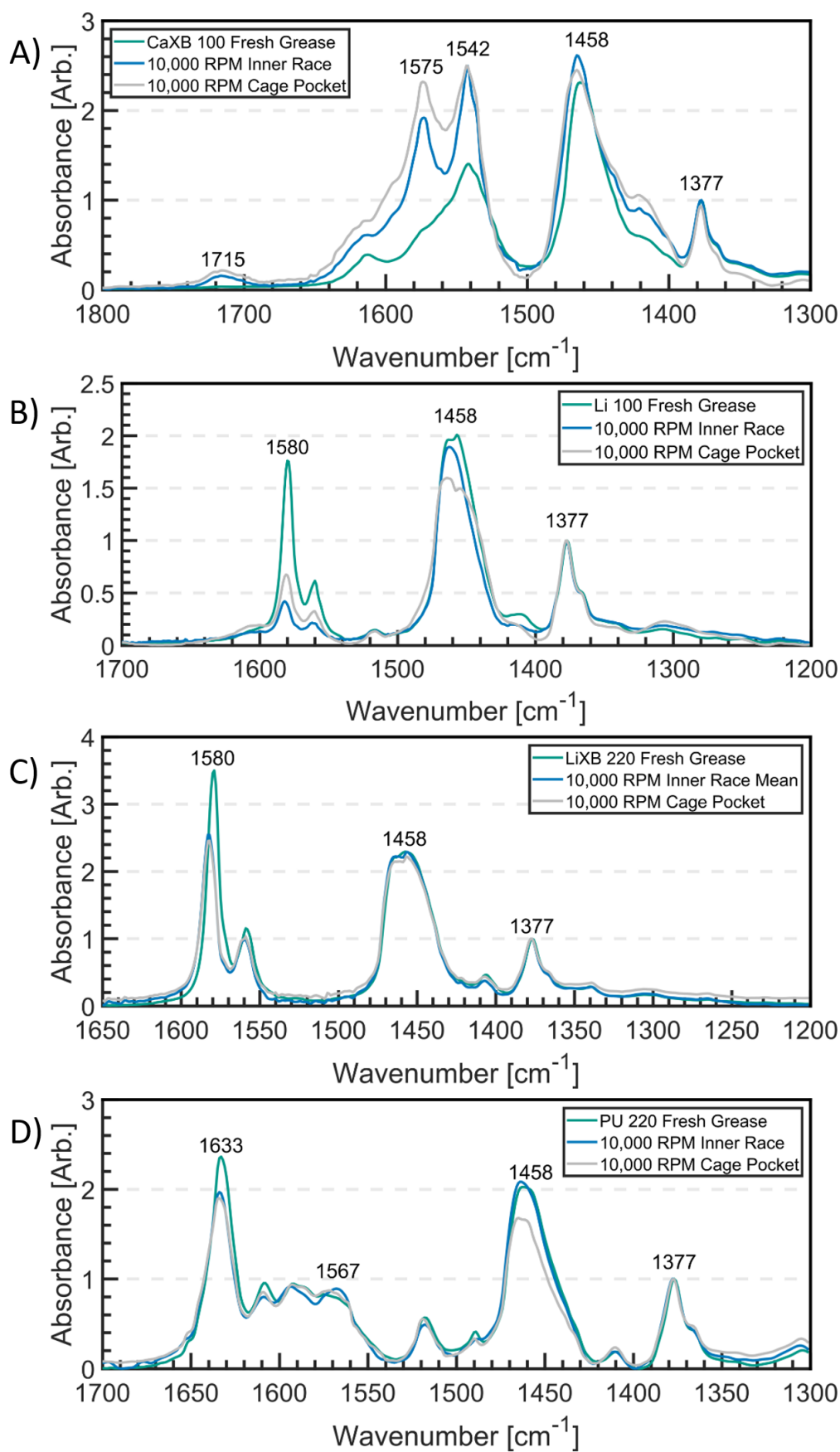


Figure 4.39: Comparisons of the IR spectra of the fresh greases, 10,000 RPM bearing race samples and the cage pocket samples. A) CaXB 100 B) Li 100 C) LiXB 220 D) PU 220.

The contact conditions are very different in the ball-race contact and the ball-cage contact which might suggest that the films retained in these areas would differ strongly. In fact, where it was possible to perform IR analysis of the films in the cage pockets, they showed strong similarity with the films in the raceway, shown in Figure 4.39. Note that these samples were typically at the limit of saturation as a result of the thick films, Figure 4.39B) and D) showing a distortion of the 1458 cm^{-1} peaks due to peak saturation. These results are shown for comparison only and would otherwise be discarded. The slight increase of the thickener peaks compared to the 10,000 RPM race sample in the Li 100 spectrum for example cannot be reliably taken to mean that the pocket sample contained more thickener as a result of the peak saturation. All that can be concluded is that the cage pocket spectra are, in general, similar to the inner race spectra, and so a high level of recirculation of the active lubricant between the cage pocket and inner race can be inferred.

4.8 DISCUSSION OF BEARING LUBRICANT FILM INFRARED ANALYSIS

The infrared spectra of the raceway samples of all four grease types at both test speeds have shown changes compared to the spectra of the fresh greases. Oxidative changes were absent in all greases except the CaXB 100 grease, which showed oxidation even at 5,000 RPM. The susceptibility to oxidation is therefore much higher than the other base grease, LiXB 220, which did not oxidise even at 10,000 RPM. The thickener-rich sample at the shield showed greater oxidation than the oil-rich sample from the race, roughly in proportion to thickener content. This suggests the oxidation is largely occurring in the thickener itself, agreeing with the conclusion of Salomonsson et al. [53], that oxidation and hydrolysis of a lithium soap were the primary thermal degradation processes. An alternative explanation could be a greater availability of oxygen at the shields.

The samples taken around the bearing have shown for two of these greases that the oil content of the grease at the shields is reduced as it releases oil which bleeds into the raceway, causing a corresponding increase in oil content of the lubricant in the raceways. Grease that remained as bulk lumps on the cage were particularly reduced in oil content. At 5,000 RPM, relatively moderate conditions, all greases except the PU 220 displayed a reduction in thickener content at the inner race. The extent of this reduction varied, with the Li 100 grease

showing the greatest reduction to approximately 25% of the original thickener content, as assessed by absorbance values. This aligns with the IR work by Cann et al. using the same IRRAS technique with R2F bearings [180]. The mechanism of this oil release may be partly driven by centrifugal forces, but also by shear degradation of grease, which has been suggested to increase the release of ‘free’ lubricant in ball-on-disc tests [130].

In addition to these results, more subtle changes have been observed that are theorised to be a result of shear degradation of the thickener. Both lithium-containing greases have displayed a very similar peak shift of the 1580 cm^{-1} peak, increasing in wavenumber, with the LiXB 220 grease shifting to a greater degree. They also showed an increase in the absorbance of the 1560 cm^{-1} peak, as well as a shift of this peak. The CaXB 100 grease showed many changes in the group of superimposed peaks that are produced by the carboxylate bonds, some of which increase in intensity while others decrease. The PU 220 grease has shown changes in the IR bands relating to the urea bonds. These bonds are also a superposition of multiple peaks and there are subtle changes to the bonds from $1610\text{--}1590\text{ cm}^{-1}$, but one of the more significant changes is the large increase in the 1567 cm^{-1} NH in-plane bending peak.

These changes have predominantly occurred at IR absorbance peaks that are caused by carboxylate and urea bonds, which are very susceptible to hydrogen bonding and are a dominant factor in the arrangement of thickener molecules to form micro-scale thickener fibres or particles [70], [71]. If these changes can be truly attributed to shear degradation the implication is therefore that most, if not all, grease thickeners undergo a significant change to their supramolecular structure during bearing operation, and that this can be assessed using IR analysis. The fibre breakage that has been observed in many bearing tests [36], [195], [196] may be the cause of these changes, allowing a greater proportion of the thickener to be surrounded by oil. The IR technique is far simpler than AFM (atomic-force microscopy) methods which could be used on samples extracted from a bearing [76]–[78], or SEM which either requires removal of the base oil, potentially altering thickener structure, or freezing of the sample which is a more complex procedure [76], [77], [213], [214]. The use of IR allows in-situ analysis of the tiny quantities of lubricant which contribute directly to film formation.

Shear degradation and subsequent release of base oil has been suggested in section 4.1 on page 95 as an integral part of bearing lubrication by enabling reflow of a small volume of active lubricant. Most greases in this study showed shear degradation and oil-rich lubricant in the track, but did not in two cases. Firstly, the CaXB 100 grease tested at 10,000 RPM showed at least the same thickener concentration as fresh, implying either the shear degradation and oil release did not occur at this speed, or that there was bulk mixing of the grease throughout the test, in other words it did not 'channel'. Work by Chatra and Lugt [108] suggests lack of channelling ability could be a cause of failure, and therefore may explain the observed failure of this test. The second case which did not show an oil-rich active lubricant was the PU 220 grease. As no temperature spikes were observed it does not appear that the grease failed to channel, which suggests in this case the 'oil release via shear degradation' mechanism does not apply, at least to the same extent. The thickener-rich deposited layer is also likely to reduce the apparent oil proportion of the total film, masking the presence of an oil-rich layer above it.

The link between these IR changes and shear degradation has not yet been confirmed to a satisfactory degree, however. There remains the possibility that at least some of these changes are in fact due to oxidation products altering the thickener interactions, certainly possible with the CaXB 100 grease. Changes to thickener content also cloud the issue. The large reduction in thickener content in the Li 100 grease, for example, may mean that relatively small shoulder peaks from the base oil now dominate the thickener peak, and cause a resulting shift in wavenumber. It should also be ruled out as a possibility that the action of applying a carboxylate grease to the potassium bromide window, as was done for all the fresh grease samples, has not caused IR spectral change due to metal substitution.

By mechanically shearing fresh samples of these greases, without reducing thickener content, and applying the same measurement techniques as were performed with the fresh greases, it can be established whether these IR changes can be attributed to shear degradation of the thickener structure.

4.9 REPRODUCTION OF THERMAL AND SHEAR DEGRADATION IN THE LABORATORY

In order to answer some of the questions posed above, and to test and understand the effects of this kind of degradation on lubrication, it was necessary to reproduce this degradation on a larger scale in the laboratory. The effects of shear and thermal degradation were kept separate, in order to understand the contribution of each to tribological properties.

The intense shearing of grease within the raceway is difficult to reproduce, with rheometers and machines based on a rotating blade either not providing sufficient shear rates and hence shear stresses or allowing only a small volume of the total sample to be continuously sheared. The yield stress and shear-thinning rheology of greases prevents easy mixing, and it is necessary to have the moving parts of the shearing machine sweep almost the entire chamber volume in order to prevent this. Alternatively, the grease can be recirculated through a small aperture at high pressure as is commonly done in homogenisation of fluids such as milk, pharmaceuticals and cosmetics, as well as greases.

While such processes can produce very high shear rates that may compare to those of an EHD contact, the grease thickener passing through a bearing contact may in fact be physically crushed, potentially reaching far higher shear stresses than can be produced via typical Couette shearing. For this reason, a process that involves high-pressure contacts was predicted to be most effective in reproducing the observed IR changes. While unable to process a large enough volume of grease for use in tribological or rheological testing, a ball homogeniser was used to shear-degrade small samples of grease. This consists of a polyethylene chamber containing stainless steel balls which are agitated rapidly, colliding with one another and the walls. For larger samples, the roll stability testing machine was used, shearing a 50g sample of grease between a heavy stainless-steel roller and a cylindrical chamber. Both systems are described in full in Chapter 3.

The thermal aging was designed to replicate the temperatures and time scales found in a bearing, as accelerated thermal aging at inaccurately high temperatures is likely to initiate reaction pathways that are not seen in bearings. Additionally, longer term tests can

potentially allow for greater loss of volatiles, an effect of aging that will increase viscosity and therefore affect lubricating ability directly. Glass petri dishes were filled with a controlled mass of grease and aged for 840 hours at 100°C.

4.9.1 Shear-Degraded Grease IR Results

The spectra from both shear methods were all sampled on a potassium bromide window. The fresh grease was placed in the ball homogeniser and run for a set time, after which a small sample was taken with a stainless-steel spatula and applied to the IR window. No change was observed between an IR sample taken immediately after shearing and one taken days or weeks later, meaning these IR changes are not the effect of temporary shear thinning which resolves upon relaxation.

The Li 100 and CaXB 100 greases were selected to be progressively sheared in the ball homogeniser for 1, 2 and 3 hours in order to observe if the spectral changes would also progressively change. This would help to indicate whether the spectral changes are linear with shear work or follow a more complex relationship. With the ball homogeniser established as a method capable of producing IR changes, the LiXB 220 and PU 220 greases were sheared for 1 hour each.

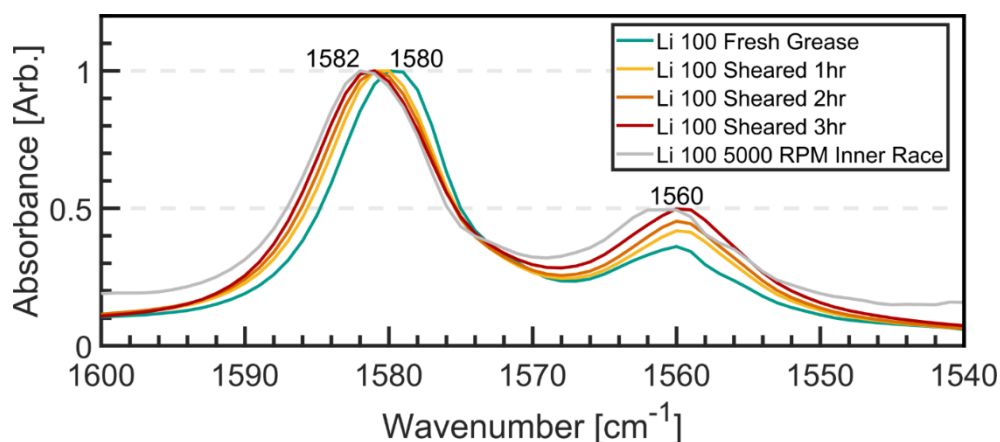


Figure 4.40: FTIR spectra of the fresh Li 100 grease and the 5,000 RPM bearing raceway film, compared to samples sheared in the ball homogeniser for incrementally increasing periods.

Figure 4.40 shows the Li 100 ball-homogenised samples, increasing from 1 to 3 hours of shearing, compared to the fresh grease and the 5,000 RPM inner race sample. The bench-sheared sample clearly shows progressive changes to the 1580 and 1560 cm^{-1} peaks, closely following the changes observed in the inner race sample. The greatest single change is within

the first hour of shearing, though the rate of change does appear constant after this, and the peak shift of the inner race sample is not reached in the 3 hours of testing. The 1560 cm^{-1} peak does, in fact, reach the intensity of the inner race sample after 3 hours, and might continue to increase under longer test times. In contrast to the inner race sample, the 1560 cm^{-1} peak does not shift in wavenumber. This difference suggests that the shear degradation of the inner race is not perfectly reproduced by the ball homogeniser, though, as a whole, the changes suggest an environment of intermolecular forces has been produced that resembles that of the inner race. As one possible cause of splitting of the carboxylate bonds into these two peaks is the formation of two separate coordination modes [201], a change in their relative heights suggests one has become more dominant, perhaps as it has a higher shear-strength or is formed under the influence of more oil, at the edges of thickener particles. The shift of the peaks to higher wavenumber is suggestive of reduced hydrogen-bonding, a natural consequence of structural breakdown. As the 1560 cm^{-1} peak has not shifted in the ball-homogenised sample, the implication is that the contributing coordination mode has not experienced reduced hydrogen bonding.

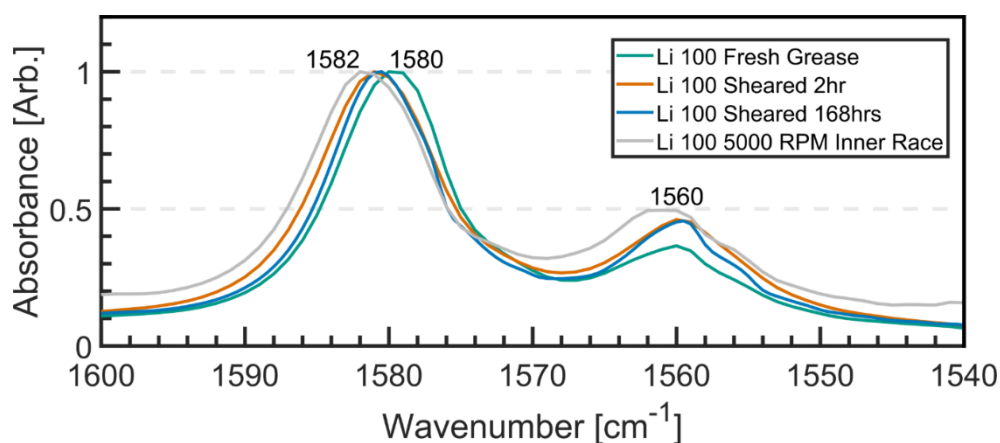


Figure 4.41: FTIR spectra of the fresh Li 100 grease, as well as samples sheared for 2 hours in the ball homogeniser, 168 hours in the roll stability tester and a sample from the inner race of the 5,000 RPM bearing.

Figure 4.41 includes the spectrum of the roll stability tester sample, displayed as '168 hrs' to distinguish from the ball homogeniser samples which were run for 1, 2, or 3 hours. The ball-homogenised samples run for 1 and 3 hours have been removed for clarity. The figure shows that the roll stability tester has induced a similar degree of change to the 2 hour-sheared ball

homogeniser sample. The peak shift of the 1580 cm^{-1} peak is slightly lower but there is a significant difference compared to the fresh grease. Both methods are therefore successful in recreating the infrared changes seen in the inner race, though to a smaller extent.

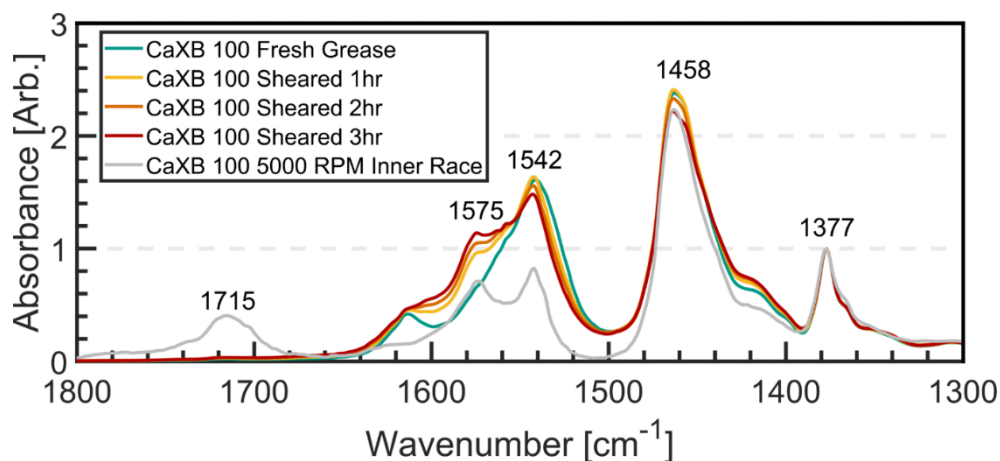


Figure 4.42: FTIR spectra of the fresh CaXB 100 grease and 5,000 RPM raceway film, compared to progressively sheared samples from the ball homogeniser.

The IR spectra of the ball-homogenised CaXB 100 samples are shown in Figure 4.42, compared to the fresh grease and inner race sample. A clear progression is shown in the samples as shearing time increases, the 1542 cm^{-1} peak decreasing in intensity, while the 1575 cm^{-1} increases. These changes appear to match some of those seen in the sample from the inner race. Two major differences are present, however. Firstly, the oxidation seen at 1715 cm^{-1} is not present in the sheared sample, a confirmation that the effects have been effectively separated. The other difference is that there is no change in the peak at 1610 cm^{-1} which reduces significantly in the bearing sample. As the bearing sample is not only subjected to a greater level of shear according to these IR markers, but also oxidation, this particular peak change may be a result of oxidation affecting thickener interactions.

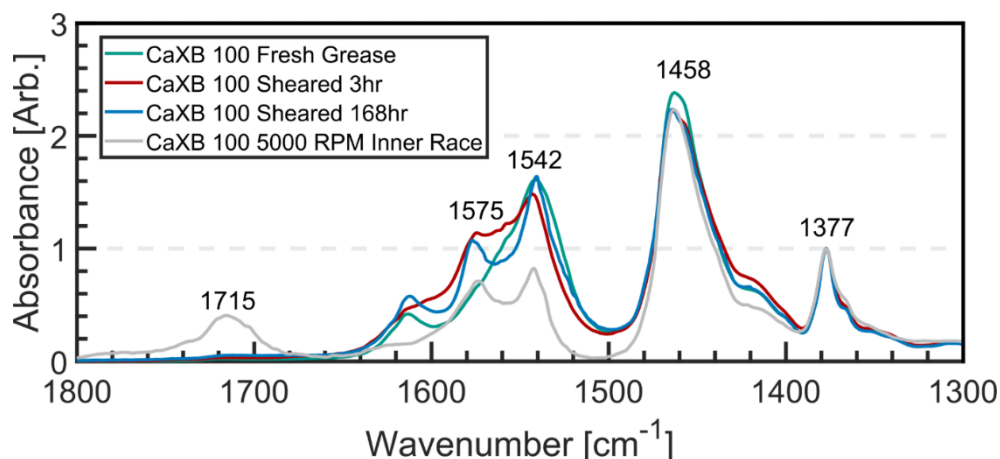


Figure 4.43: FTIR spectra of the CaXB 100 fresh grease and 5,000 RPM bearing film, compared to the two sheared samples.

The CaXB 100 sample that was sheared in the roll stability tester for 168 hours is shown in Figure 4.43. Interestingly, the peak changes are slightly different to the ball homogeniser sample. There appears to be no decrease in the 1542 cm^{-1} peak, and the 1610 cm^{-1} peak appears to have increased in intensity. This is likely a consequence of the slightly different modes of shearing. Whereas the ball-homogeniser crushes a very small contact area per collision but produces extreme shear stresses, the roll-stability tester subjects a large volume of the grease to a relatively mild shear stress constantly. There may be localised high-shear regions if the separating film thickness breaks down, but in general the shearing is likely to be Couette predominantly. These differing processes may have degraded the thickener structure in different ways, the latter separating thickener lumps or fibres from each other, the former breaking apart those lumps or fibres individually. A consequence is that the changes in intermolecular forces differ between the two processes.

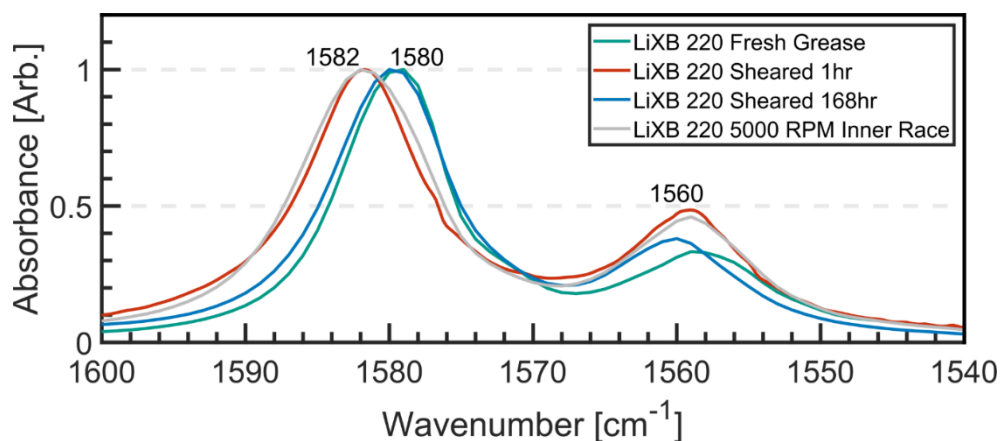


Figure 4.44: FTIR spectra of the LiXB 220 fresh grease and 5,000 RPM bearing film, compared to the two sheared samples.

In Figure 4.44 the two sheared LiXB 220 samples are compared to the fresh grease and inner race sample. Here, the ball homogeniser sample was sheared for one hour only. Despite this short time, the peak shift of the inner race sample has been repeated almost identically. In contrast, the roll stability-sheared sample shows very little change at all. There is an indication that the 1580 cm^{-1} peak has shifted slightly, but it is not significant. The 1560 cm^{-1} peak has increased in intensity slightly, like the inner race sample, but not to the same extent. These results suggest that the intense shearing of the ball-homogeniser is reproducing the same thickener interactions present in the inner race sample, but the roll-stability tester is failing to do so in the same way. It is shown in the next chapter that the roll stability-sheared sample has, in fact, undergone rheological changes that suggest some level of thickener breakdown. Again, the likely explanation is that the ball-homogeniser and bearing race are causing destruction of the individual thickener particles to a severe degree, whereas the roll stability tester is separating particles or causing only minor damage to individual particles. For a fibre thickener structure this may mean that the former process is crushing and tearing apart fibres into many parts, while the second process separates fibre bundles or splits fibres into two or so parts.

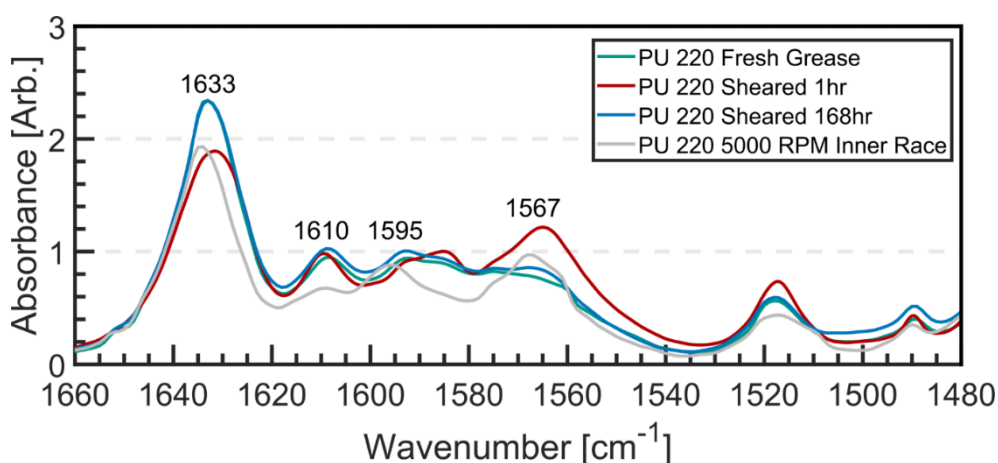


Figure 4.45: FTIR spectra of the PU 220 fresh grease and 5,000 RPM bearing film, compared to the two sheared samples.

As with the LiXB 220 grease, the PU 220 sample was only sheared for one hour in the ball homogeniser in order to compare that process to the roll stability shearing. Figure 4.45 shows these samples, compared to the inner race and fresh grease samples. Again, the 1-hour ball homogeniser sample appears to replicate more of the IR changes that were observed in the

bearing sample, including the increase in intensity of the 1567 cm^{-1} peak and the reduction in intensity of the 1633 cm^{-1} peak. Smaller IR peaks in the 1600 cm^{-1} region that were altered in the bearing appear unchanged in the ball homogeniser sample, however. The roll stability tester and fresh grease samples appear extremely similar, though there is a very slight increase in the 1567 cm^{-1} peak which may indicate a small amount of the same degradation process has occurred. It again seems that the ball homogeniser has been more effective in reproducing the same kind of shear degradation as seen in the bearing inner race.

4.9.2 Thermally Degraded Grease IR Results

The thermally aged Li 100 grease is shown in Figure 4.46, compared to the inner race and fresh grease samples. The thermally aged sample is relatively unchanged compared to the fresh grease. The only apparent change is an increase in the intensity of the thickener peaks around 1580 cm^{-1} . This is likely to be caused by volatile loss over the long aging time. Oxidation changes would be expected around 1715 cm^{-1} , but there is no change to observe.

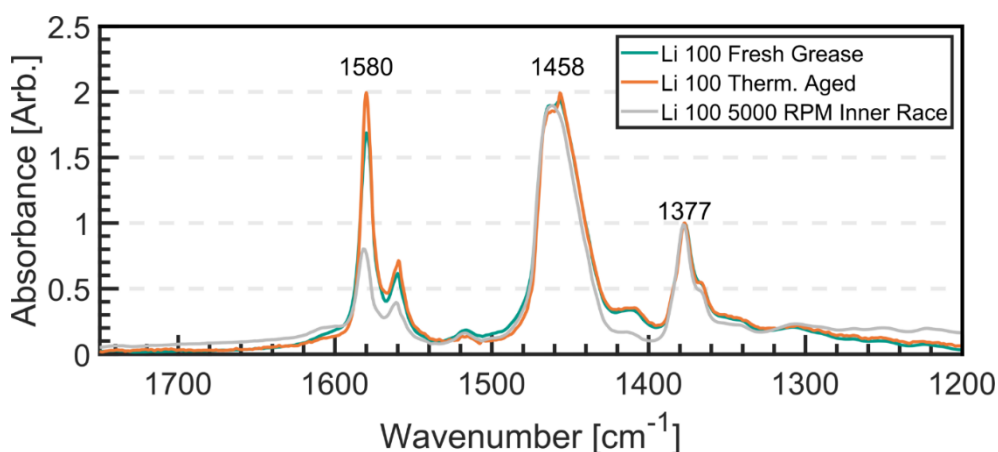


Figure 4.46: FTIR spectra of the fresh Li 100 grease, thermally aged sample and 5,000 RPM raceway film.

The IR spectra of the thermally aged CaXB sample is shown in Figure 4.47, compared to the fresh grease and inner race sample. The changes due to thermal aging are numerous and indicative of severe oxidation. The broad group of peaks at 1715 cm^{-1} are due to a range of oxygen-containing oxidation products, while the region near the 1172 cm^{-1} peak may be due to production of esters. Clearly the extent of oxidation is greater than that of the inner race, a consequence of longer aging at higher temperature. Interestingly, the thickener region appears to have undergone similar changes to the bearing film. As the shearing process was

able to produce these changes (to a lesser degree) without signs of oxidation, the evidence suggests that both processes have caused similar changes to the thickener structure. This may be because the changes indicate structural breakdown, which is the end result of both processes.

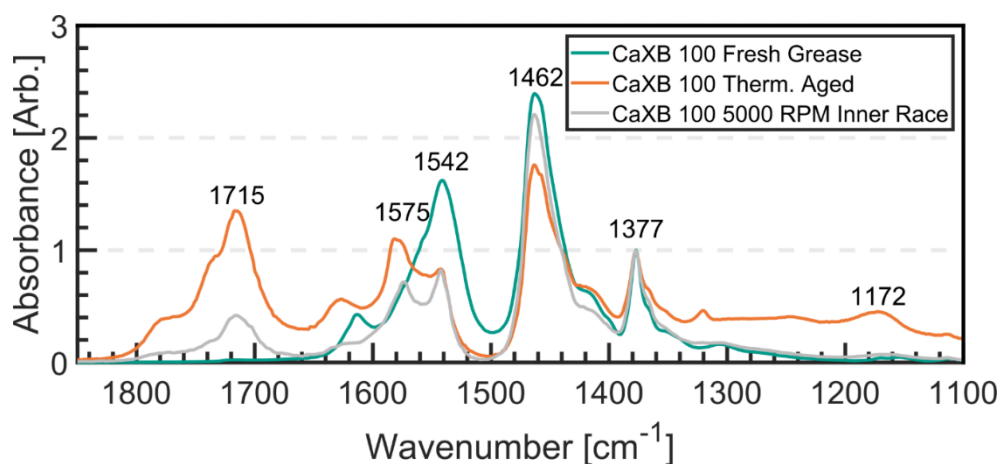


Figure 4.47: FTIR spectra of the CaXB 100 fresh grease, thermally aged sample and 5,000 RPM raceway film.

As with the Li 100 grease, oxidation of the LiXB 220 grease, shown in Figure 4.48, has not caused clear changes compared to fresh. There is no real change in the 1715 cm⁻¹ region, and the thickener region has not increased in intensity significantly, possibly due to the higher base oil viscosity which would reduce the evaporative losses. Depending on the production of the base oil, the distribution of molecule sizes may be significantly lower than that of the Li 100 grease, which would also reduce the number of molecules that are able to evaporate.

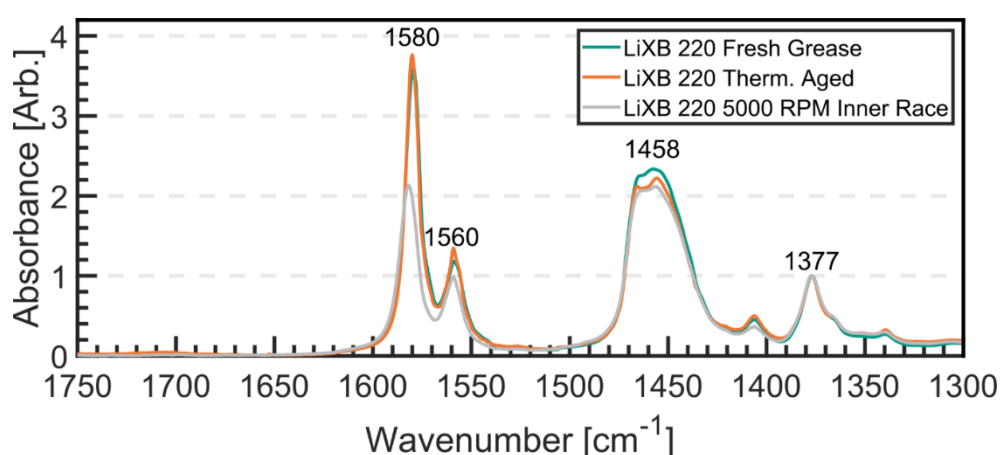


Figure 4.48: FTIR spectra of the LiXB 220 fresh grease, thermally aged sample and 5,000 RPM raceway film.

Finally, the PU 220 thermally aged sample is shown in Figure 4.49, again, displaying minimal changes compared to fresh. A small increase in thickener content due to volatile loss appears

to be the only change as a result of thermal aging, with no observed increase in the 1715 cm^{-1} region.

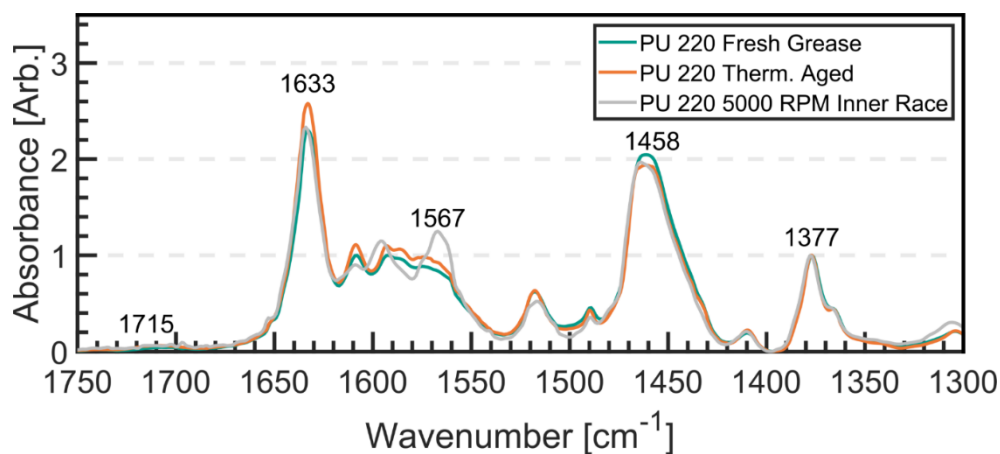


Figure 4.49: FTIR spectra of the PU 220 fresh grease, thermally aged sample and 5,000 RPM raceway film.

These bench methods of producing thermal and shear degradation in greases have largely been successful in reproducing the changes observed in samples taken from the inner races of bearings. Thermal degradation was not seen to great extent in most bearing samples, but the CaXB 100 grease which did experience severe oxidation did so to a greater extent in the bench test. Shear degradation appears to be a difficult process to reproduce, particularly for large volumes of grease.

The ball homogeniser, which provides extreme shear stress by crushing the lubricant between steel balls, was the more successful of the bench methods, appearing to induce at least some of the same IR changes as the bearing sample in every grease. The roll stability tester, which is widely used as a means of shearing greases to assess their resistance to loss of consistency, was less effective in creating the same changes to the thickener structure, as assessed by IR analysis. This is likely to be a consequence of the completeness of the shear degradation, with the ball homogeniser destroying the thickener by crushing and intense shearing as might occur in the ball-raceway contact, whereas the roll stability tester produces less intense shear and likely degrades the thickener by breaking down larger particulates. This is supported by observations by Renshaw, who noted that a lithium grease subjected to different shearing conditions appeared to undergo different changes to the fibre structure [195]. The fact that the ball homogeniser better replicates the inner race degradation suggests that a significant

proportion of the thickener within the active lubricant may be as free molecules or extremely small particles after crushing, rather than solely the larger fibre fragments that are also observed.

4.10 CONCLUSIONS

This chapter has described an analysis of the raceway lubricant films of a set of grease-lubricated bearings operating under realistic conditions in an effort to understand how fresh grease is degraded by shear and thermal effects. This has involved observing the distribution of the lubricant film under microscope, as well as analysing the chemical composition of the lubricant using FTIR. The small range of greases were chosen to represent the most common thickener systems in use, and allow conclusions to be drawn about grease lubrication of bearings in general, rather than specific mechanisms of thickener types.

On dismantling, the bearings showed a similar distribution of relatively fresh grease on the shields, more fluid lubricant in the raceways and cage pockets, and grease that appeared hard and dry attached to the cage. The infrared analysis suggests that under normal operation, most greases develop an oil-rich lubricant in the raceway as oil is released from the grease elsewhere in the bearing, likely aided by shear degradation. This is in agreement with much published work. Not all of the greases showed this effect, the PU 220 did not reduce in thickener content at either test speed. This could mean that polyurea greases undergo a modified lubrication mechanism, in which they resist shear-induced oil bleeding. The observed thickener-rich film could also be influencing the thickener-content measurements and may be integral to the performance of polyurea greases. The CaXB 100 grease failed in the support bearings at 10,000 RPM, appearing to never achieve effective ‘channelling’ and experiencing high temperatures as a result.

The IR analysis has also shown that all greases undergo changes in the IR bonds associated with the thickener, theorised to be a result of shear degradation changing the intermolecular bond environment such as the prevalence of hydrogen bonding. These changes vary depending on thickener type, but appear to be shared within that type, with both lithium-based greases displaying very similar changes.

To establish whether these changes can be confidently attributed to shear degradation, shearing of the grease samples was attempted in bench procedures, as well as thermal aging in long-term oven tests. The two shearing methods employed showed very different results for certain greases, suggesting the shearing process and the resulting intermolecular forces experience by the thickener are closely linked. The more intense shearing process appeared to be closest to the shearing at the inner race, implying physical crushing and extreme shear stresses are necessary to closely reproduce bearing shear degradation. The limited oxidation seen in most greases was also observed under long-term thermal aging, while the CaXB 100 grease which experienced severe oxidation in the bearing test did so also during the oven aging.

5 EFFECTS OF SHEAR AND THERMAL DEGRADATION ON GREASE RHEOLOGY AND LUBRICATION PROPERTIES

This chapter presents the results of rheological and tribological testing of greases that have been shear and thermally degraded in a manner representative of the processes that occur in bearings. These results are compared to fresh greases, aiming to identify the ways in which the testing of fresh greases may fail to truly represent grease lubrication in bearings.

The rolled tracks of the MTM friction testing device are analysed with IR spectroscopy and compared to the raceways of bearings, allowing assessment of the extent of degradation that occurs during ball-on-disc testing.

It has been established in the previous chapter that there is significant shear degradation of the working lubricant in bearings operating under relatively normal conditions. Thermal oxidation was not found to a significant extent in most greases analysed, but is known to occur in bearings operated at elevated temperatures [136] which are strongly negatively associated with grease life [82]. It is necessary to understand how these forms of degradation affect the lubrication properties of the grease, specifically those that influence bearing performance in life and efficiency.

The rheological properties of a set of greases were measured, including the fresh greases, samples that had been sheared for 168 hours in a roll-stability test machine, and samples that had been thermally aged in an oven for 840 hours at 100 °C. These greases include those that were analysed in the bearing tests of the previous chapter, as well as some additional greases. These tests were aimed at assessing the contribution of the thickener to solid-like behaviour, with the expectation that a reduced solid rheology would contribute to improved resistance to starvation. The term ‘solid rheology’ here is used to describe not only the yield stress, but also other properties such as the storage modulus, representing stiffness of the grease, discussed in detail in Chapter 3.

In addition to rheological testing, the tribological performance of these greases and their base oils was assessed. The MTM was used to measure traction in a rolling ball-on-disc contact

and the EHD rig was used to measure film thickness in a very similar ball-on-disc configuration. These metrics in a bearing have a direct influence on efficiency and time-to-failure, and it is therefore essential to attempt to understand how they can change when the grease degrades while operating in a bearing.

The test greases are shown below in Table 5.1. In addition to the four greases subjected to bearing tests in the previous chapter, two additional greases are included in these bench tests. The LiB 100 grease uses the same base oil and thickener system as the Li 100 grease but does not contain additives and underwent entirely separate production, making the properties of the two greases align only slightly. The CaX 100 grease is an additised version of the CaXB 100 grease, originating from the same production batch, with additives included post-manufacture.

Abbreviation	Thickener	Base Oil Viscosity at 40°C [cSt]	Additised	Sheared 168 hrs	Thermally Aged 840 hrs
Li 100	Lithium 12-Hydroxystearate	100	Yes	Yes	Yes
LiB 100	Lithium 12-Hydroxystearate	100	No	Yes	Yes
CaXB 100	Calcium complex	100	No	Yes	Yes
CaX 100	Calcium complex	100	Yes	No	Yes
PU 220	MDI diurea	220	Yes	Yes	Yes
LiXB 220	Lithium complex	220	No	Yes	Yes

Table 5.1: Properties of the test greases.

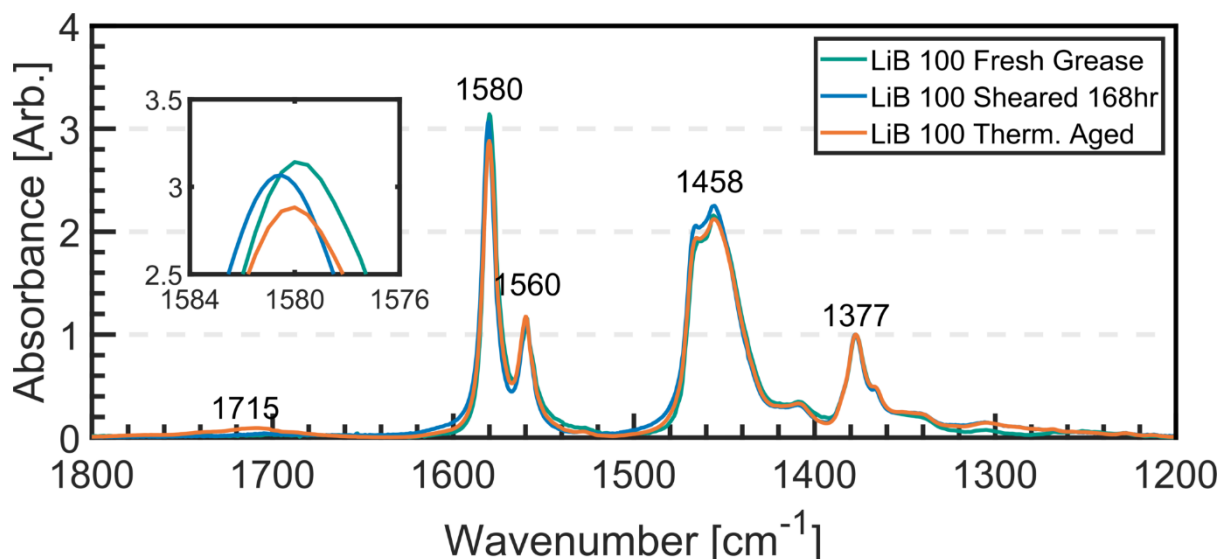


Figure 5.1: FTIR spectra of the LiB 100 fresh grease, sheared and thermally aged samples.

The infrared effects of the thermal aging and shearing of the LiB 100 grease are shown in Figure 5.1. There are few obvious differences between any of the samples, with the small changes in peak heights of the 1580 cm^{-1} band likely to be measurement error rather than a real change in thickener content. The position of this peak does appear to shift slightly upon shearing, as was observed in the Li 100 and LiXB 220 greases, though to a smaller extent. Another subtle change is the slight increase of the 1715 cm^{-1} peak in the thermally aged sample, indicating a small amount of oxidation.

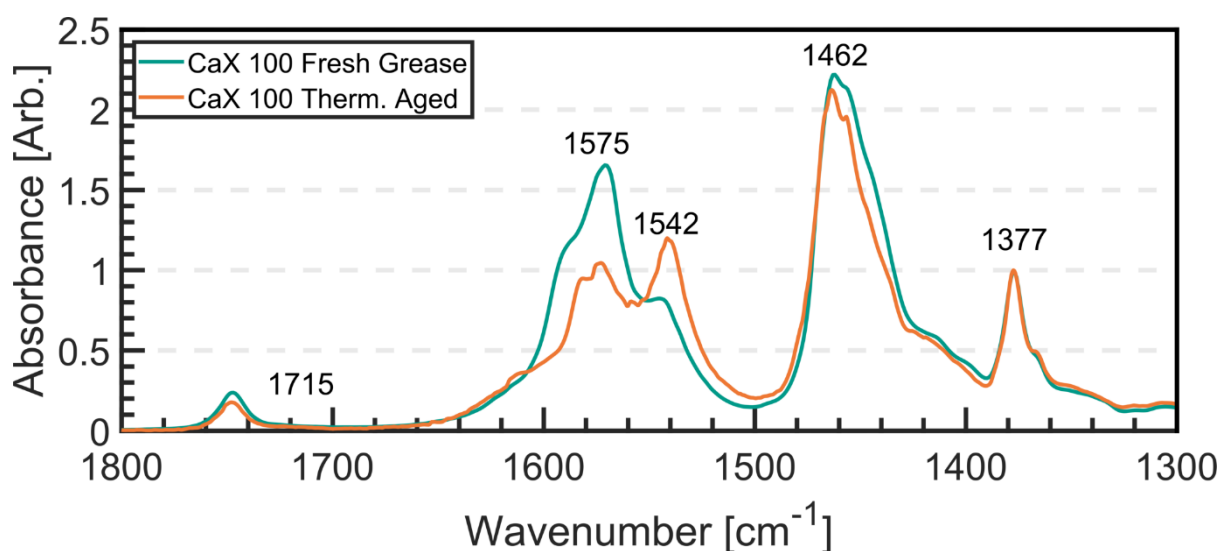


Figure 5.2: FTIR spectra of the CaX 100 fresh grease and thermally aged sample.

As shearing was not performed on the CaX 100 sample, Figure 5.2 shows the fresh grease compared to the thermally aged sample. The thickener region is very different to the CaXB

100 grease, with a much larger 1575 cm^{-1} peak, and reduced 1542 cm^{-1} peak. In fact, upon thermal aging, the grease appears to resemble the base grease and its sheared sample much more. It is therefore possible that both greases constitute an unstable thickener structure in their fresh state, which is able to radically alter upon heating or shearing to a common, more stable, structure. The peak at 1750 cm^{-1} which appears to reduce upon thermal aging may be due to an antioxidant which is partially consumed over the long-term test.

5.1 EFFECT OF DEGRADATION ON RHEOLOGY

Thermal and shear degradation can cause changes to grease rheology that may then influence tribological characteristics such as film-forming ability. An increase in solid-like rheology may reduce the resistance to starvation at high speeds which could cause bearing failure. Alternatively, reduction in the yield stress may lead to grease leaking from the bearing and starvation due to insufficient lubricant. The test greases and their degraded samples were tested according to the oscillation method specified in Chapter 3. This involved subjecting the grease to oscillatory stress which increased over time, eventually reaching a point where the thickener structure no longer responded elastically but began to behave with more viscous characteristics. These results are presented here.

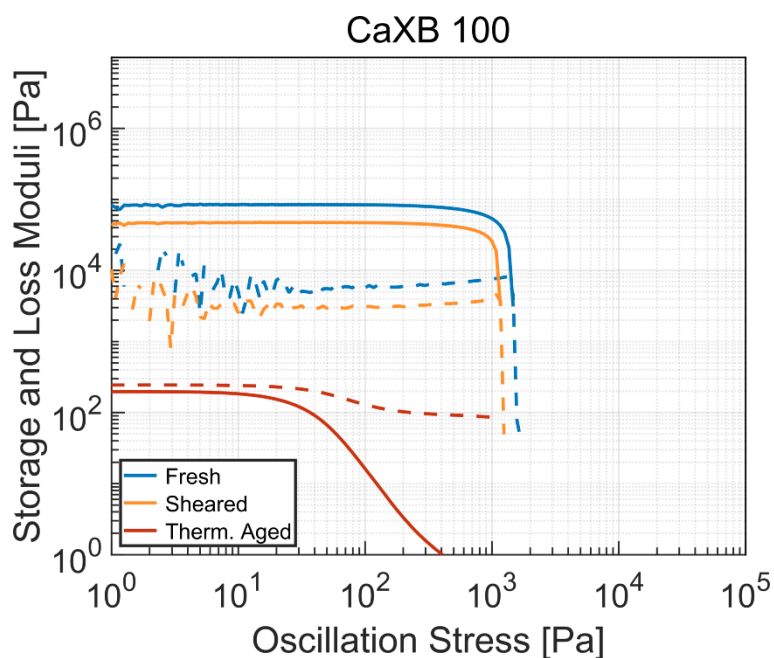


Figure 5.3: Storage and loss moduli for the CaXB 100 grease, comparing the fresh samples to the sheared and thermally aged samples. Storage modulus shown with solid lines and loss modulus shown with dashed lines.

Figure 5.3 shows the storage and loss moduli for the CaXB 100 grease. These metrics are discussed in Chapter 3, the storage modulus being a measure of the elastic or solid behaviour of the sample, while the loss modulus is a measure of the viscous or fluid behaviour. The plot shows the characteristic shear-thinning property of greases, with storage and loss modulus of the fresh grease reducing sharply at a stress of just over 1000 Pa. The storage modulus is significantly larger than the loss modulus (shown in dashed lines) for the fresh grease at low shear stress, implying a solid rheology. Once the 'yield stress' has been reached and both storage and loss moduli fall, the grease behaves more like the base oil, and the storage and loss moduli cross over. It is at this point that the yield stress can be reliably defined.

The large amount of noise in the data at low stresses, particularly for the loss modulus, is a consequence of the low stress and relatively stiff grease deforming very little, producing a low signal-to-noise ratio. As stress increases, the signal-to-noise ratio improves. The oscillations increase in stress and consequently strain, particularly once the yield stress is reached. The tests were stopped not long after this point as large strains tend to pull grease out from within the gap in the rheometer test geometries, leading to erroneously low stress measurements.

In comparison to the fresh grease, the sheared CaXB 100 sample has lower storage and loss moduli in the linear viscoelastic region (LVE region). In this region the oscillation stress is too small to break the forces between thickener particles and the thickener network is being elastically deformed. The storage modulus in this region is therefore a measure of the stiffness of this matrix. The yield stress has also been significantly reduced.

The thermally aged sample has also reduced in loss and storage moduli, however the reduction is extreme, reducing by approximately 400 times. Clearly the severe oxidation of the thickener found in the previous chapter has caused a loss of consistency. In fact, unlike the fresh grease, the loss modulus is now larger than the storage modulus, implying largely fluid behaviour at low stresses. This also means, by the definition used in this work, there is no yield stress as the two moduli do not cross. Not only has the grease lost the shear-thinning property provided by the thickener, but the viscosity at higher shear stress is far higher than the fresh, indicated by the loss modulus not reducing significantly as shear stress increases,

and appearing to intersect and continue beyond the loss moduli of the fresh and sheared samples.

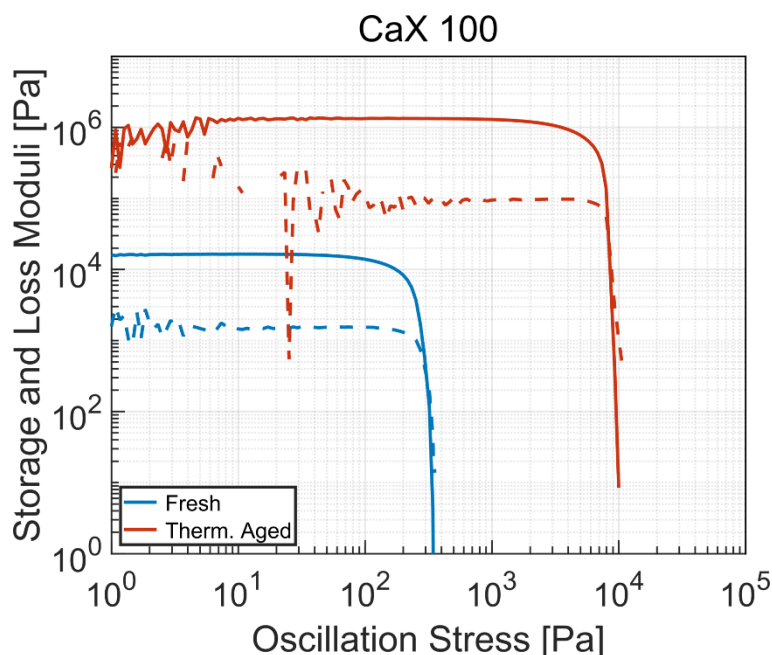


Figure 5.4: Storage and loss moduli for the CaX 100 grease fresh and thermally aged samples. Storage modulus shown with solid lines and loss modulus shown with dashed lines.

The rheometry results for the CaX 100 grease are shown in Figure 5.4, lacking a shear degraded sample as the other greases have. The base grease has a significantly higher storage modulus in the LVE region, as well as a higher yield stress. The loss modulus has also reduced due to inclusion of additives, demonstrating that at low shear stress, the dominant loss mechanism is due to the thickener rather than the base oil which has not been altered. Considering that this grease and the CaXB 100 grease have the same thickener and base oil and differ only in additive content, the difference between the rheology of the fresh greases is somewhat surprising, though the literature suggests a reduction in consistency is to be expected. Work comparing base greases and a sample containing the antioxidant antimony dithiocarbamate has shown a looser thickener structure in the additised grease [135], and a comparison of various additives in Li and LiX greases has shown they generally reduce consistency [215]. However, the exact effect of different combinations of thickener and additive cannot easily be predicted. The thickener interaction is likely to change as a result of the additives, which can be understood when considering the generally highly polar nature of many additives. In order to react or adhere to the contacting metal surfaces, many classes

of additive have an ionic head and an oleophilic tail [61], which is very likely to interfere with the similar, surfactant-like, thickener.

The presence of additives has clearly prevented the loss of consistency seen in the base grease, either via prevention of oxidation by antioxidants, or potentially by a stabilisation of the thickener due to the additive-thickener interactions mentioned above. Rather than a reduction in solid rheology, the opposite has occurred, with a drastic increase in storage modulus of approximately two orders of magnitude and associated increase in yield stress. This significant change is suggestive of a major transformation in the thickener-thickener interactions, with a great increase in hydrogen bonding or formation of a stiffer thickener structure. The FTIR results in Figure 5.2 suggest a drastic change in the carboxylate bonds upon aging, reaching a state that more closely resembles the CaXB 100 grease. The additives were mixed into the grease in a high-speed mixer post-manufacture at room temperature, and therefore had not been exposed to the thickener at high temperature until this aging step. The solid thickener may have resisted changing under the influence of the polar additives while at room temperature, but was able to interact and reorder during thermal aging, forming a stronger structure.

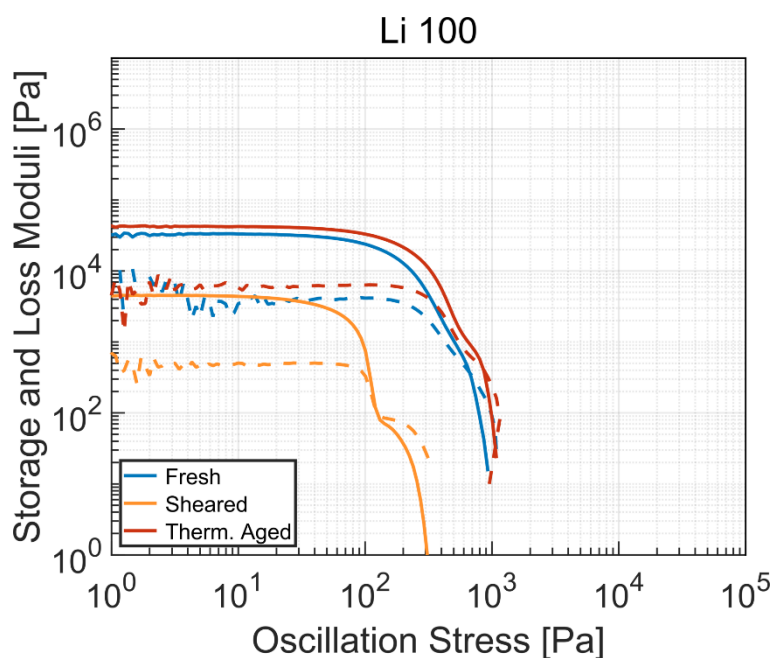


Figure 5.5: Fresh, sheared and thermally aged rheometry results for the Li 100 grease. Storage modulus shown with solid lines and loss modulus shown with dashed lines.

Figure 5.5 shows storage and loss moduli of the Li 100 samples. In comparison to the CaX greases, the Li 100 fresh sample appears very similar to the additised CaX, with similar storage modulus and yield stress values. Where it does differ is in the manner of yielding. Both CaX greases yield suddenly, with a sharp decrease in storage and loss moduli, whereas the Li 100 grease decays more gradually. In simple terms, this suggests a less-sudden breaking of the thickener interactions. This could be due to a wider distribution of particle sizes, with shorter particles breaking contact earlier while longer ones withstand larger stresses before separating. Alternatively, particle shape could play a role. Lithium greases are known to have thickener fibres which might slide over one another under increasing strain, retaining an elastic resistance. CaX greases can also have fibres but are sometimes described as having a 'foam-like' structure [84] which implies a different failure under shear.

As with the CaXB 100 grease, the sheared Li 100 sample shows lower storage modulus and yield stress than fresh, but also has a slightly different behaviour at the yield point, yielding more suddenly. If the particle size has been reduced by shearing then the particle size distribution may now be narrower, preventing the longer fibres from continuing to resist shear when the shorter ones have already been sheared apart. The thermally aged sample is relatively unchanged in comparison to the fresh. Only a slight increase in storage and loss moduli, with a corresponding increase in yield stress. As this grease contains additives including antioxidants this is not surprising. Volatile loss over the long-term aging may explain the increase in stiffness and loss modulus. The IR results for this aged grease, shown in Figure 4.46 on page 145, do show an increase in intensity of the thickener peaks around 1580 cm^{-1} which suggests an increase in concentration relative to the base oil.

Interestingly, around the yielding point there appears to be a second region where storage and loss module are approximately constant. They do not cross so there is no second yield point by the definition used in this work, however, there has been research into 'two-step' yielding [216], [217] which suggests this behaviour is explained by two mechanisms of yield. The initial yield appears as a rupture of the solid network, while the second appears when the individual particles break apart. How these dual mechanisms manifest in a thickener network composed of fibres is unclear, but it could be a similar process of fibre bundles

separating, then decomposing into fibres, or fibres themselves separating, then fracturing. The fact that this effect is more pronounced in the sheared sample, which is likely to have fewer fibre bundles as they would be pulled apart under shear, suggests it is the latter explanation. Regardless, this behaviour occurs over a very narrow stress range and does not appear to significantly effect properties above or below this range, making it unlikely to affect lubrication behaviour.

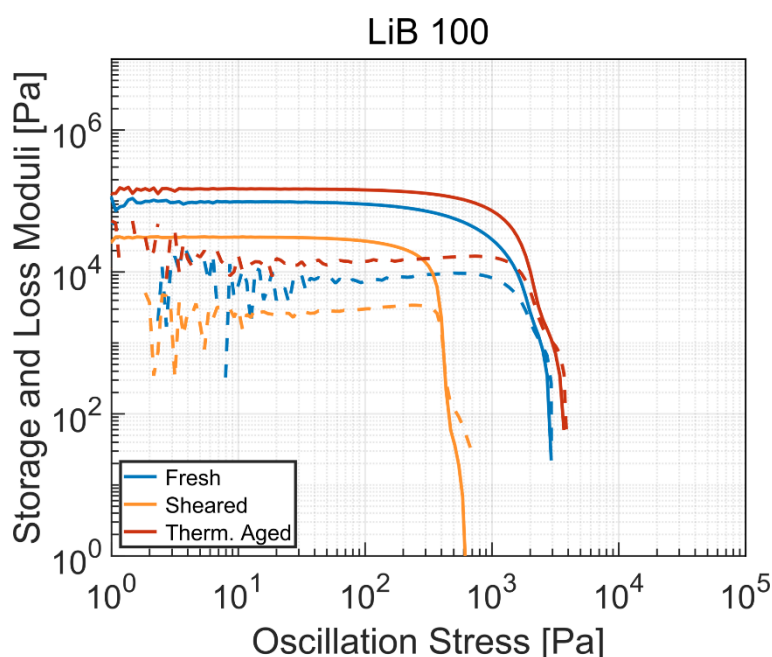


Figure 5.6: Rheometry results for the fresh LiB 100 grease and its sheared and thermally aged samples. Storage modulus shown with solid lines and loss modulus shown with dashed lines.

The LiB 100 grease displays very similar behaviour to the Li 100 grease, though with slightly higher storage and loss moduli and significantly higher yield stress. The effect of shear degradation is similar, lowering stiffness and yield stress while also causing yield to occur over a narrower stress range. Thermal aging has increased storage modulus and yield stress to a greater degree than seen in the Li 100 grease, though the change is relatively small compared to the change caused by shearing. It may be the lack of antioxidant that has meant greater numbers of oxidised reaction products now alter thickener interactions.

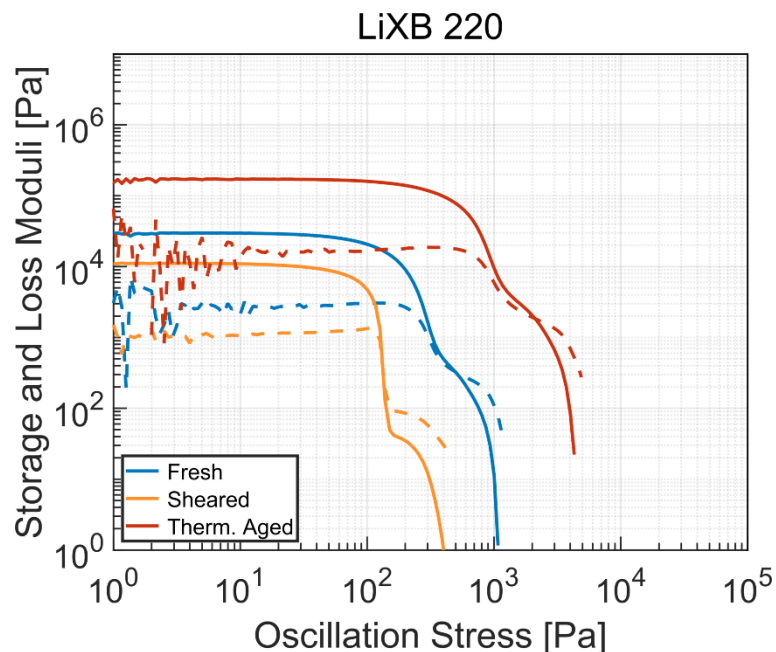


Figure 5.7: Storage and loss modulus for the LiXB 220 grease and shear and thermally degraded samples. Storage modulus shown with solid lines and loss modulus shown with dashed lines.

The LiXB 220 fresh grease appears to be very similar to the Li 100 fresh grease in absolute values of storage and loss moduli and yield stress, but also in the way these values change with shear stress. Where they differ is in the response to shear and thermal degradation. Shear degradation has reduced these values but to a lesser degree than the previous two lithium greases, while thermal degradation has increased these rheological metrics by a much larger degree. The additised lithium grease showed the least change with thermal aging which can be understood as a consequence of less oxidation. The increased numbers of oxidation products which are more polar and potentially can contribute greater intermolecular interactions through hydrogen bonding will cause stiffening of the thickener structure, assuming total breakdown does not occur as in the CaXB 100 grease. It is not clear why the complex grease showed a larger change, though this grease appeared to have a greater thickener content than the other lithium greases in the previous chapter, which would presumably increase shear stability but also amplify any increase in thickener interaction.

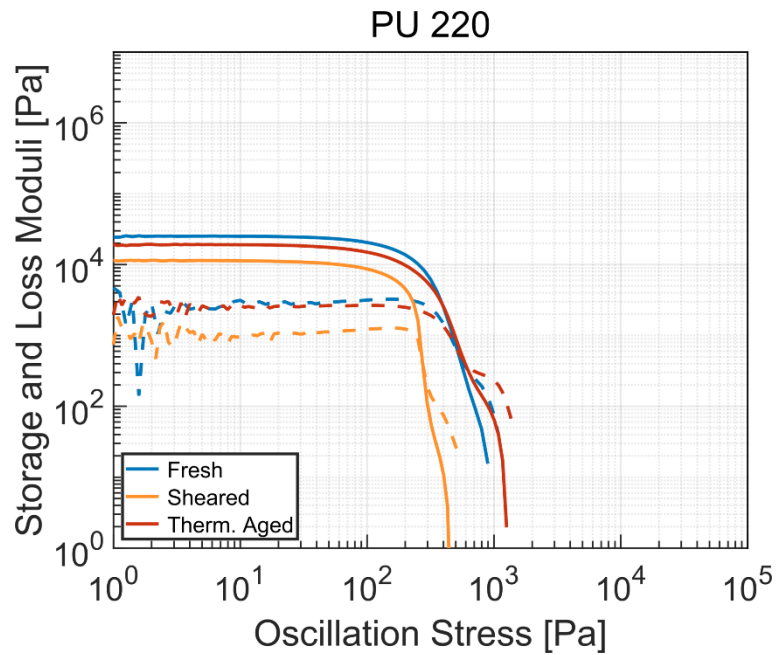


Figure 5.8: Rheological results for the PU 220 fresh, sheared and thermally aged samples. Storage modulus shown with solid lines and loss modulus shown with dashed lines.

The polyurea grease, PU 220, shows relatively little change in rheology due to shearing, though still a halving of the storage modulus. In similar fashion to the other greases, the yielding of the sheared grease occurs more suddenly, in fact beginning at a similar stress to the fresh grease, but yielding completely at a much lower stress. It is notable that other definitions of yield stress might show no change due to shearing. Of more interest, however, is the thermally aged grease which, rather than increase in storage modulus, has decreased. This is despite the yield stress marginally increasing. Physically this means the grease is less stiff at low shear stress but yields at roughly the same stress. As previously discussed, the yield stress is likely to be the more important factor when it comes to resistance to starvation, so this grease may be unaffected in that regard by thermal degradation. Polyurea greases are known for their suitability for high-temperature operation, often explained as due to inherent antioxidant properties [5], [43], though these results tentatively suggest an additional factor. Thermal aging has appeared to almost universally increase yield stress of the test greases which would reduce lubricant reflow under the various forces that act to do so. If this grease is characteristic of other polyureas, performance at high temperature may be, in part, due to this resistance to temperature-induced reflow reduction.

Discussion

It is premature to draw firm conclusions about rheological changes of specific grease types as a result of shear or thermal degradation. These results can be cautiously interpreted in this manner, but a more complete test matrix of greases should be examined to investigate specific changes due to degradation. Instead, these results serve to demonstrate clearly that most grease thickener types (specifically all of those tested here which covers the majority of grease thickeners in use) will undergo significant rheological changes upon the shear and/or thermal degradation that is likely to take place in bearings.

Figure 5.9 presents the yield stresses, as defined by the crossover point of storage and loss moduli, of all the grease samples. This method of estimating yield stress has been criticised as being an overestimate, marking the point where viscous losses dominate, but where flow is already occurring [103]. It is, however, a method that is simply defined and easy to implement, not relying on a subjective definition. It is therefore useful as a comparative measure but less useful in direct application. As the CaXB 100 thermally aged sample showed loss modulus greater than storage modulus consistently, it did not have a defined yield point.

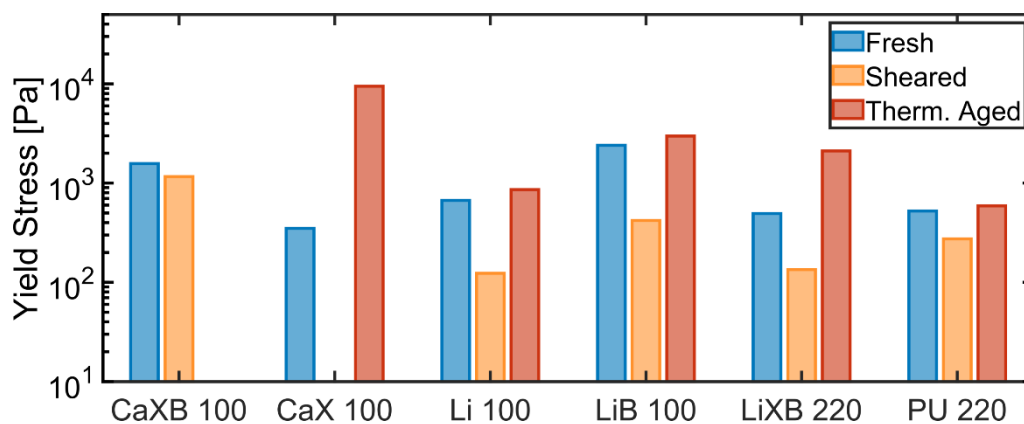


Figure 5.9: Yield stresses of the fresh, sheared and thermally aged samples of each grease. The CaXB 100 thermally aged sample did not have a defined yield point, and no sheared sample of the CaX 100 grease was available.

Shearing has universally decreased the solid rheology of these greases, specifically the storage modulus in the LVE region and the yield stress. These properties are likely to control the ability of a grease to flow back to the contact after being displaced, and therefore the extent of starvation at higher bearing speeds. Experimental work has shown the consistency (and, therefore, yield stress) of a grease to negatively correlate with film thickness in a bearing [14], likely due to a reduction in reflow rate. Rheological analyses of shear-degraded grease

rheology in the literature has found a reduction in consistency [105], suggested to be a direct result of the breakdown of thickener particles [134]. These two changes will practically mean that the grease will deform to a greater extent under stresses exerted on it and also will begin to flow under lower stresses, leading to higher film thicknesses under starved conditions. The latter is likely to be more important in bearing lubrication, controlling whether a grease flows under centrifugal force at the shields or capillary forces adjacent to the contact, with Zhou et al. finding that shear-degraded grease provided thicker films in a bearing test rig [14]. The authors also note that shear degradation increases the oil bleed rate, also acting to maintain film thickness under starved conditions.

The opposite effect was generally observed for thermal aging of greases in this work. Thermal aging tended to increase these rheological metrics, though two greases deviated from this trend. The CaX 100 grease appeared to undergo a complete destruction of thickener, losing the yield stress entirely, and is therefore a specific exception and should be considered separately. The PU 220 grease underwent no significant change due to thermal aging, while the extent of aging of the other greases varied greatly.

Rheological analyses of thermally-aged greases in the literature generally report a reduction in yield stress/solid-like rheology [105], [165] with Couronne finding a reduction in yield stress for Li and LiX greases, but an increase for polyurea greases [218]. The majority of the tests cited involved aging at 120°C. One explanation for the increased yield stresses in this work is that the majority of these greases contained antioxidants and therefore experienced limited oxidation, shown in the FTIR spectra of the thermally aged greases in the previous chapter, as well as in the introduction to this chapter. Changes in rheology must be caused by other mechanisms then, possibly the reconfiguring of thickener molecules into more cohesive structures. Salomonsson observed thickener agglomerating into thicker, shorter, fibres after thermal aging [53], demonstrating that continued restructuring of these fibres is possible, potentially allowing greater interaction than the initial case. Additionally, the increased viscosity caused by loss of volatile base oil molecules will have a large effect over long aging times, with many researchers opting to seal the samples to prevent this, removing this yield-stress-increasing effect [105]. The thermally aged IR spectra presented in section

4.9.2 on page 145 generally show an increase in relative thickener content, most likely due to volatile loss.

The changes due to degradation were, in some cases, larger than the variation between greases. This has the obvious implication that care in selecting a particular grease for an application based on its properties while fresh may be misguided if the degradation it is likely to experience alters these properties beyond those of other candidate greases.

As the shear degradation experienced by these grease samples appears to be milder than that experienced in bearings after 100 hours at 5000 RPM, yet has caused such large changes, we can conclude that these are underestimates of the rheological changes likely to occur in the ‘working’ lubricant on a bearing raceway. Similarly, the thermal aging of 860 hours at 100°C is a fraction of many bearings’ expected lifetimes, and this temperature is typical of many applications, though on the higher end of the wide range of operating conditions bearings are used in.

With these changes quantified, it is possible to analyse the changes in tribological properties that are critical to a bearing’s performance in energy efficiency and lifetime and attempt to explain these changes in terms of rheology. The rheological findings would suggest that the sheared greases would better resist starvation compared to the fresh, and the thermally aged samples would experience greater starvation/an earlier onset of starvation.

The caveat of this analysis is that the shear rates and shear stresses achievable in a rheometer are several orders of magnitude below those experience in an EHD contact inlet. The LVE region simply does not appear in the vicinity of the contact, though it is dominating in other areas of the bearing. It is in starvation that the rheological metrics discussed here have greatest influence, as starvation is dominated by the quantity of lubricant that is able to flow from areas outside of the contact vicinity in towards the inlet.

5.2 EFFECT OF DEGRADATION ON TRIBOLOGICAL PERFORMANCE

The tribological properties of film-forming ability and contact friction are of great importance for a lubricant and while they are studied in depth for fresh lubricants, the degraded lubricant

that operates in a bearing contact must also be understood. In particular, it is necessary to understand how these properties change with degradation.

5.2.1 EHD – Film Thickness Under Fully Flooded Conditions

The film thickness testing that is described in detail in Chapter 3 produces results such as those shown in Figure 5.10. Nine data points are produced at each speed value as the film thickness can vary drastically, particularly at low speeds or with intermittent starvation. Figure 5.10 shows this variation of film thickness for the CaXB 100 grease at low speeds, tending to reduce at higher speeds. Also shown is a point of intermittent starvation at around 0.2 ms^{-1} at 40°C . The information provided by plotting the raw data points can also be shown effectively with a shaded confidence interval, while reducing the clutter and allowing easier comparison with other results. Figure 5.10 shows the 99% confidence interval for the grease at both test temperatures, 40°C and 80°C . The shaded region at each speed value represents a range of film thickness values that contains the true mean to a 99% probability. As the confidence interval is directly proportional to the variance of the data set, it is also a useful indicator of variance. Also shown is the same data without the scatter plot for clarity.

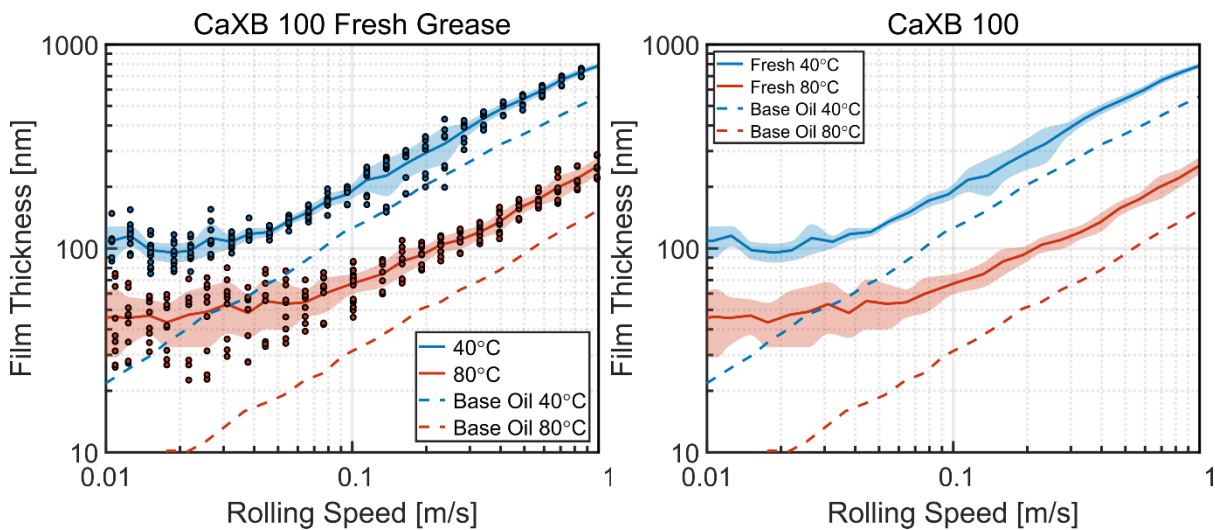


Figure 5.10: CaXB fresh grease film thickness at 40°C and 80°C , showing 99% confidence interval and individual data points.

Figure 5.11 shows the film thickness results for the sheared sample, compared to fresh. The film thickness of the base oil is shown with dashed lines. While the base oil film thickness increases with speed in accordance with the power law correlation, the fresh grease shows very different behaviour. At low speeds, the film thickness forms a plateau region, relatively

constant with speed. At higher speeds the film thickness tends towards behaviour like that of the base oil, shifted however, to much higher film thickness values. This may be due to a continuing effect of viscosity increase created by the thickener, as greases are known to provide [51], [219], but also should be considered as a consequence of experimental error in controlling temperature, discussed in Chapter 3. It is impossible to seat the rolling element in a bath of temperature-controlled grease as is done for oil testing, making it much more difficult to accurately control the temperature of the test grease which strongly influences viscosity and, as a consequence, film thickness.

At the lower temperature, the variance of the film thickness is relatively low, especially at the highest speed. At 80°C however, the variance is much higher, particularly at the low speed. The gain of film thickness over the base oil is proportionally much higher at the higher temperature. This phenomenon of high film-thickness at low speed has been well-described in the literature [85], [173], [209] and is sometimes termed the ‘thickener effect’ [220], [221], a consequence of thickener lumps being entrained into the contact, both increasing absolute film thickness and film thickness variance due to the inhomogeneous nature of the thickener.

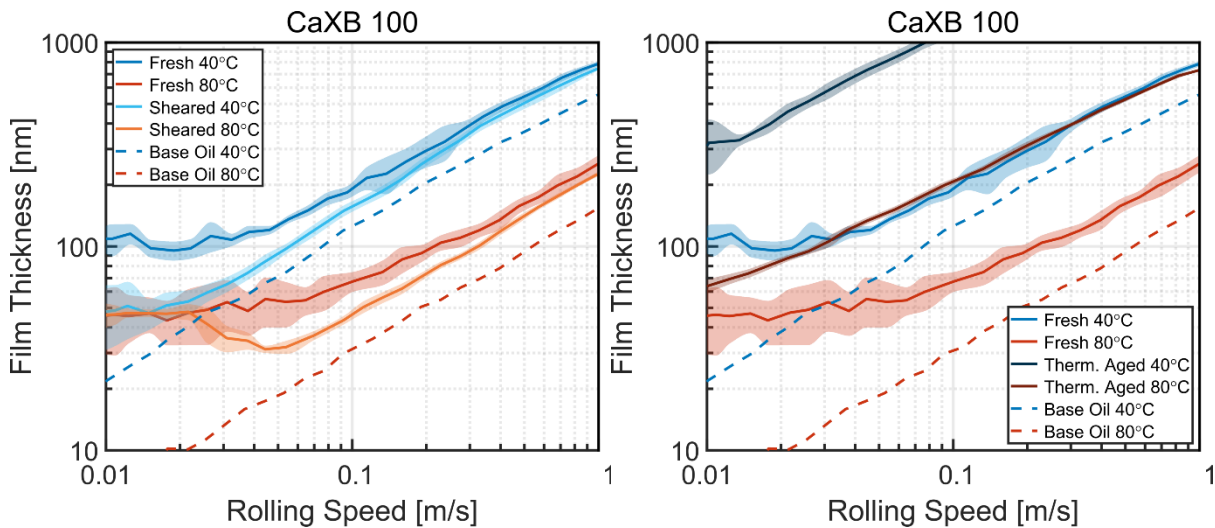


Figure 5.11: CaXB 100 film thickness plots showing results for the sheared sample, compared to fresh, as well as the thermally aged sample, compared to fresh.

Looking at the sheared sample in comparison to the fresh, it is clear that the ‘thickener effect’ has been reduced, particularly at the lower temperature and mid-speed range from approximately 0.03–0.5 ms⁻¹. The grease behaves much more like the base oil, deviating from the base oil line at a much lower speed. Despite this, the behaviour at high speed is still closer

to that of the fresh grease than the base oil, though has reduced, particularly for the higher temperature. This result also reduces the likelihood of poor temperature control being the dominant contribution to thicker grease films at high speed. If shearing, without removal of the thickener, is able to reduce the film thickness so much, it is possible that the discrepancy between base oil and grease at this speed can be largely explained by thickener content.

It is interesting to note that all samples except the fresh 40°C test have converged on the same film thickness value at the lowest speed. This suggests that the dominant effect at this particular speed is independent of shearing, perhaps due to a minimum thickener particle size that could be produced via shearing.

Figure 5.11 also shows the results for the thermally aged CaXB 100 sample. Clearly the oxidation described in the previous chapter has dramatically affected the film-forming properties of the grease. The film thickness for both samples has increased hugely due to a large increase in viscosity. In fact, the results at 80°C coincidentally match closely to those of the fresh grease at 40°C. Whether there is any display of the ‘thickener effect’ is impossible to say as the minimum film thickness may simply be too great to reveal this, however the rheological changes observed in this sample show a loss of yield stress which implies a loss of solid thickener.

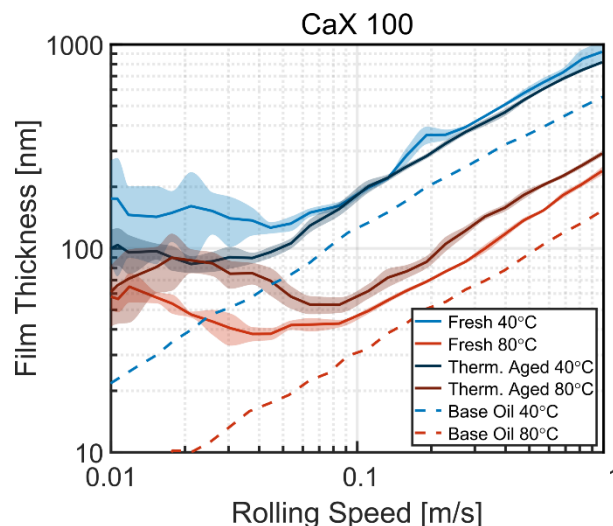


Figure 5.12: Film thickness results for the CaX 100 fresh grease and thermally aged sample.

The film thickness results for the additised version of this grease are shown in Figure 5.12. In comparison to CaXB 100, CaX 100 provides even higher film thickness at high speeds.

Additionally, while the base grease transitions smoothly between the oil-dominated higher speed region and the thickener-dominated low-speed region, the additised grease shows a marked increase in variance for the 40°C sample at 0.05 ms⁻¹. Rather than a constant film thickness value at low speed, the 80°C test reaches a minimum before increasing again. These differences are caused only by the presence of additives, suggesting that their interaction with the thickener can cause significant changes to tribological properties. The thermally aged CaX 100 sample does not show the dramatic increase in viscosity seen in the base grease, though significant changes are seen. The 80°C test shows higher film thickness at all speeds, while the 40°C sample shows the opposite, though to a far lesser extent. Both samples converge on a film thickness value of around 90 nm at low speeds. This could be a symptom of transitioning from a regime where viscosity-affected shear stress is controlling thickener entrainment and hence film thickness, to one where thickener entrainment is relatively constant, and it is thickener particle size that is now controlling film thickness.

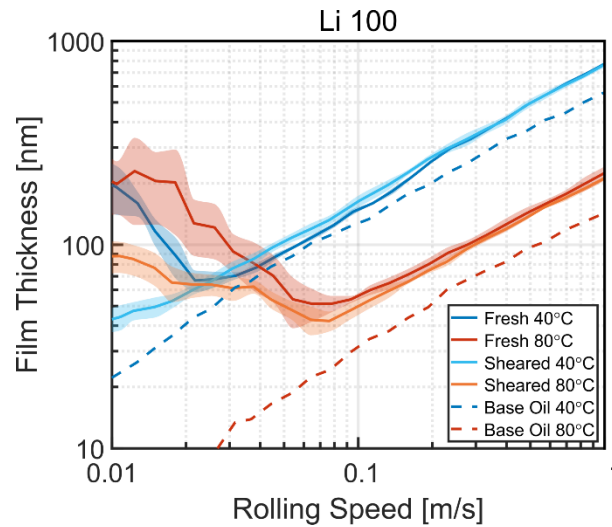


Figure 5.13: Film thickness results for the Li 100 fresh grease and sheared.

The Li 100 fresh grease, shown in Figure 5.13, shows a distinctive V-shaped curve at both temperatures, also seen by [222] in a range of lithium greases. This ‘inverse-Stribeck’ [209] behaviour directly counters the decreasing film thickness afforded by the base oil. This also coincides with a large increase in the variance at this point, indicating a relatively sudden change in lubricating mode.

In contrast to the previously shown greases, the 80°C test actually shows higher film thickness in the low-speed region. This is due to the crossover point between the lubrication modes occurring at a much higher speed, leading to a greater effect at the lowest speeds. The reason for this shift could be a complex rheological change as temperature increases, or more likely, an effect of the reduced viscosity of the base oil. A reduction in shear stress within the contact inlet that is provided by lowered viscosity may reduce the extent of thickener particle destruction, and consequently increase the size of particles that enter the contact.

The sheared sample shows a reduction in the ‘thickener effect’ as with previous greases, with the 40°C result now conforming quite closely to the power-law behaviour of base oils. At 80°C the effect remains but is greatly reduced, appearing more like a plateau than the steep-sided V-curve of the fresh grease. Given the shear degradation is likely to have destroyed many thickener particles and reduced their size, the reduction in film thickness at low speed can be understood simply as a result of fewer and smaller thickener particles entering the contact.

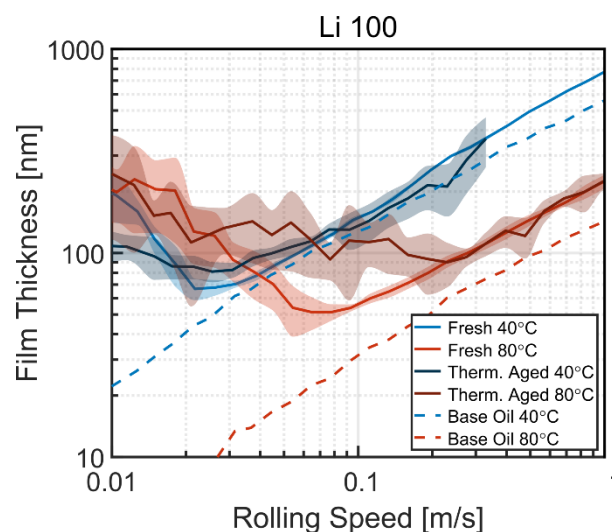


Figure 5.14: Film thickness of the thermally aged sample against rolling speed, compared to fresh grease.

The thermally aged Li 100 sample, shown in Figure 5.14, shows very different behaviour. Firstly, the film thickness variance is much higher across the speed range. For most of the speed range this is due to greater thickener particle entrainment but at high speed a significant factor was incipient starvation. As an ostensibly fully flooded test, this was avoided wherever possible, however, for some of the thermally aged greases at low temperature it was extremely difficult to maintain fully flooded conditions at all times. In fact,

the 40°C test of this grease was not possible to complete as starvation at the higher speeds was unavoidable. The 80°C sample was easier to manage as the reduced viscosity at this temperature aided reflow around the contact, and potentially also aided flow within the grease scoop itself. While the fresh grease gives a V-shaped curve, both the depth of the V and the height of the low-speed film thickness peak appear to have converged towards a more constant value of approximately 100 nm. Huang et al. [165] observed fibre destruction upon thermal aging and a reduction in fibre length, while Salomonsson et al. [53] observed fibres becoming shorter and thicker. These reduced particle sizes can explain the lower film thicknesses seen. The loss of volatiles over a long-term thermal aging will increase base oil viscosity and can be expected to increase film thickness across all speeds. These two effects could explain the more constant film thickness values, however the much larger variance, particularly at 80°C, suggests there is simply more thickener being entrained into the contact.

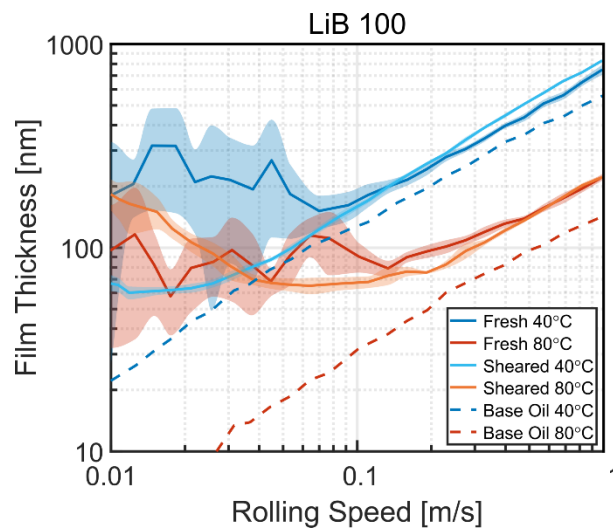


Figure 5.15: Film thickness of the fresh LiB 100 grease and the sheared sample.

The base lithium grease displays a very large variance at low speed, indicative of large thickener lumps entering the contact. Rather than the V-shaped curve of the additised grease, this grease appears to give a more constant but very high film thickness at low to medium speeds. When sheared, this variance reduces enormously, however the ‘thickener effect’ remains to some extent at 40°C, and at 80°C actually provides an increase over the fresh grease. This result contrasts with other grease behaviour; usually a reduction in thickener particle size causes a reduction in the film thickness when those particles enter the contact. It is clear, though, that the behaviour is now much more like that of the Li 100 grease, with an ‘inverse’

Stribeck region at low speed. As grease homogenisation can often initially increase consistency by separating clumps of thickener and allowing them to form a more effective thickener structure, it may be that the shearing of this grease has homogenised the thickener.

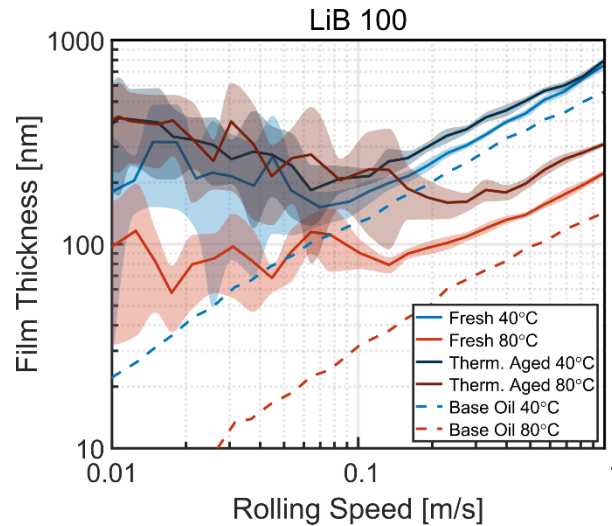


Figure 5.16: Film thickness of the thermally aged LiB 100 grease and the thermally aged sample.

The thermally aged LiB 100 sample has provided a roughly uniform increase in film thickness at all speeds. The effect is larger at 80°C than 40°C, and for much of the speed range the two temperatures are equivalent, providing thick films of around 250 nm at low speeds. The thermal degradation may cause agglomeration of thickener particles which consequently increases film thickness when they are entrained, though it is unclear why the effect is comparatively reduced for the fresh grease at 80°C.

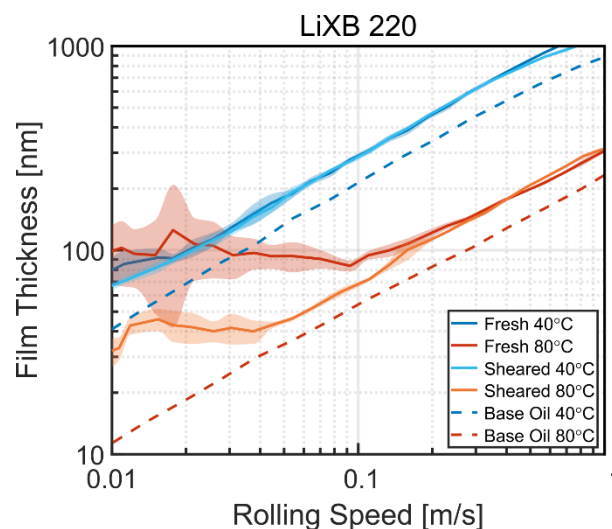


Figure 5.17: Film thickness results for the LiXB 220 fresh grease as well as the sheared sample.

While behaviour of the LiXB 220 grease at 80°C is quite typical, the film thickness at 40°C is unusual in that there is little thickener effect observed. This is simply due to the base oil viscosity which is high enough that the modest thickener effect for this grease is obscured by the already thick films. The change upon shearing the grease is therefore expected to be small, and indeed the sheared sample at 40°C differs very little to the fresh grease, behaving in a similar manner as a more viscous base oil. At 80°C, where the thickener effect is observed, the sheared sample does differ and shows a reduction in film thickness at low speed, as well as a reduction in film thickness variance.

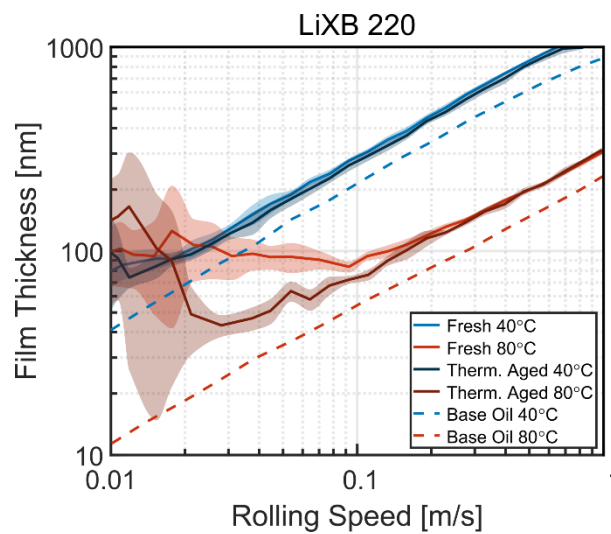


Figure 5.18: Film thickness for the LiXB 220 fresh grease and thermally aged sample.

The thermally aged samples of the LiXB 220 grease in fact appear to be very similar to the sheared samples. For this grease, the thickener effect reduces at low to medium speeds. At the very lowest speeds at 80°C, however, a sharp increase in film thickness indicates a sudden increase in entrained thickener particles. This may be the formation of a V-shaped curve as seen in other lithium-based greases, or a unique consequence of an unusual thickener particle size distribution that has developed on thermal aging.

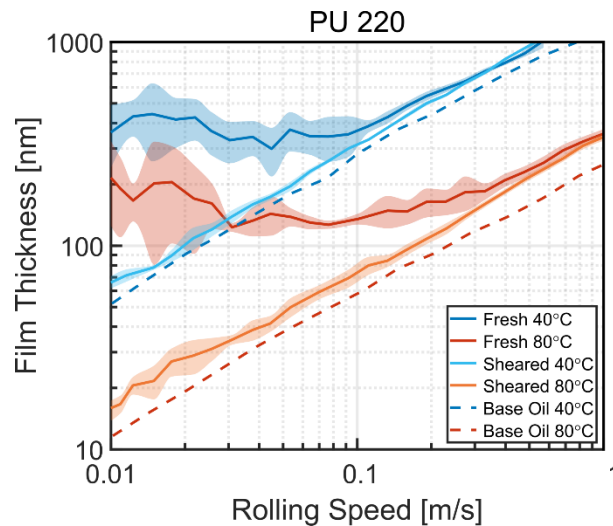


Figure 5.19: Film thickness results for the PU 220 fresh grease and sheared sample.

The polyurea grease is an extreme example of the thickener effect, not only large enough to appear at 40°C with the more viscous base oil, but rising to more than 10 times the film thickness of the base oil at the lowest speed at 80°C. Even at the higher temperature, when oil viscosity is at a minimum, the film thickness does not dip below the 100 nm level, perhaps due to an abundance of thickener particles which are of sufficient size to maintain this surface separation. The results of the sheared sample are very different, with the thickener effect vanishing entirely. This is surprising not only because it was so dominant an effect in the fresh grease, but the rheological results suggested the PU 220 grease was resistant to shear degradation. This is a clear demonstration that the behaviour in the LVE region (the region in which the rheometry tests were conducted), while clearly thickener-dominated, is not correlated with the thickener effect of high film thickness at low speeds. In the first case it is bulk rheology that is being examined, while the thickener film thickness effect appears to be due to individual thickener particle size. In some greases this may correlate with bulk properties as larger particles or fibres may interact with one another more strongly, but in others such as this one, the relationship is absent.

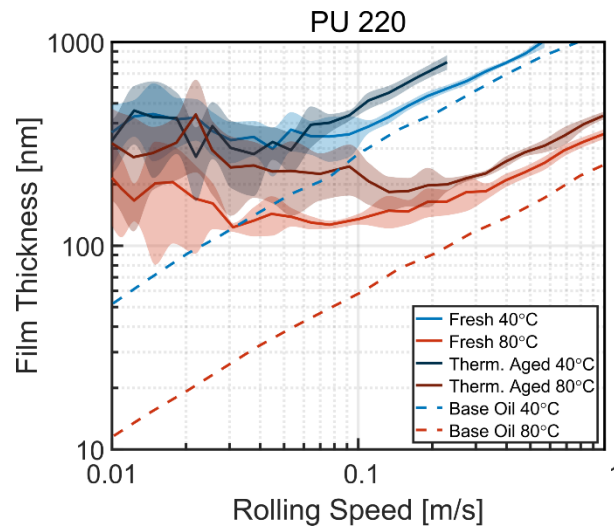


Figure 5.20: Film thickness for the PU 220 fresh grease and thermally aged sample.

The thermally aged sample of the PU 220 grease did not show drastic changes to rheology, like the sheared sample. In terms of EHD film thickness, however, this grease behaves in a similar manner to others, with an increase of film thickness across the speed range. The exception is at 40°C, where low speed film thickness does not increase. In fact, a maximum value appears to have been reached which does not increase upon thermal aging. This effect is quite similar to the LiB 100 thermally aged sample, where the fresh and thermally aged samples at 40°C and the thermally aged sample at 80°C all showed very similar film thickness at low temperature. In that case the difference was slightly larger than in the PU 220 grease which may be due to the lower base oil viscosity which reduced film thicknesses and provided more ‘headroom’ below the apparent film thickness maximum.

Summary of Fully-Flooded Film Thickness

The fully-flooded results shown here have demonstrated clearly that there are considerable changes to grease film thickness after both shearing and thermal aging. Shearing has generally decreased the extent of the thickener effect, likely a direct result of the decreased particle size observed after shearing [80], [89], [108], [134], [193], [195] as the effect is thought to be driven directly by particle entrainment [52]. Similar observations have been made by researchers analysing film thickness of shear degraded greases [52], [80], [173]. Another factor that may be involved in the reduction of this effect is the increased oil bleed observed in shear-degraded greases [14]. This will allow free oil to reflow, which may result in an active

lubricant that has a decreased thickener content and hence reduced thickener entrainment. The mixing effect of the grease scoop may prevent this, but it is not guaranteed. The increase in film thickness at low speeds seen with the LiB 100 grease at high temperature is unusual and also suggests that the size of the entrained particles is not the only factor in this effect. The shear-induced particle size reduction has not resulted in a loss of film thickness, but rather a smooth transition to a thick-film region, possibly because many more particles are now being entrained, even if they are smaller in size individually. In general, these shear-induced changes have correlated with the reduced yield stress observed in rheological testing, both stemming from destruction of the thickener structure.

Thermal aging has been shown to increase film thickness under starvation when accompanied by a decrease in consistency [165]. In this work thermal aging had a mixed effect on fully flooded film thickness, in some instances increasing it, while in others reducing it. The inability to maintain a fully-flooded state for the Li 100 and PU 220 thermally aged greases at 40°C is an important indicator that there is a resistance to flow, matching the increased yield stress seen after thermal aging. This did not coincide with the greatest increases in yield stress, however, suggesting the phenomenon is more complex than simply the stress at which the grease yields.

5.2.2 EHD – Film Thickness Under Starved Conditions

As the film thickness in a bearing is certainly not always fully flooded, and in fact may spend most of the bearing's life being limited by starvation, as suggested by Zhou [14], it is important to not only consider fully flooded results and attempt to allow starvation to influence film thickness. This is a difficult challenge, as starvation can be affected by many factors which may be in unique configuration in a bearing but are difficult to reproduce in a single ball-on-disc contact. The quantity of lubricant surrounding the contact, the forces upon it and the geometry of the contact are some of these factors which cannot be accurately reproduced. Nonetheless, the fully flooded film thickness results do not provide a full picture of the effects of degradation on film thickness in a bearing and therefore the set of greases were tested in a starvation mode.

The methods Chapter 3 describes this procedure in detail, but it is summarised here. All greases were tested under fully flooded conditions at 40°C, fresh grease was applied to the disc and the test was repeated at 80°C. After this, the rig was allowed to cool to 40°C and the grease scoop was removed, leaving a distribution of grease around the disc. Prior trial testing using freshly applied grease was highly variable and this allowed a more repeatable result. Speed was then increased, and a single data point taken at each speed value, rather than the three taken in fully flooded testing. This test procedure attempted to reduce the effect of time on the results, which is known to be a strong factor in starvation film thickness [221]. By testing after the ‘running-in’ period of the 80°C fully flooded test the reservoir of lubricant beside the contact was already established, and by reducing the time taken in each speed sweep, the difference between each sweep was intended to be reduced. Three sweeps from 0.01 ms⁻¹ to 1 ms⁻¹ were performed at 40°C, the cooler temperature selected to exacerbate starvation.

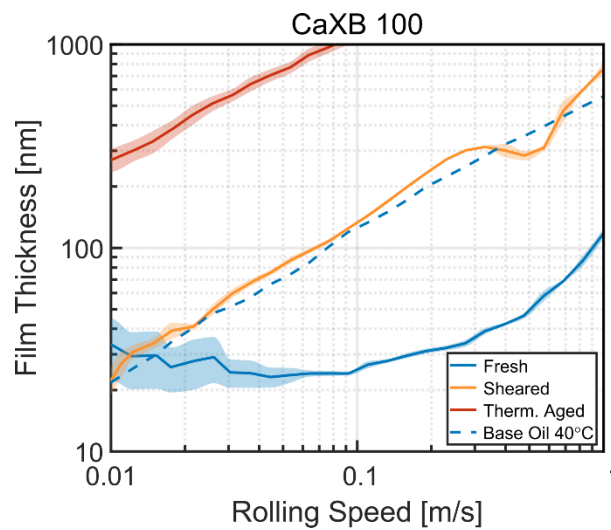


Figure 5.21: Film thickness of the CaXB 100 grease and degraded samples, under starved conditions.

The starved film thickness results for the CaXB 100 grease are shown in Figure 5.21, with the thermally degraded sample showing next to no change from fully flooded. As the rheometry showed, thermal aging of this grease caused a loss of yield stress which may have contributed to the reflow here, despite the obviously high viscosity. As film thickness achieved very high values before 0.1 ms⁻¹ and testing had to be halted at that point it is not possible to say conclusively that starvation was effectively resisted by this rheological change. The fresh grease starved result has changed significantly compared to fully flooded behaviour. Firstly,

the base level of film thickness is reduced compared to fully flooded which is a result of lubricant reflow now only occurring through passive means. Rather than channelling fresh, thickener-rich grease into the contact with the scoop, it is oil-rich lubricant that is likely to be preferentially reflowing [126]. Thickener particle sizes in this local region are likely to be smaller due to shear degradation after previous testing. This film thickness value of 20 – 30 nm remains roughly constant as rolling speed increases, with film thickness falling by approximately 75% relative to the level of the base oil. It is only at higher speed that a gradual increase of film thickness occurs. This is in contrast to most research, which shows that film thickness under starved conditions generally decreases with speed due to reduced time for lubricant reflow [15]. This effect has been observed in bench ball-on-disc film thickness tests, with Vengudusamy et al. suggested the higher speed is causing higher shear rates which degrade the grease and allow reflow [17], while Fischer et al. explain similar behaviour as a result of centrifugal force on the rotating disc [219]. In the ball-on-disc configuration the lubricant on the disc is subject to a centrifugal force which increases with the square of rotation or rolling speed. If the lubricant is able to yield under this force, it would provide a constant supply of lubricant to the contact in a specific way that is not present in most bearings. Even in thrust bearings, which would experience a similar force on lubricant in the raceway, this behaviour may exhaust lubricant supply in the centre of the bearing, rather than solely increase it. The smoothly increasing film thickness and low variance suggests a base-oil rich lubricant is reflowing, one that does not yield at a specific point but simply increases in flow rate.

The sheared CaXB 100 sample shows very different behaviour and is quite similar in behaviour to the fully flooded condition. The thickener effect is slightly reduced from the low level seen in fully-flooded conditions, likely for the reasons described above, and the grease provides a steadily increasing film thickness much like an oil would. Only near the top speed is there a deviation from this behaviour, where film thickness plateaus at ~300 nm, before jumping back up to greater-than-base-oil levels. This behaviour is remarkably repeatable across the three sweeps, indicated by the low variance. The cause is therefore not likely to be random intermittent starvation, but may show the apparent speed limit of lubricant reflow,

at which point film thickness might have begun to decay with increasing speed, however this process was interrupted by a sudden increase in available lubricant due to centrifugal force.

The shear stress due to centrifugal force acting on a film of fluid on a rotating disc is represent by equation 13, where τ is shear stress, ρ is density of the lubricant, r is the radius, h is film thickness and ω is angular velocity.

$$\tau = \rho r h \omega^2 \quad (13)$$

If we assume a density of 900 kgm^{-3} , set r to the typical value of 0.04 m , ω to 25 rads^{-1} (equivalent to a 1 ms^{-1} rolling speed) and the thickness of the lubricant film to 1 mm then we calculate a shear stress of just 23 Pa . This is far lower than the typical yield stress for these greases, as assessed in this work, which is around 1000 Pa for fresh grease and perhaps 500 Pa for the sheared samples. Using these values, it would require a speed of 6.7 ms^{-1} in this setup for a 1 mm film of fresh grease to flow under purely centrifugal force. As mentioned previously, the definition of yield stress as the crossover of storage and loss modulus is an overestimate, the grease beginning to flow plastically at a significantly lower stress. Values of $\sim 100\text{-}1000 \text{ Pa}$ have been reported for yield stress of similar, fresh, NLGI grade 2 greases using various methods [103], with $\sim 100\text{-}500 \text{ Pa}$ being typical for a method defining yield as the end of the LVE region [103], [110], bringing centrifugal yield within possibility. A discrepancy still remains, and if this explanation of the jump in film thickness at high speed is correct, it must act as just part of the reflow mechanisms that supply the contact. For example, the capillary force acting on lubricant that pulls it into the converging contact may be augmented by this centrifugal force and begin to flow at a further distance from the contact, increasing the lubricant flow rate. Another factor is the oil/thickener content, with the reflowing lubricant likely to contain less thickener and hence have a much lower yield stress, which may cause it to directly yield under these conditions.

It is clear that the shear degradation has had a profound impact on resistance to starvation for this grease. The rheometry has shown that yield stress fell by 26% upon shear degradation which may explain the increase.

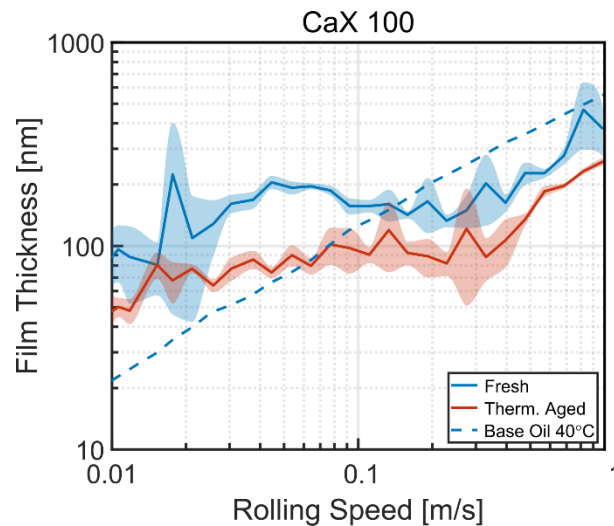


Figure 5.22: Starved film thickness results for the fresh CaX 100 grease and thermally aged samples.

The starved results for the CaX 100 grease are shown in Figure 5.22, lacking the sheared sample which was not available for this grease. Until the mid-speed range the fresh grease appears similar to the fully-flooded condition, however after this point the film thickness falls below that of the base oil before recovering slightly at higher speed. The thermally aged sample behaves extremely similarly to the fresh sample, but shifted down to lower film thickness. It is rather surprising that the thermally aged sample is able to produce consistent films of approximately 100 nm, given the extreme change seen in the rheometry, where yield stress increased by more than 25 times. While the changes in starvation do not seem proportional to changes in yield stress, they are aligning in a general sense for the greases discussed so far.

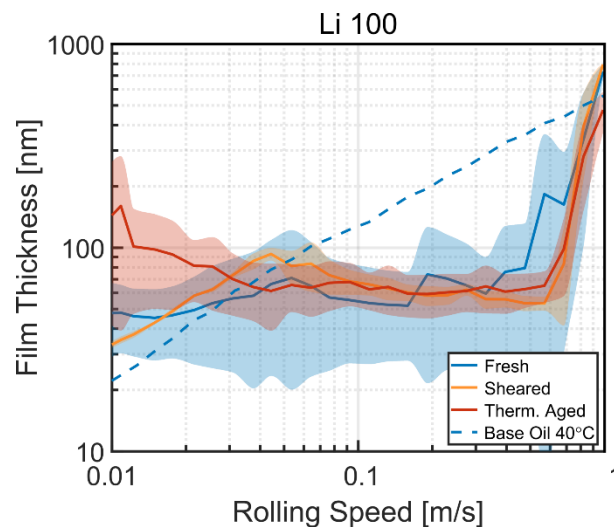


Figure 5.23: Starved film thickness results for the Li 100 grease and degraded samples.

The remaining greases, including the Li 100 sample shown in Figure 5.23, all show the same general behaviour in the starved state, giving a relatively constant film thickness until the high-speed region, where film thickness jumps by around 10 times. There are two main factors to compare, then: the plateau film thickness value and the apparent ability to return to thick films at higher speeds. The first is affected by both the lubricant's rate of reflow as well as the film-forming ability of the lubricant that makes it to the contact, mainly the thickener content which contributes to large film thicknesses. The second is only a measure of how the lubricant responds to the increased reflow forces acting at higher speeds.

None of the Li 100 samples appear to show the extreme V-shaped thickener effect that was clear in the fully flooded results, implying that it was only through artificially delivering thickener to the contact that this behaviour was seen. Once the scoop was removed and passive reflow mechanisms took over, it is likely far less thickener was carried to the contact and this led to lower film thickness. All three samples appear to have very similar plateau film thicknesses, with the sheared sample reaching a slightly higher point before decaying, and in fact reaching the lowest film thickness of the three at 0.6 ms^{-1} . This plateau value may, however, be influenced by the initial film thickness, of which the sheared sample had the lowest. Another possible contribution to the plateau film thickness are deposited thickener films which have been observed in ball-on-disc testing [162], [181], [209]. Efforts to measure the thickness of this film by recording the static film thickness at the end of testing were unsuccessful due to the variable thickness of this film, and its strong dependence on time when static. It can take on the order of half an hour to fully dissipate oil within the contact, precluding repeat measurements.

The thermally aged sample showed very thick films at low speed but tended downwards as speed increased. It is possible that the remaining thickener effect of the thermally aged sample boosted this plateau value, while the sheared sample did not benefit from this effect. The fresh sample showed enormous variance in the starved state, a product of deteriorating film thickness in successive sweeps. This was seen as a general trend in all greases, however not to the extent displayed here. This possibly suggests the first run had not settled into the

starved state as effectively as most of the other starved tests, and that the film thickness was decaying from the fully-flooded state, increasing the measured value.

At the highest speed, the rebound in film thickness occurs first in the fresh grease, and the same value is reached by the fresh and sheared sample. The thermally aged sample appears to respond less strongly and does not increase above the base oil level. The results from the Li 100 starved test are interesting as the rheometry suggested a significant reduction in yield stress after shearing which has not manifested as greatly improved starvation response. In fact, the fresh and sheared samples appear similar, though the absent thickener effect in the sheared sample may be obscuring an improved reflow rate. The thermally aged sample was only slightly more solid-like in rheology compared to fresh, but the results suggest a diminished response to the increased reflow forces at high speed.

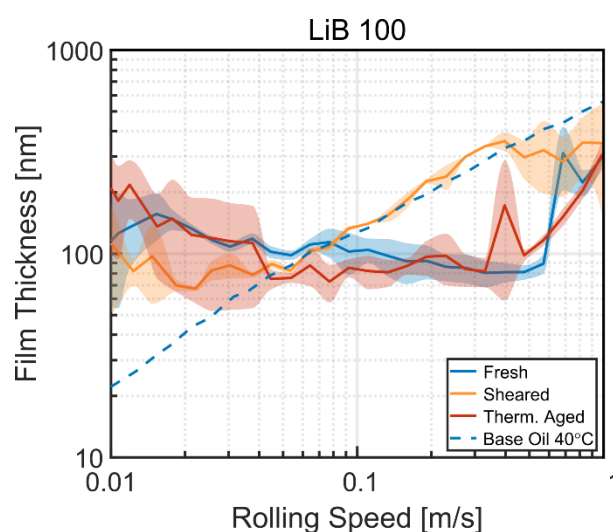


Figure 5.24: Starved film thickness results for the LiB 100 grease and degraded samples.

The fresh LiB 100 grease shows a similar plateau in film thickness to the Li 100 grease under starved testing. The sheared sample behaves in a similar way to the CaXB grease, increasing in film thickness as if fully flooded, until a maximum point is reached, with intermittent starvation and high variance. Clearly the shear degradation has, in this case, greatly increased resistance to starvation. The significant thickener effect in the fully flooded results has diminished here, but remains strong in the thermally aged and fresh samples. The sheared sample retains a boost over the base oil film thickness at low speed. The thermally aged

sample behaves in a similar manner to the fresh grease, though appears to respond slightly less to the film increase at high speed.

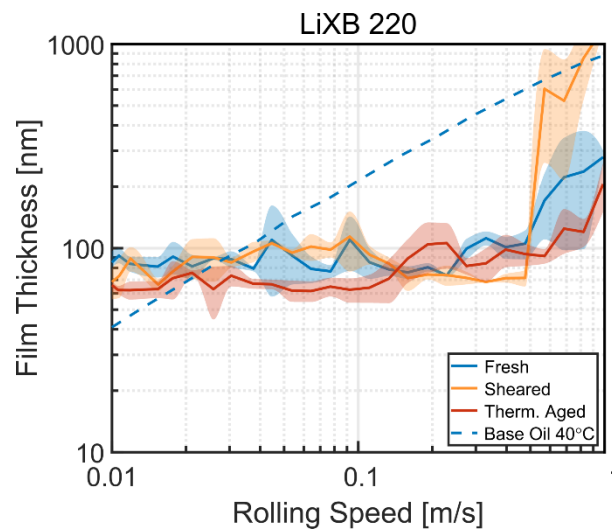


Figure 5.25: Starved film thickness results for the LiXB 220 fresh grease and degraded samples.

The LiXB 220 grease shows relatively little difference in the plateau film value for the three samples, though the thermally aged sample is generally the lowest. At the highest speed, however, the three samples are clearly very different in their response. The sheared sample rebounds in film thickness earlier and to a greater extent than the other two samples, with the thermally aged sample increasing only very little. This greater distinction may be due to the increased base oil viscosity of the grease which will exacerbate starvation by reducing reflow rate [223]. These results correspond reasonably to the rheological changes measured. The proportion of change between samples was measured to be relatively large in the LiXB 220 grease, and certainly the effect at high speed is large, however the sheared sample does not show the base oil-like behaviour seen in the LiB 100 and CaXB 100 sheared samples.

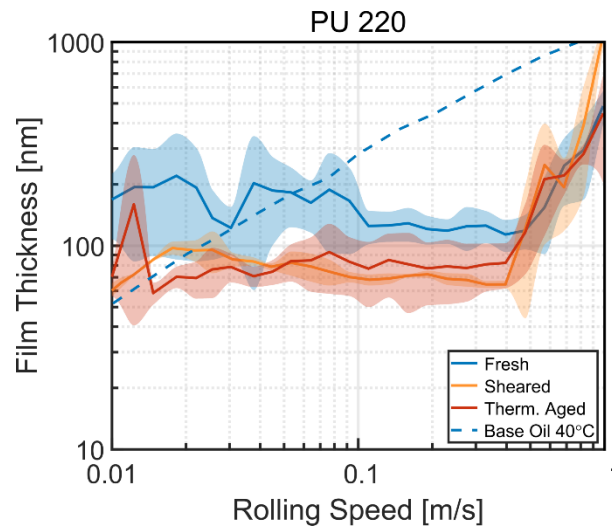


Figure 5.26: Starved film thickness results for the PU 220 grease and degraded samples.

The fresh PU 220 sample under starved conditions, shown in Figure 5.26, displays a strong thickener effect, like in the fully flooded condition. The thermally aged sample does not, unlike the fully-flooded condition which suggests that the thermal aging has prevented thickener reflow in the same way as in fresh grease. The sheared sample does not show this thickener effect at all, and it is perhaps for this reason that it decays to the minimum value of all three samples, around 70 nm. The fresh grease maintains a film of over 100 nm on average but it could simply be that a viscous, thickener-rich layer of at least 30 nm is providing this boost in film thickness. It is important to know that fresh grease is capable of depositing such a layer, while sheared grease seems unable despite no change in thickener content, but it is also important to know if this effect is relevant to bearing lubrication. If it is not, then comparing plateau film thickness as has been done here will lead to a misunderstanding about how degradation affects starved film thickness. As film thicknesses are much higher at the high speed and the thickener effect is proportionally much smaller, it is clearer here that the sheared sample provides a benefit in responding to the reflow forces. It is unfortunate then that these forces are not an accurate emulation of those in a bearing due to the difference in geometry. At this high speed, the thermally aged sample does not appear to differ much at all from the fresh, possibly a result of the yield stress remaining very close to the fresh value (and in fact reducing by a small amount).

Summary of Starved Film Thickness

The starved results have been difficult to interpret due to the competing effects of thickener entrainment increasing film thickness (thickener effect) and reduced yield stress causing increased lubricant reflow. As shear degradation progresses, the former effect is reduced (corroborating work by Cen et al. in similar conditions [52]) while the latter is increased. This has led to two modes of behaviour in these tests. For greases like the CaXB 100 and LiB 100, the increased reflow has been sufficient to maintain a film thickness close to the fully flooded case for the majority of the speed range. For the other greases, the lack of thickener effect has meant a low film thickness was reached as speed increased but reflow had not yet increased significantly. Only at higher speed, likely due to the additional influence of centrifugal force, did reflow for the sheared sample suddenly increase beyond that of the fresh and thermally aged samples and increase film thickness to the highest of the three. This combination of effects likely explains why the PU 220 plateau film thickness was lower in the sheared sample than the fresh. In general, the shear degradation has improved contact replenishment of the test greases, agreeing with the results of other researchers [130]. Given that shear degradation is known to increase oil bleed rate, and the strong evidence that resistance to starvation is improved by a higher bleed rate [164], [224], this finding is not surprising.

The extent of the effect has not, however, correlated clearly with changes in yield stress. The Li 100 grease, for example, did not show a clear improvement in starved film thickness compared to fresh, but underwent very similar yield stress changes to the other greases upon shearing. The balance of lubricant feed and loss that is widely described as controlling starved film thickness [120], [122], [131], [225], [226] can be tipped to the side of higher film thickness by increasing reflow through rheological changes. These changes must not be simply described by yield stress. Instead, oil-release, ability to carry thickener to the contact and oil viscosity changes might all be controlling film thickness to differing extents.

The thermal aging of the samples generally decreased film thickness, and where film thickness appeared unchanged this was likely due to the increased thickener effect that occurred in some greases due to thermal degradation. As discussed in section 5.1, the rheological changes due to thermal aging have not followed the general trend found in the

literature which is a reduction in consistency/yield stress [105], [165], [218], which could be due to volatile loss or the presence of antioxidants. Some work has shown that thermal aging can cause agglomeration/widening of thickener particles [53], which would explain why the thickener effect was generally increased upon thermal aging.

The rebound of film thickness at high speed was reduced in the thermally aged samples, likely a direct effect of limited reflow. A more cohesive thickener lattice would limit the rate of reflow and tip the feed-loss balance to thinner films. Oil bleed, on the other hand, is thought to be sourced from oil in between thickener particles, far enough from the thickener molecules to not be ‘immobilised’ by strong intermolecular forces [227]. This would imply that agglomeration, which would reduce thickener surface area, would also reduce the volume of immobilised oil and increase the volume that is able to bleed. Whether or not oil bleed is reduced or not cannot be ascertained from this work, but, if it has been increased as this model would suggest, is clear that increased yield stress has been the dominant factor in controlling film thickness.

While low shear stress rheological behaviour may be a strong influence in lubricant reflow, the rheometry data such as yield stress has not appeared to correlate well with starvation behaviour. The absolute proportion of yield stress change has varied significantly, but this did not seem to directly affect starvation behaviour. Despite this, the direction of change has consistently correlated with an improvement or reduction in starvation ability. Similarly, the rheometry of greases when compared to one another does not indicate performance under the starved condition. There are likely to be many other properties that thermal and shear degradation have influenced that are not assessed through rheometry. Clearly the yield stress is not the only factor controlling starvation. Increase in viscosity, for example, will directly reduce reflow rate but will not clearly affect the rheological parameters measured here. The potentially increased effect of oil bleed was not assessed and could vary significantly between the studied greases. This suggests that rheological tests are not a reliable means of assessing a grease’s change in resistance to starvation after undergoing degradation. The film thickness testing performed here may be a better test, but fails to correctly emulate the conditions of a

bearing, with a significant centrifugal force influencing film thickness at higher speeds, when starvation is most dominant.

5.2.3 MTM – Friction Under Fully Flooded Conditions

The MTM was used in friction testing of the greases, as described in Chapter 3. Figure 5.27 shows the results for the CaXB 100 fresh grease and sheared samples, as well as the base oil results for comparison. The base oil demonstrates clearly the transition between the mixed and EHD regimes, with a steady increase in coefficient of friction (COF) as speed reduces. At high speed, the higher temperature tests show the lowest COF as they have a lower viscosity and produce a lower shear stress in the contact as a result. This oil, and consequently the grease, produce particularly low COFs. The fresh grease displays a remarkably constant film thickness value as speed increases, clearly protecting against the COF increase when entering the mixed regime, an effect well-described in the literature [161]–[163], [222]. This is likely to be a direct result of the thickener effect increasing film thickness above that of the base oil at low speed. As with the base oil, the COF of the fresh grease falls as temperature increases. At high speed and temperature, the fresh grease shows a greater COF than the oil, likely due to the increased viscosity that a grease has over its base oil, even at high shear rates.

The sheared sample appears to behave in the same way as the fresh grease only at high speed. At lower speed the thickener effect has been greatly reduced and, in fact, the sheared grease mirrors the base oil curves, shifted to a higher COF. As the film thickness thickener effect was observed to greatly decrease in the sheared sample, so does the friction thickener effect, suggesting a direct link between them.

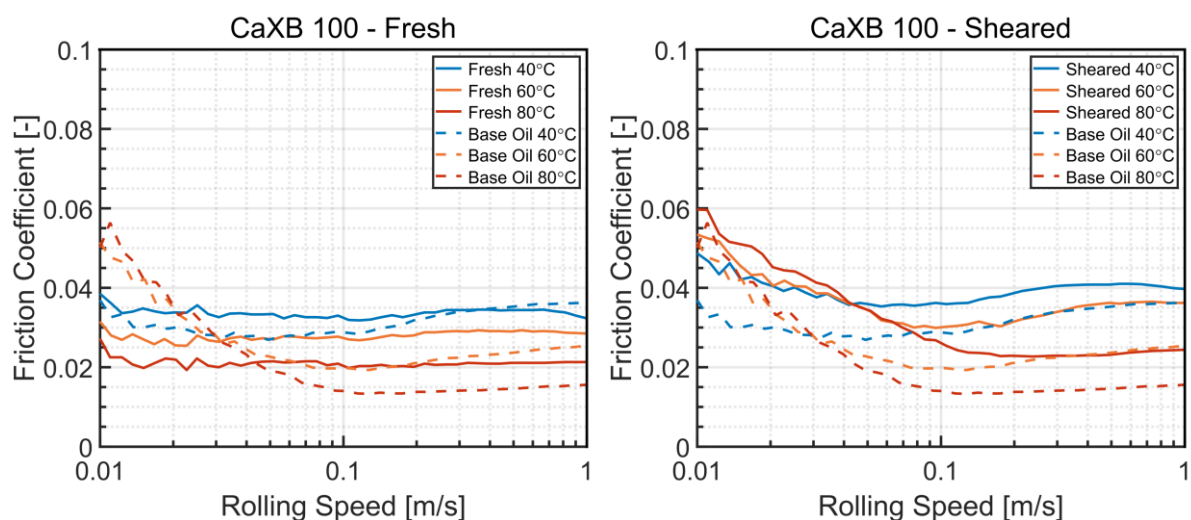


Figure 5.27: Friction results for the CaXB 100 grease, showing fresh and sheared samples, compared to the base oil.

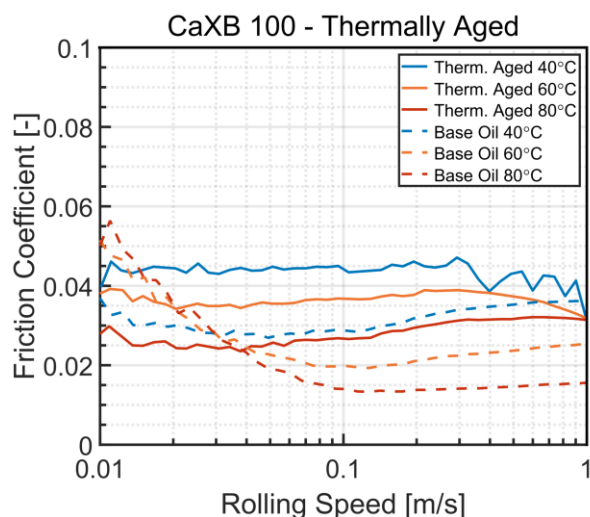


Figure 5.28: Friction results for the CaXB 100 thermally aged sample.

Figure 5.28 shows the friction results for the thermally aged CaXB 100 sample which showed such large viscosity increases in film thickness and rheometry testing. Here, the change does not appear quite so extreme, representing a shift to higher COF for all temperatures. Clearly the high viscosity prevents any surface contact at the low-speed region, but at higher speeds the viscosity does cause an increased COF compared to the fresh sample, approximately 50% for the 80°C sample at 1 ms^{-1} .

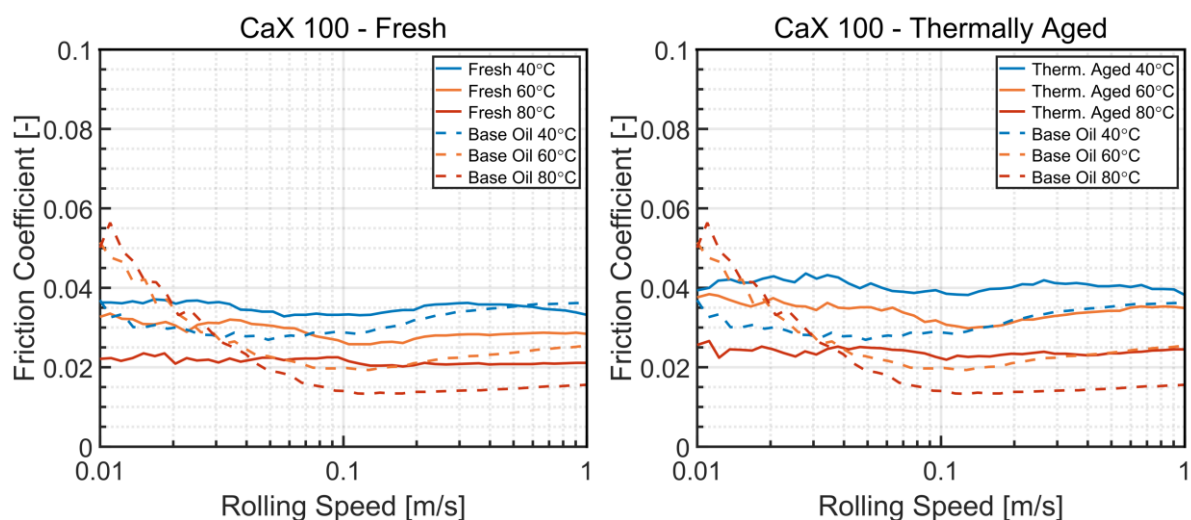


Figure 5.29: Friction results for the CaX 100 fresh grease and thermally aged sample.

The CaX 100 grease in Figure 5.29 unsurprisingly shows very similar friction behaviour in the fresh state to the CaXB 100 grease. The effect of additives is minimal, with both greases showing relatively constant friction at all temperatures. With a sheared sample of CaX 100 unavailable, the only comparison is with the thermally aged sample. This aging has increased COF uniformly, as with the base grease, but the effect is much smaller as the same extreme changes in properties were not observed.

Figure 5.30 shows the friction results for the Li 100 grease, both fresh and shear degraded samples. The fresh sample is unlike the two CaX greases shown previously, as instead of remaining constant in friction at low speed, friction actually decreases from the high-speed value, an effect that becomes more apparent at higher temperature, reaching an extremely low COF value. This must be considered in tandem with the V-shaped film thickness profile observed for this grease. It appears that the film thickness increase afforded by the thickener effect directly relates to friction at that speed. This follows from the simple observation that, for a given speed, an increase in film thickness will reduce the shear rate and consequently shear stress in the contact.

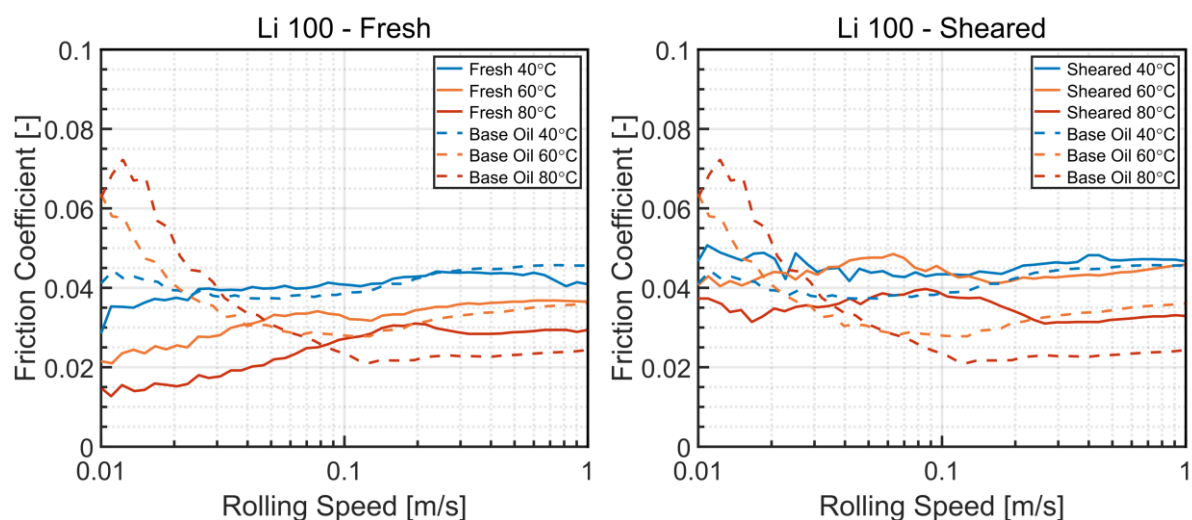


Figure 5.30: Friction results for the Li 100 fresh and sheared samples.

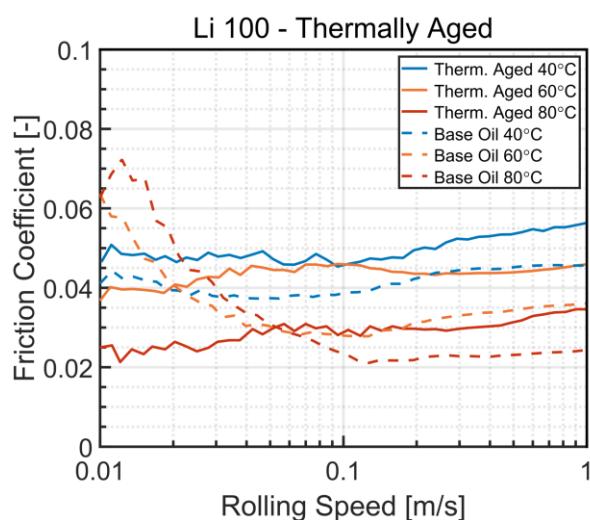


Figure 5.31: Friction behaviour of the thermally aged Li 100 sample.

For the Li 100 grease, shearing reduced the film thickness thickener effect, but it still remained relatively strong and retained the V-profile. This appears to directly correspond to the sample retaining a friction thickener effect, reduced but still apparent. The friction behaviour of the sheared sample is in fact close to that of the two CaX fresh samples.

The thermally aged Li 100 sample, shown in Figure 5.31, is quite similar to the fresh grease, though the thickener effect appears reduced and COFs are higher at high speed. Thermal aging may not cause drastic changes to film thickness, yet appears to increase COF fairly uniformly, possibly by a combination of effects that dominate separately at low and high speed. Firstly, this behaviour at low speed suggests an increase in shear strength of the thickener, resisting shear despite no change in film thickness. Secondly, an increase in

viscosity due to oxidation or volatile loss will increase friction but may have been obscured in film thickness testing due to unintentional intermittent starvation, which this grease suffered from.

In a similar way to the Li 100 grease, the LiB 100 fresh sample in Figure 5.32 displays an extreme thickener effect but to even lower COF values. In this case the transition point between low and high speed behaviour, which occurred at 0.6 ms^{-1} at 80°C for the Li 100 fresh sample, appears to take place at much higher values, not even being reached by 1 ms^{-1} for the 80°C test. Though the film thickness profiles for the two greases appear quite different, with no clear V-shape for the LiB 100 grease, it may be that the thickener particle size was so great that it obscured the transition, as the minimum point was never reached and the maximum film thickness was limited by other mechanisms, preventing the clear V-shape appearing. In support of this argument, the sheared LiB 100 sample does show the V-profile quite like the Li 100 grease and is very similar in friction behaviour to the fresh Li 100 grease. The shear degradation may have brought the thickener particle size in line with that of the Li 100 grease and, as a result, emulated its film thickness and friction behaviour.

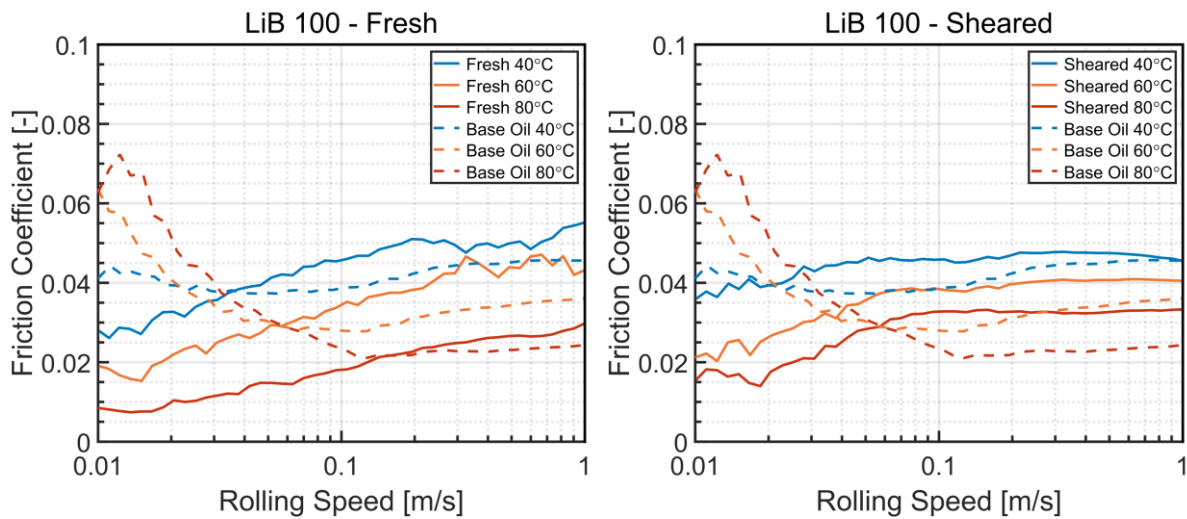


Figure 5.32: Friction results for the LiB 100 fresh grease and sheared sample.

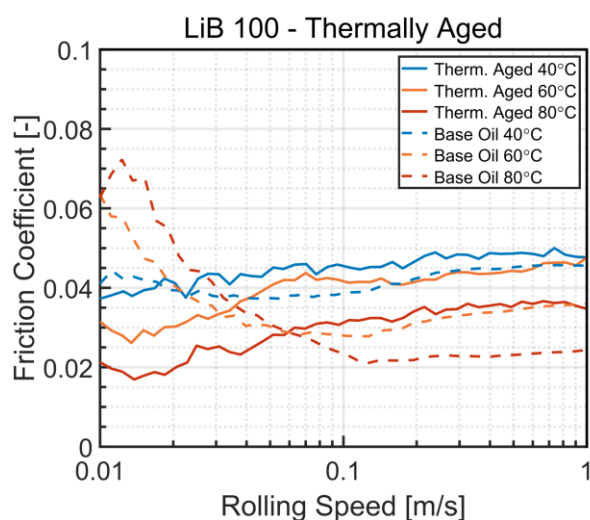


Figure 5.33: Thermally aged LiB 100 friction results.

After thermal aging, the LiB 100 grease retains the thickener effect but has increased in friction uniformly, as with the other greases.

The LiXB 220 fresh grease in Figure 5.34 also appears to show a slight decrease in COF with reducing speed, however this is a smaller effect than seen previously and does not appear to show a transition speed, as with the LiB 100 grease. Perhaps for the latter reason, the film thickness results for the LiXB 220 fresh sample did not show a clear transition point either. Looking at the sheared results, the thickener effect has been significantly reduced, but the COF does remain well below that of the base oil so there appears to be some ability to resist the mixed lubrication regime. This corresponds to a reduced, but still apparent, film thickness thickener effect.

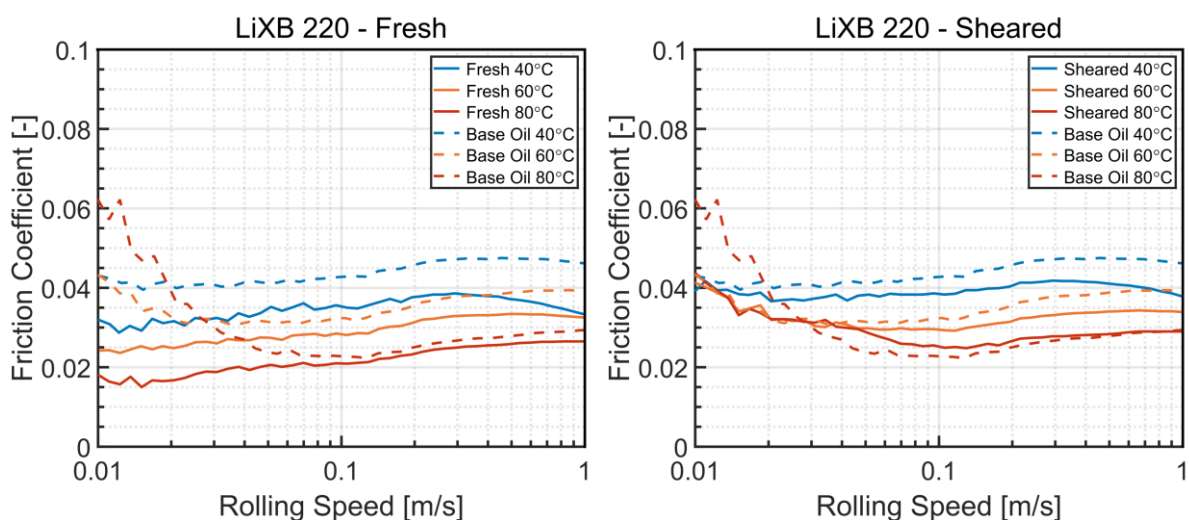


Figure 5.34: Friction results for the LiXB 220 fresh and sheared samples.

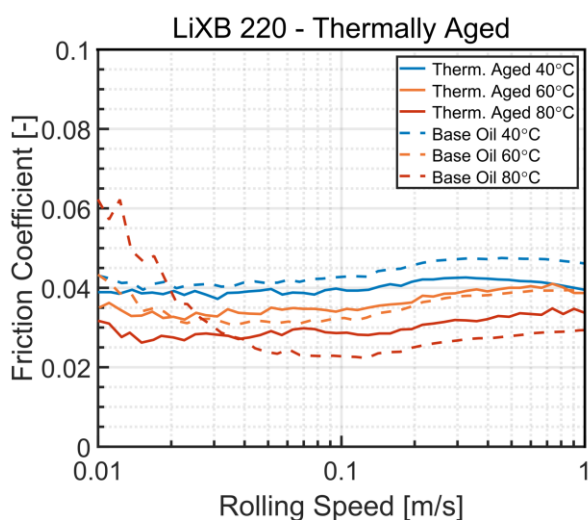


Figure 5.35: Friction for the thermally aged LiXB 220 grease.

For the thermally aged LiXB 220 sample, shown in Figure 5.35, there appears to be a reduction in thickener effect not seen in other thermally aged samples. COF appears slightly increased at higher speeds also. The loss of thickener effect is also observed in the film thickness results which is unusual for a thermally aged grease but appears to correlate well with the friction results.

The fresh polyurea grease PU 220, shown in Figure 5.36, shows fairly uniform friction across the speed range. The absolute value of COF is relatively high compared to the other greases, an effect clearly inherited from the base oil which also shows high friction, even when outside of the mixed regime. This is a result of a high naphthenic content of the base oil, naphthenic molecules having a high pressure-viscosity coefficient [228] due to their ring-based structures

which do not easily slide past one another in the high-pressure EHD contact. As viscosity within the contact is increased, so does shear stress across the contact and, consequently, friction. The grease COF values appear to change relatively little with temperature compared to the base oil or even other greases. The reason for this is not clear but is likely to be due to the polyurea thickener, potentially due to a decrease in thickener shear-strength as temperature rises.

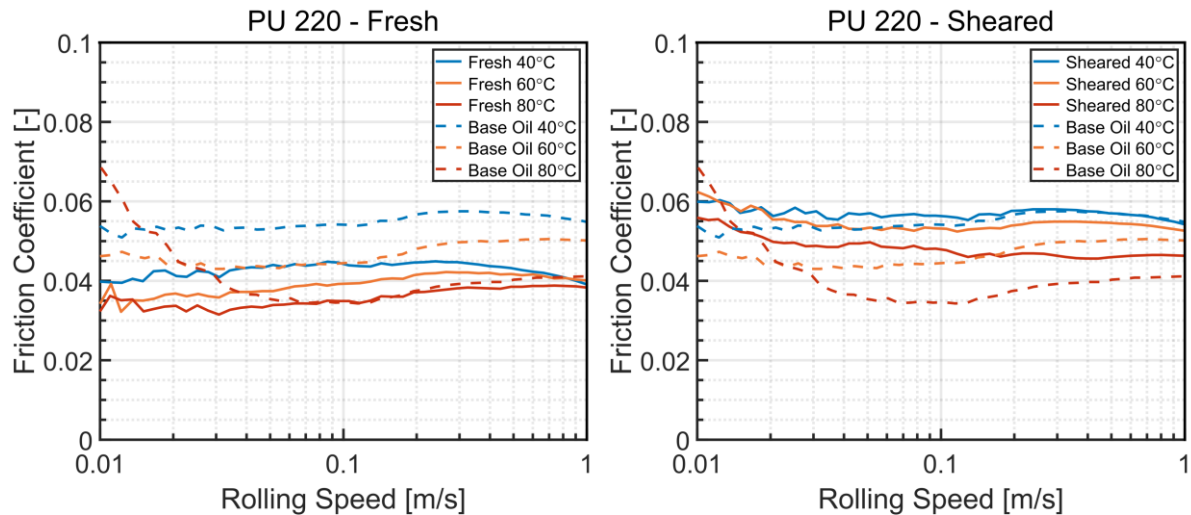


Figure 5.36: Friction results for the PU 220 fresh and sheared samples.

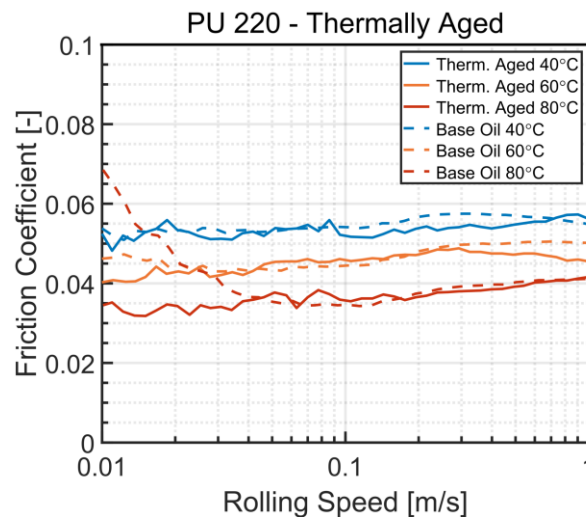


Figure 5.37: Thermally aged PU 220 friction results.

The sheared sample is interesting to analyse in combination with the film thickness results. After shearing, the PU 220 grease did not show a film thickness thickener effect in the same way as other greases, appearing much like a base oil of increased viscosity. Here, however, the rise of COF due to entering the mixed regime when film thickness falls is fairly mild. This

is despite the lambda ratio apparently falling to ~ 1 at 80°C and 0.01 ms^{-1} . Also intriguing is the rise in COF in the mid-to-high speed region. For the other greases this has remained unaffected by shearing. The behaviour of this grease due to shearing has been unusual. The rheological properties appeared to be relatively unaffected implying the thickener structure remained coherent and able to resist shear, yet film thickness showed a complete loss of thickener effect, which suggests the thickener particle size has been greatly reduced. As the fresh grease appeared to show thickener entrainment all the way up to 0.3 ms^{-1} in the film thickness results, it may be that this boost in film thickness was providing low friction throughout most of the speed range. Once the particle size was reduced by shearing, this no longer occurred at such high speeds and COF increased as a result.

Figure 5.37 shows the PU 220 thermally aged friction results, appearing quite similar to the fresh grease at high temperature, however, the 40°C test showed an increase in COF compared to fresh. In this regard the 40°C test appears similar to the sheared sample at 40°C . As suggested by the starved results, it may be that the thermal aging reduces the ability of the grease to entrain thickener, but this effect reduces with temperature and viscosity, returning to the level of the fresh grease at 80°C .

Summary of Fully-Flooded Friction

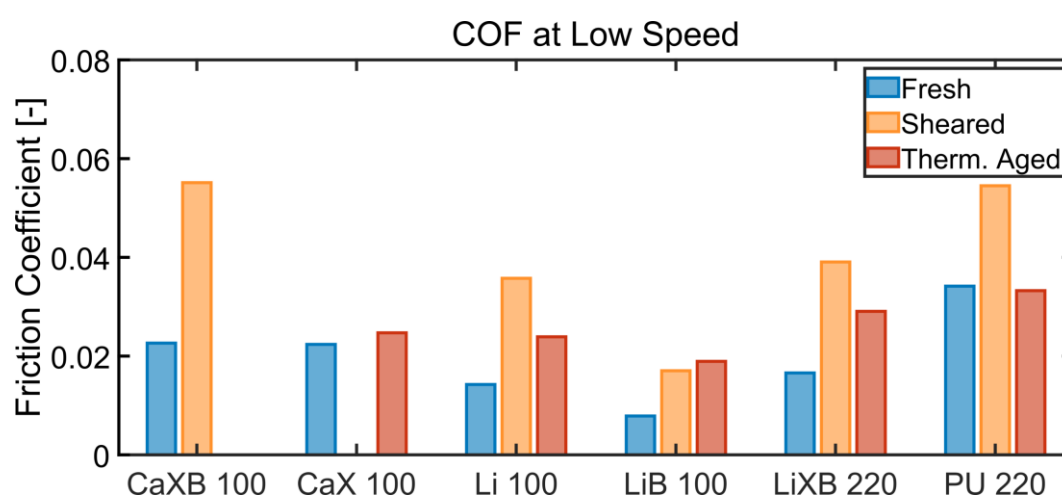


Figure 5.38: Friction coefficient of the test greases and their sheared and thermally aged samples averaged over a speed range of 10-15 mm/s. This shows data only from the 80°C test.

Figure 5.38 compares the COF of the grease samples averaged over the lowest test speeds of 10-15 mm/s at 80°C . This temperature was chosen to provide the largest degree of thickener

effect. It is clear from this plot that shear degradation has a large effect on COF at low speed due to the reduction in thickener effect. Thermal aging has also increased friction generally, but this varies between the greases, the PU 220 grease showing no friction increase due to thermal aging at low speed.

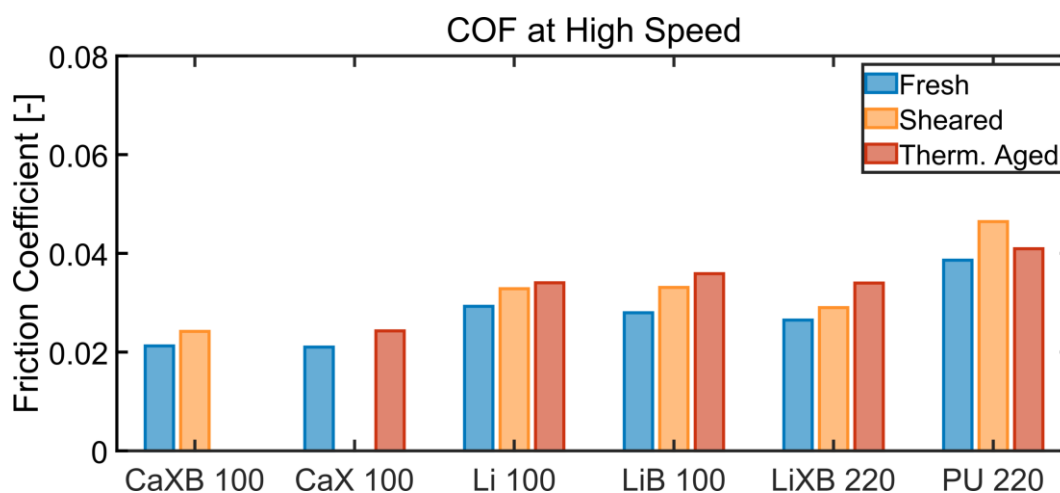


Figure 5.39: Friction coefficient of the test greases and their sheared and thermally aged samples averaged over a speed range of 0.66-1 m/s. This shows data only from the 80°C test.

Figure 5.39 shows a similar comparison, but with COF averaged over the highest speeds, from 0.66 to 1 m/s. Here the effects of aging are less pronounced. Shear degradation has consistently increased friction by a small amount, while thermal aging has increased it slightly more. Again, PU 220 is the exception regarding the thermally aged performance, showing the smallest increase compared to fresh.

The friction results have shown that shear and thermal degradation have consistent effects on grease friction. After shearing, the thickener effect of reduced friction at low speed displayed by greases is reduced. If it was mild initially, it can reduce to a level barely above that of the base oil. If it was initially strong, it can reduce to a level comparable with other fresh greases. There is generally little effect of shear degradation at higher speeds.

Thermal degradation has almost universally increased friction, though this effect can be quite mild. It does not appear that antioxidants provide particular protection against friction increase due to thermal aging, suggesting the cause is not directly linked to oxidation but may simply be the result of volatile loss over long periods increasing viscosity.

5.3 FTIR MTM TRACKS

To evaluate the effectiveness of ball-on-disc tests in reproducing the shearing conditions of a bearing, the rolled tracks of used MTM discs were analysed in the same way as the bearing inner races of the previous chapter. The same four greases that featured in the bearing tests were analysed here: the Li 100, CaXB 100, PU 220 and LiXB 220 greases. Initially, the goal was to test a best-case system, with a long test at the highest possible speed, with the highest possible reflow of lubricant. This system is most like a bearing and would allow lubricant on the track to undergo the maximum shearing and hence be most likely to show changes in the IR spectrum. This would most likely work best with removal of the grease scoop, as it will introduce fresh grease by nature of its role in channelling grease into the contact.

This prolonged test began with 1 hour of running at 0.5 ms^{-1} and 80°C , with a grease scoop in order to establish stable resupply. After this time, the grease scoop was removed and the test continued for 2 more hours at the same speed. The initial step with the grease scoop provided an opportunity for the ‘working’ lubricant to form, and gave the highest likelihood of preventing complete starvation in the remainder of the test.

Unfortunately, this procedure was only successful for the Li 100 and CaXB 100 greases. The PU 220 and LiXB 220 greases repeatedly starved in the part of the test without the grease scoop, presumably a direct consequence of their higher base oil viscosity which will reduced reflow rate. The results from the starved EHD testing do suggest that these two greases have reduced ability to regain film thickness at high speeds, compared to the Li 100 grease. As the severely starved lubricant films are far too thin to measure using IRRAS, these results could not be analysed. Instead, the discs used during standard testing were analysed. The two analysed were also tested at 80°C in the standard manner, amounting to approximately 25 minutes of time under contact, with speeds from $0.01 - 1 \text{ ms}^{-1}$.

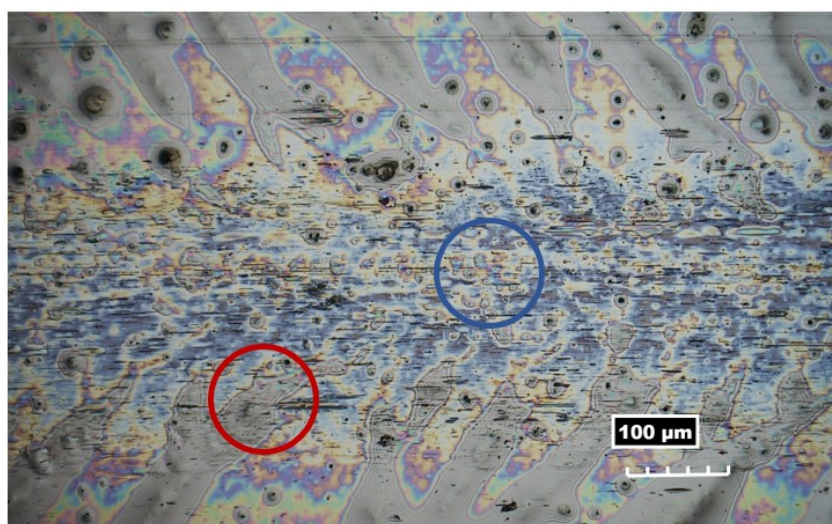


Figure 5.40: An image of a rolled MTM track from a test with the Li 100 grease, indicating where ‘centre-track’ and ‘edge-track’ measurements were taken, in blue and red respectively.

Figure 5.41 shows the IR spectra of the Li 100 MTM rolled track, as well as a measurement from the edge of the track, just out-of-contact. This was a prolonged test, with 2 hours of running without a grease scoop. In contrast to the bearing inner race, the thickener content of the MTM track, as shown by the 1580 cm^{-1} peak intensity, has risen significantly above that of the fresh grease, as has the measurement at the track edge. This is consistent with the thickener-rich films that have been observed in ball-on-disc tests previously [162], [181], [209] and have been described in various papers as a feature of grease lubrication, extending to bearing lubrication [17], [124], [172]. The discrepancy with the bearing inner race is suggestive of a very different process occurring compared to the bearing. The reflow mechanism in a bearing appears to preferentially allow oil to reflow, while in a ball-on-disc test, the reflowing lubricant contains sufficient thickener to build up a deposited film.

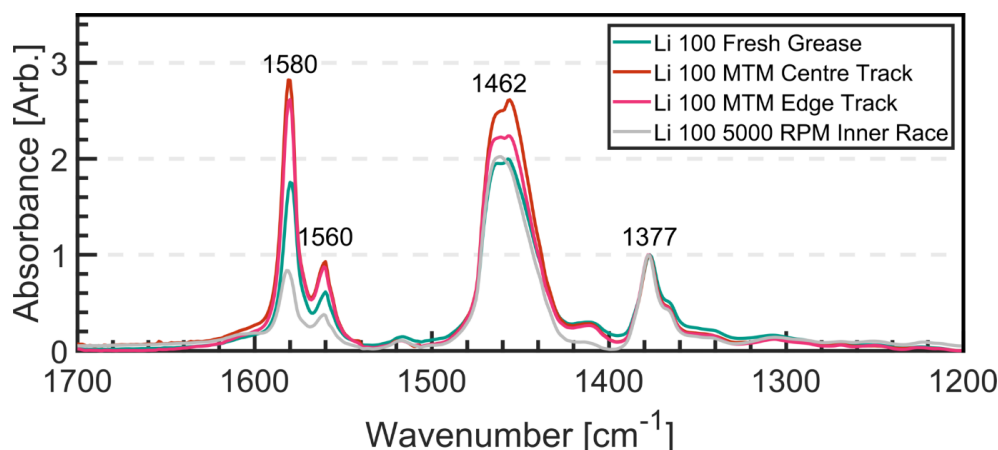


Figure 5.41: FTIR spectra of the Li 100 fresh grease compared to the MTM rolled track and bearing samples.

In addition to the altered thickener content, the MTM track samples do not show a shift of the 1580 cm^{-1} peak to the same extent as the bearing race. They do, however, show a difference compared to the fresh grease, with the centre track measurement displaying a greater shift than the edge of track measurement. This aligns with the expectation that it would have experienced greater shear. It is important to make the point that it is the lubricant measured in the ‘edge track’ sample that will be reflowing and providing hydrodynamic pressure at the contact inlet, hence controlling film thickness. While the apparent degradation of the centre track measurement suggests the contact itself has shear degraded the grease, it does not mean that the lubricant entering the contact is necessarily shear degraded, as it would be in a bearing.

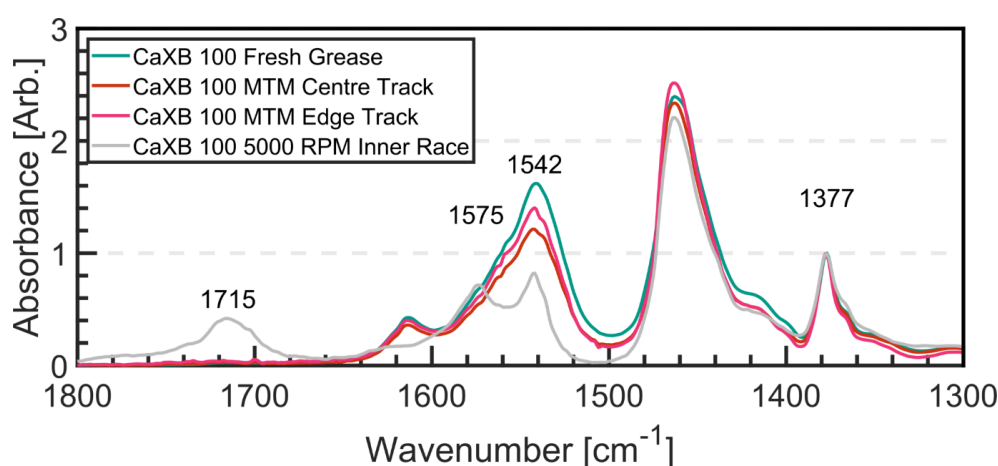


Figure 5.42: FTIR spectra of the CaXB 100 fresh grease compared to the MTM rolled track and bearing samples.

The MTM IR measurements for the CaXB 100 grease are shown in Figure 5.42. This was also a prolonged test with 2 hours of running without a grease scoop. The samples taken from the

MTM track bear a strong resemblance to the fresh grease sample, diminishing slightly in the intensity of the 1542 cm^{-1} and 1610 cm^{-1} peaks. In the bearing sample these peaks have significantly reduced, implying the shearing action of the MTM has produced a small amount of shearing, however the 1575 cm^{-1} peak has not increased in the MTM samples as it does in the bearing. There is also no change in the 1715 cm^{-1} peak suggesting no significant oxidation has occurred over the test. While the shear-induced changes appear to be small, as with the Li 100 grease they are greater in the sample taken in centre of the track which has directly undergone shearing in the contact.

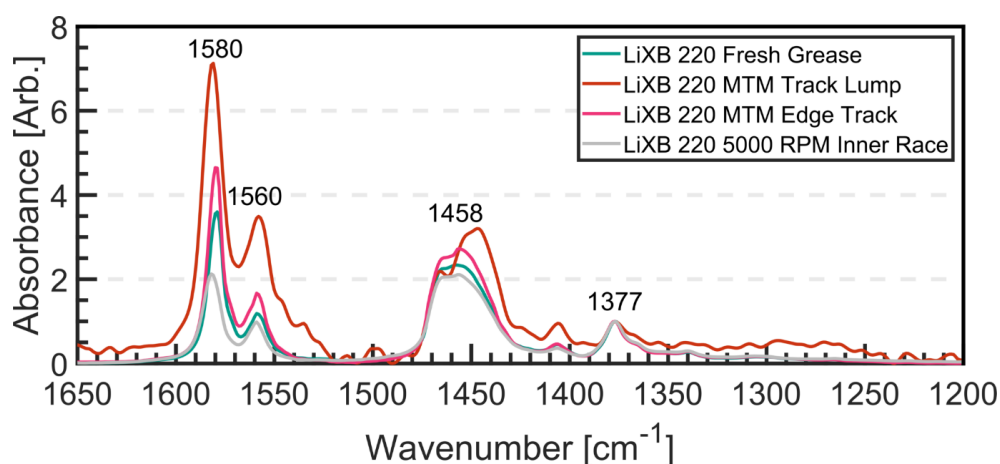


Figure 5.43: FTIR spectra of the LiXB 220 fresh grease compared to the MTM rolled track and bearing samples.

The LiXB 220 grease is one of the two greases that was unable to be tested for long times without the grease scoop and so the MTM spectra shown in Figure 5.43 are taken after a standard friction test at 80°C . Despite using the grease scoop, the rolled track featured very little lubricant and very thin films in general. These were too thin to take an FTIR sample from, however there were also lumps of deposited thickener which could be measured. One such measurement is shown above, clearly containing significantly more thickener than the fresh grease, as assessed by the 1580 cm^{-1} peak, as well as the right-hand shoulder of the 1458 cm^{-1} peak which is a contribution of the thickener.

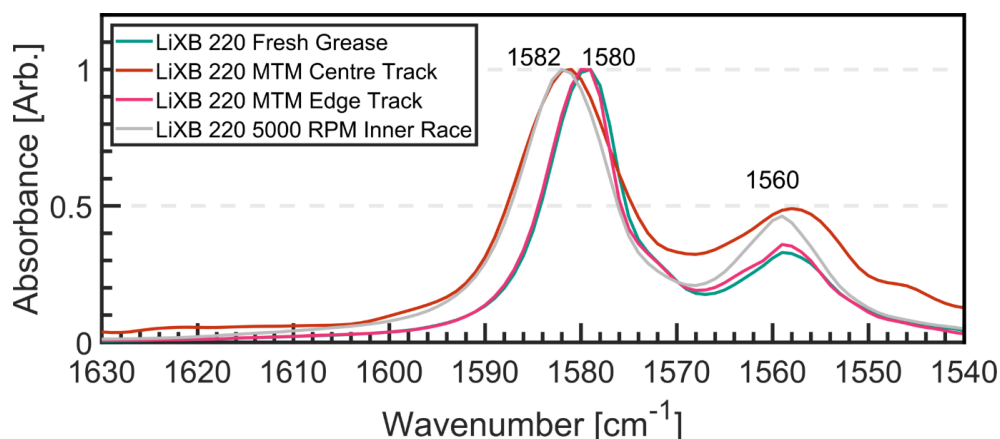


Figure 5.44: Magnified thickener region of the LiXB 220 MTM FTIR spectra, compared to fresh and bearing samples. All normalised to the peak near 1580 cm^{-1} .

The thickener region is shown more clearly in Figure 5.44, with all spectra normalised to the larger of the two peaks here. The thickener lump shows a peak shift equal to that of the bearing, indicating severe shear degradation. The lump has passed through the contact and has been crushed, subjected to immense pressure and shear stress. The large increase of the 1560 cm^{-1} peak may suggest even greater changes to the thickener structure than has been seen in the bearing. This sample is relatively concentrated compared to the bearing raceway lubricant which has been sheared and mixed with less intensely sheared lubricant for 100 hours. The sample measured at the edge of the track is quite different, it contains far less thickener, though more than the fresh grease, and is essentially unsheared according to the FTIR spectra. This may be a consequence of using a grease scoop which channels relatively fresh grease continually into the contact path.

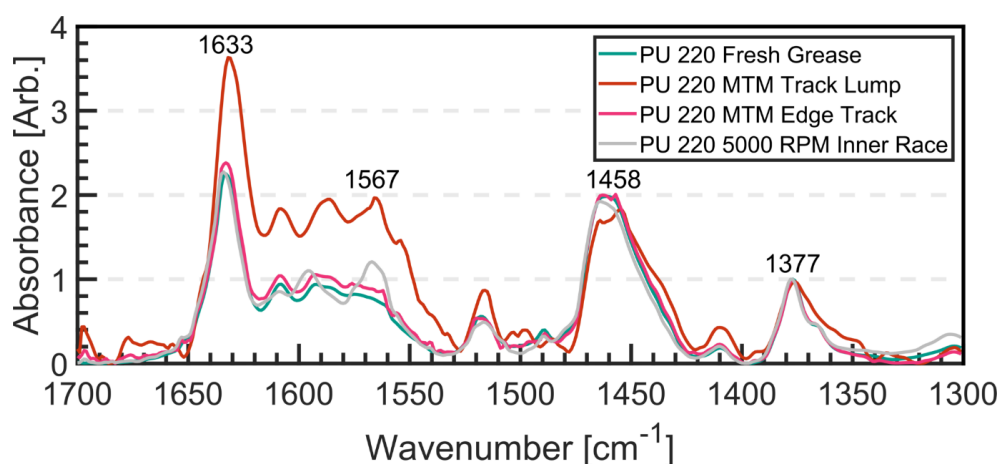


Figure 5.45: FTIR spectra of the PU 220 fresh grease compared to the MTM rolled track and bearing samples.

Figure 5.45 shows the MTM results of the PU 220 grease, compared to the fresh and bearing race samples. As with the LiXB 220 grease, this was taken after a standard MTM friction test at 80°C, and the raceway film was too thin to measure, with large, deposited, lumps of thickener. The track lump spectrum clearly shows a greater thickener content, with increased absorbance in the 1600 cm⁻¹ region. In terms of shear degradation, this sample also shows an increase in the 1567 cm⁻¹ peak, as seen in the bearing sample. Other, smaller, changes to the peaks around 1600 cm⁻¹ are not seen, however, suggesting this grease did not degrade as heavily as it did in the bearing. The spectrum from the track edge appears essentially identical to that of the fresh grease.

The two greases tested using a grease scoop show a similar result of relatively fresh grease beside the track, probably a direct result of the action of the scoop which is necessary to maintain fully flooded conditions. These greases were particularly susceptible to starvation without a scoop, most likely due to their shared higher-viscosity base oil, and it is perhaps because of this that they demonstrate similar morphology of their rolled tracks. Both appear to have extremely thin films remaining in the track which could be a result of lack of reflow. Their rolled tracks are also covered in deposited thickener-rich lumps which contain heavily degraded grease. This may also be a result of the use of the grease scoop, which will prevent the formation of an oil-rich lubricant that is able to reflow by continually introducing thickener into the contact.

There are many effects such as base oil viscosity, shear stability, thickener particle size and the use of the grease scoop that all influence these results. The conclusions drawn from this work must be limited as a result. It has been shown that in the most bearing-like test using no grease scoop and long test times, the lubricant within the rolled track shows shear degradation of a similar kind to that seen in a bearing. It is possible that with extremely long test times, these changes may be reproduced fully. Despite this, the deposition of thickener-rich films was observed with the Li 100 grease, which differs from the oil-rich films seen in bearings lubricated with the same grease. This suggests that the lubrication mechanism may be different, or that the contact is not as severe as a bearing in its ability to remove this film once deposited. Testing with a grease scoop may remove the effect of shear degradation of

the reflowing lubricant, as it is displaced by fresh lubricant continually. The implications are that the standard method of testing greases in fully flooded conditions using a grease scoop does not produce the same shear degradation of the working lubricant as observed in bearings.

5.4 CONCLUSIONS

This chapter has described the effects of bench-top techniques of mechanical and thermal grease degradation on the properties of a range of greases. The way in which the properties influencing lubrication change is important to understand, as these forms of degradation are present in a grease-lubricated bearing and will influence the friction and lifetime of that bearing.

The rheology of the test greases was significantly changed by degradation. Shearing consistently decreased yield stress in all greases, though some were more susceptible to this decrease than others. Thermal aging generally increased yield stress, though this varied depending on thickener type. The PU 220 grease did not appear to increase in yield stress much at all, while the CaXB 100 grease underwent a complete loss of yield stress as a result of thickener breakdown. These changes can be expected to significantly affect film thickness under starved lubrication in a bearing.

The tribological properties of film thickness and friction were also significantly affected by degradation. The thickener effect that contributes to high film thickness and low friction at low speeds is drastically reduced after shear degradation, while thermal aging appears to increase it, and increase the film thickness variance at low speed in particular. Despite the increased thickener effect in thermally aged greases, this did not translate to lower friction, friction generally being higher for thermally aged greases across the speed range. Starved behaviour was also assessed and it appears that shear degradation increases reflow to enable thicker films, particularly under the influence of centrifugal force in ball-on-disc tests. The opposite was generally the case after thermal degradation, though this effect was less clear. It was found to be challenging to reliably test lubrication under starvation using the ball-on-disc setup as reflow does not appear to occur as readily as in a bearing.

Infrared analysis of rolled MTM tracks suggests that only long-term tests without the use of a grease scoop are capable of producing the shear degradation changes that are observed in bearings. Even then, these changes are not seen to the same extent and require inconveniently long running times of many hours. When a grease scoop is used, as is usually necessary to prevent complete starvation, the changes are only visible within the rolled track itself and not in the lubricant beside the track, meaning that the contact inlet is supplied with non-degraded grease. When the effects of degradation demonstrated in this chapter are considered, it is clear that the use of fully flooded ball-on-disc grease tests does not directly represent the friction properties of grease under normal bearing conditions. This is also likely to extend to ball-on-disc film thickness testing. Baly et al. [18] describe a good correlation between bearing and bench film thickness tests under starved conditions, while they do observe small increases in film thickness with speed for some greases, they did not observe the sudden, large, increase in film thickness at high speed seen in this work and others [17], [221]. It appears that the use of a grease scoop should be avoided where possible, and longer test times should be used, or grease samples sheared prior to testing, in order to improve the predictive power of these forms of testing.

In addition to the lack of emulation of bearing-like shear phenomena, ball-on-disc tests appear to produce thickener-rich films in the rolled track which can reduce friction and increase film thickness. Some of the same greases tested in bearings in fact show a reduction in thickener content in the raceway lubricant, likely due to preferential reflow of oil-rich lubricant into the raceway as grease is displaced. Only the polyurea grease showed thickener-rich films both in the MTM rolled track and in the bearing as well.

These findings suggest that ball-on-disc testing is an inappropriate model for greased bearing lubrication, with testing of fresh grease using a grease scoop being a particularly poor emulation of real bearings. Ball-on-disc setups lack the innate reflow mechanisms present in bearings, and so testing without a scoop allows the misleading centrifugal reflow to dominate. There are large gains to be made by improving this form of model testing, specifically by bringing geometry closer to that of a bearing.

6 SINGLE-CONTACT BEARING RIG - METHODS

This chapter outlines the design and challenges involved in the development of a novel single-contact bearing rig. This covers the mechanical and electrical design, as well as the control system and microscope optics. Also described is a second machine that was built in order to allow deposition of the crucial semi-reflective film that enables thin-film interferometry on the non-standard cylindrical test specimens.

Testing greases using the ball-on-disc rigs such as the MTM and EHD rigs and comparing the rolled films to the R0F+ full bearing test showed that the composition and distribution of the lubricant film in the rolled track was dissimilar. This implies that there are differences in lubricant entrainment and perhaps ongoing processes of lubricant degradation. As a result, the friction and film thickness results from the ball-on-disc rigs may not be valid and representative of behaviour in a bearing.

There are significant differences in the tribological contact of a ball-on-disc rig and those of a rolling element bearing. The contact pressures and entrainment speeds are typically much lower than can be found in operating bearings. Often, slide-roll-ratio is higher than in bearings in order to produce a large enough tangential force to measure with sufficient signal-to-noise ratio.

The geometry of the contacts differs significantly also. The ball-on-disc contact is much more concentrated than the invariably highly conformal contacts of bearings. This not only reduces the size of the contact area but also greatly reduces the size of the highly sheared zones surrounding the contact. Both contacts are shown in the diagram in Figure 6.1. The shearing work done on lubricant surrounding the contact in a ball-on-disc rig is very small as a result of the tiny shear zones beside the track, and so the lubricant that is entrained is relatively fresh. This is in contrast to a bearing where the high volumetric rate of lubricant shearing means that the lubricant entering the contact has been degraded to some degree after only a short time of running. It was shown in the previous chapter that shear degraded lubricant is better able to resist starvation and it is therefore likely to reflow preferentially.

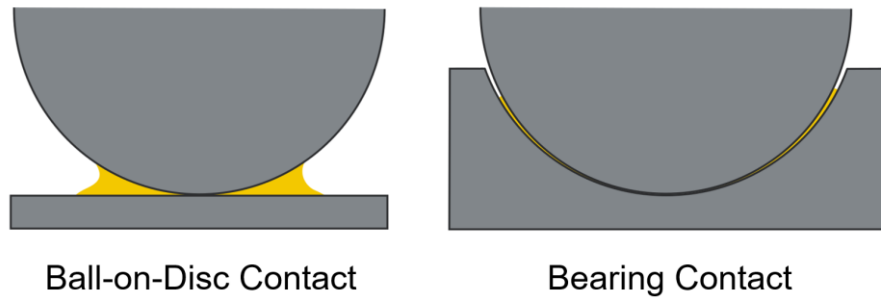


Figure 6.1: Illustration of a ball-on-disc and deep-groove ball bearing contact.

Additionally, the orientation of the contact relative to the axis of revolution in a ball-on-disc rig creates a centrifugal force that becomes significant at higher speeds. This can act to resupply the contact with fresh lubricant in a process that is only applicable to thrust bearings and other angled bearings.

The lack of a bearing cage will also alter resupply processes as it has been shown that a bearing cage can increase the speed at which starvation occurs [133]. This may be a result of the cage redistributing grease from the sides of the track into the centre, or the increased shearing of bulk grease between roller and cage acting to shear degrade the grease which may then aid reflow.

Another major difference is the number of contacts, clearly the single contact of a ball-on-disc rig will produce a fraction of the shearing work that multiple contacts do. Each contact may influence its neighbours, displacing lubricant from the rolled track which must reflow in order to supply the next rolling element. Fischer et al. found that introducing a second rolling element in a ball-on-disc test system reduced film thickness in starved conditions, as did reducing the distance between the rolling elements [221].

While film thickness has been measured in full bearings using capacitance or resistance techniques, these measure the average film thickness across all contacts of the bearing and are not as accurate as the optical techniques used in ball-on-disc setups [229]. By inserting a sapphire window into the outer race of a bearing, it is possible to use optical techniques to analyse film thickness at a single contact [230]. However, sapphire is an expensive and difficult material to work with due to its extreme hardness. The machining must be extremely precise in order to leave no step change between sapphire and steel, otherwise significant

stresses may crack the sapphire or influence the lubrication in other ways. It is also necessary to accurately trigger image capture with very short exposure times in order to capture the contact as it passes the window, without introducing blur. De Laurentis et al. utilised a rig composed of a bearing with the outer ring replaced by a cylindrical sapphire ring which displayed similar film thickness with time to measurements from real bearings [231]. This rig does require accurate timing to synchronise image capture with the passing of the ball and it is not possible to observe the same contact continuously.

The issue of centrifugal resupply was the motivation for the construction of the only rolling single-contact ball-on-ring rig found by the author in the literature [232]–[234]. This work enabled high speed film thickness measurement of oils, analysing the effects of inlet shear heating, but the authors do not consider starvation or grease lubrication.

The correlation of bench tests and full bearing tests in film thickness and friction has previously been reviewed [18]. The authors found that there are similarities in behaviour and concluded that this type of testing is worthwhile in understanding the underlying processes of lubrication. Both model and full bearing tests showed a transition to a starved regime. There were, however, differences in the speed at onset of starvation. This suggests that any conclusions regarding the specifics of test conditions cannot be extrapolated to full bearing tests. The authors do conclude that the two types of test are complementary and model tests are not replacements of full bearing tests, but this does not aid the grease manufacturer, who in general is not interested in running twice as many tests. It is suggested that a more useful test is one that accurately replicates the mechanisms under play in a bearing, allowing both an observational understanding of prototype grease behaviour, and a reasonable prediction of performance in a bearing. This is something that ball-on-disc model tests are unable to do. Again, such a test would not be a replacement of the full bearing tests, but a more useful step toward them, enabling faster exploratory grease development.

The objective of the latter part of this PhD project was to develop a simple film thickness test with a ball-on-ring geometry that would provide a step towards the model test described above – closer emulation of bearing lubrication mechanisms and more predictive power for

bearing performance. The rest of the chapter discusses the design and development of the ‘Single-Contact Bearing Rig’ (SCBR).

6.1 ELECTROMECHANICAL DESIGN

6.1.1 Principle

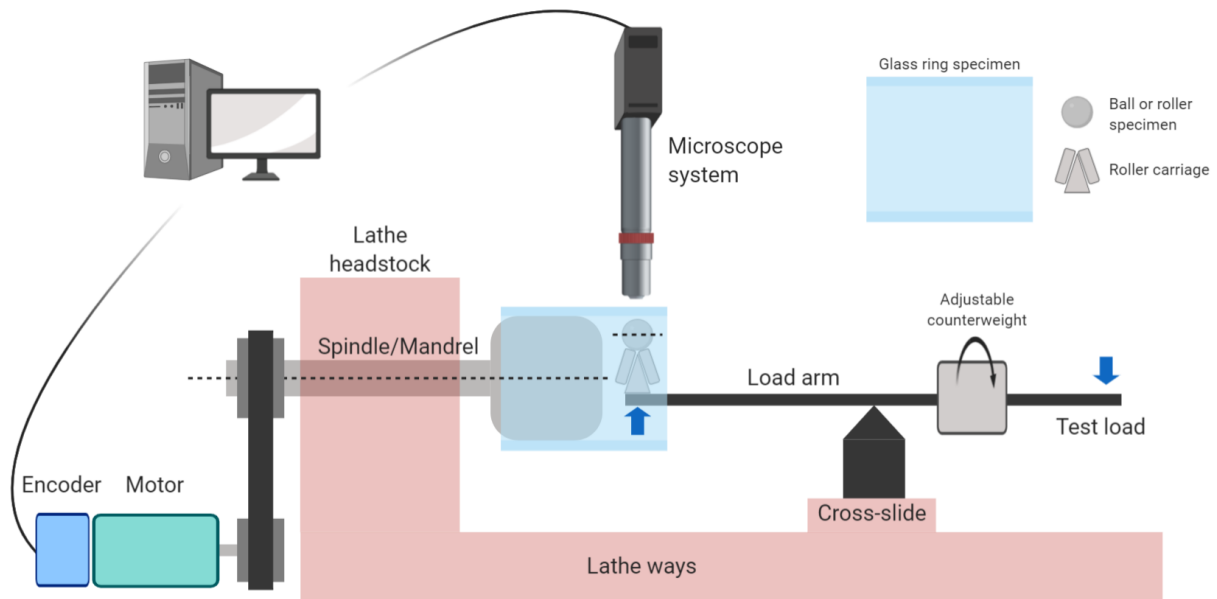


Figure 6.2: Diagram of the overall SCBR, showing the main structure in red, the load arm which supports the carriage and ball and the drivetrain which rotates the ring.

The rig is built around a benchtop lathe which provides many of the necessary functions for this machine. The machined and ground surfaces of the bed (the lathe ways) provide a means of locating the rolling element while the spindle and transmission are designed to operate at a suitable speed range with minimal runout or deflection under load. The cast iron bed is also beneficial in minimising vibrations.

The glass rings are made from borosilicate precision-bore tubing. Their manufacturing process involves shrinking the hot glass over a cylindrical form of specified diameter, resulting in a precisely controlled inner diameter. Borosilicate glass is suitable for its toughness and optical characteristics. This glass ring is securely gripped internally by an expanding mandrel. The mandrel fits directly into the MT3 taper of the spindle, ensuring excellent concentricity of the spindle and internal surface of the ring and consequently low runout.

A rolling element, either ball or barrel roller, is loaded against the glass ring, supported by a carriage of ball bearings. A microscope images the contact, and these images are post-processed into film thickness data using a similar process to the SLIM method [235].

Control of the rotation speed and imaging of the contact is performed by a connected PC, using MATLAB. Figure 6.3 shows a technical illustration of the assembled rig, omitting the microscope, load weight, pulley/motor and electronics which are attached to the DIN rail at the base of the machine. Further details of the rig are outlined in Table 6.1 below.

Test Parameter	Value
Load [N]	25
Ball Diameter [mm]	19.05
Barrel Major Diameter [mm]	70
Barrel Minor Diameter [mm]	9.5
Specimen Material	AISI 52100, borosilicate glass
Maximum Contact Pressure [GPa]	0.23
Slide-to-Roll ratio	Uncontrolled
Rolling Speed [m/s]	0.03 – 9.5
Temperature (°C)	Room temperature - 25

Table 6.1: Test conditions of the SCBR.

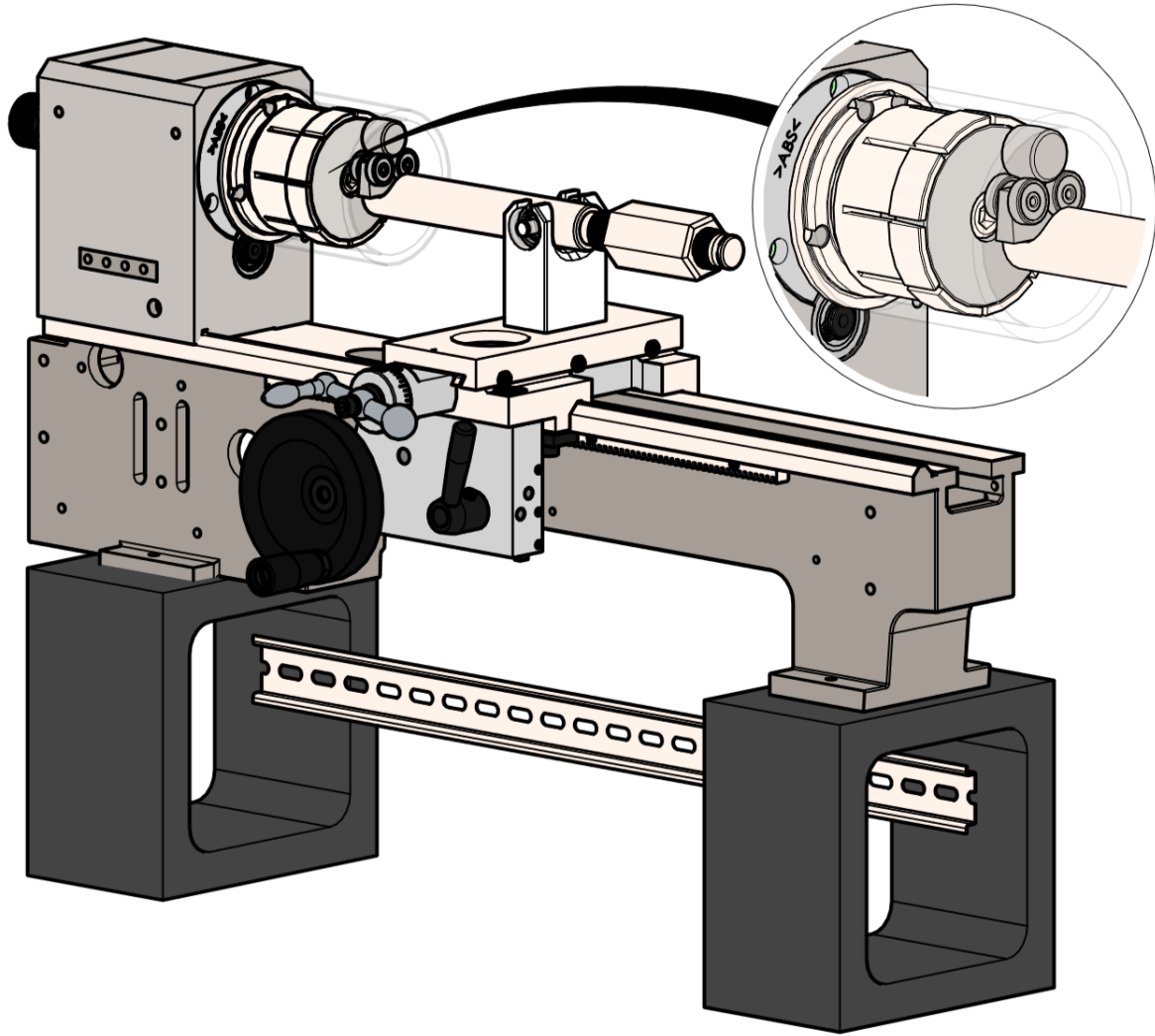


Figure 6.3: Technical illustration of the SCBR. Two cast iron blocks are used as mountings to provide suitable elevation as well as mass to resist vibration. Between them a DIN rail is attached for mounting of electronics. The load arm is seated on the saddle in the centre of the diagram and applies load through the roller onto the glass ring. This is shown in the inset diagram. The ring itself is supported by the expanding mandrel mounted in the spindle.

6.1.2 Transmission

The spindle is driven by a two-speed gearbox, which is used in both positions to enable testing at low speed with minimal speed fluctuation but also high speeds in the high-gear position. A belt and pulleys connect the motor to this gearbox. The motor is an ElectroCraft S286-1A\T8 servomotor, with a combined encoder for position and speed feedback. The motor is controlled by an ESCON 70/10 servo controller, providing excellent speed control. A speed setpoint is provided to the motor controller via the MCP4725 12-bit DAC chip, controlled with the I²C interface of an Arduino Uno. A MATLAB application connects to the Arduino as a

data acquisition (DAQ) device and is then able to deliver speed commands. These components are shown in Figure 6.4.

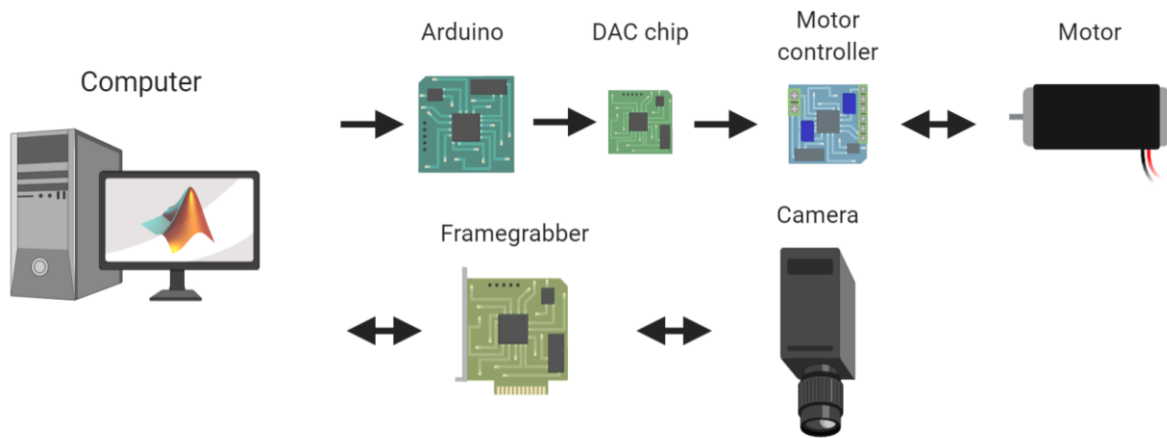


Figure 6.4: Diagram showing the information flow in the electrical hardware.

The glass ring itself is gripped by an expanding mandrel which applies an even pressure to the inside of the ring and locates it accurately to maintain a high concentricity with the spindle. The leftmost edge of the glass ring sits against a shoulder on the spindle which supports it and resists the deflection moment created by the contact load.

6.1.3 Loading System

The rolling element is supported by a carriage of 4 ball bearings, as used in the PCS Instruments EHD rig. This allows it to roll with minimal resistance, ensuring the contact is close to pure rolling. The carriage is mounted on the load arm, resting on two locating pins. The load arm itself is a stainless steel rod with a press-fit shaft halfway along its length. The other end of the load arm is threaded, allowing a counterweight to be moved accurately until the centre of gravity of the load arm, ball, carriage and counterweight lies directly in line with the pivot point. This allows a known load to be hung at a notch equidistant to the pivot point, directing a load through the contact. Such a system offers considerable simplicity compared to other means of loading but does require some care in order to ensure the system is balanced prior to loading.

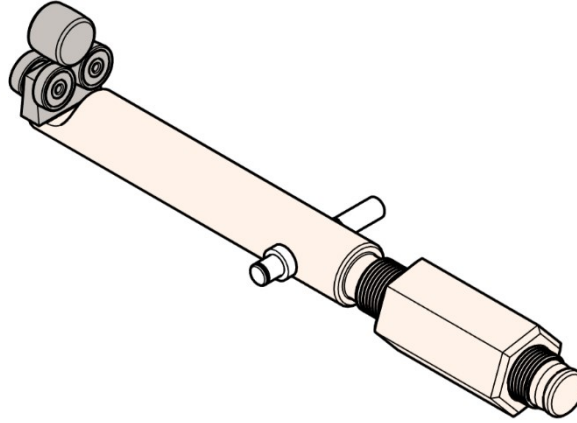


Figure 6.5: Technical illustration of the load arm, showing the barrel roller and carriage on the left and the adjustable counterweight on the right.

6.2 OPTICS

6.2.1 Camera and Light Source

A JAI CV-M9 CL camera is used to image the contact, featuring 3 CCD (charge-coupled device) sensors, giving superior colour discrimination compared to a standard colour camera. These types of cameras divert the incoming light onto separate CCD sensors according to the colour channel red, green and blue. With this method the colour crosstalk, the extent to which red light may trigger the green channel etc, is greatly reduced compared to the more common method of colour filters covering each pixel of a single CCD.

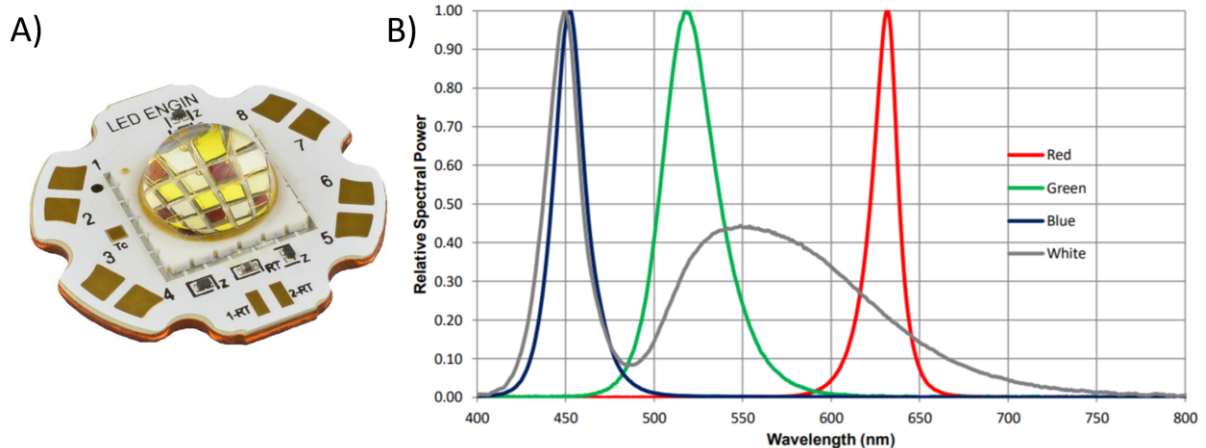


Figure 6.6: A) The LZR RGB LED array. B) The spectral distribution of each colour channel of the LZR chip, including the unused white channel.

The contact is illuminated with an RGB LED light source built around an LZP-L0MD00-0000 LED array, shown in Figure 6.6. This chip includes many individual LEDs and can draw up to 80W. Each colour channel is driven by an adjustable constant current circuit, allowing power of each channel to be balanced according to the camera's spectral response.

The advantage of using such a system is, firstly, that the extremely bright source enables short exposure times which are necessary when imaging very high-speed contacts. Secondly, the pseudo-monochromatic nature of LEDs is beneficial when imaging thick lubricant films. As the interference intensity is directly used to determine film thickness, it is ideal to have strong contrast between the light and dark fringes. The light emission from an LED can be described as pseudo-monochromatic (the spectral intensity is centred about a central point and rapidly diminishes away from that point) and it is this property, in contrast to broadband white light, that aids interference contrast. The interference between two out-of-phase waves will continue indefinitely if they are truly monochromatic but, as their bandwidths increase, the shorter wavelengths will interfere at different points to the longer wavelengths. This will result in loss of interference contrast and is demonstrated in Figure 6.7A, where the interference intensity of white light against film thickness is modelled for the real conditions of the lubricant contact. Figure 6.7B shows the same simulation but for the emission spectra of the LED array, providing distinct fringes up to 2 microns film thickness, enabling reliable film thickness measurement in this range. Note that it is not solely the light source emission that dictates this behaviour, but the product of the spectral emission and the camera's spectral response. This results in a non-gaussian distribution, particularly for the blue channel in the white light case, and consequently the interference intensity in Figure 6.7A does not diminish smoothly.

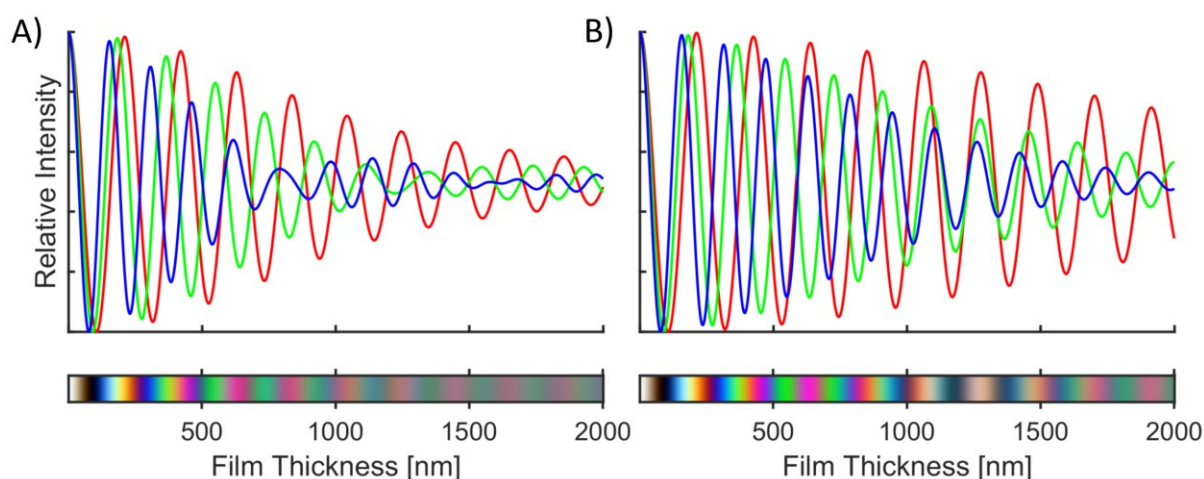


Figure 6.7: A) Simulated red, green and blue channel intensities against film thickness when illuminated with white light. B) Simulated intensities, illuminated by RGB LED light.

6.2.2 Microscope Optics

The use of a glass ring specimen, rather than the more common disc, creates a problem when using a microscope to image the contact. As the ring is curved in one direction but not the other it produces an anisotropic magnification, or astigmatism, resulting in a distorted image of the contact in which only one of the x and y axes may be focused at one time. This may not be a problem for spectroscopic measurement of the contact centre film thickness but prevents mapping of the film thickness across the whole contact using image analysis techniques.

Such an issue arose in the very first EHL film thickness measurement when Kirk analysed the contact between two cylinders and used a ‘rider’ to conform closely to the upper cylinder and effectively produce a flat upper surface [236]. This approach is not practical, however, when high speeds are involved.

Zhang et al. describe their solution to this problem when constructing their ball-on-ring rig [232]. By using the optical transfer matrix approach to analysing the optical system, they calculated the optimum position of a cylindrical lens that would compensate for the magnification and bring the focal point in the x and y directions together. Their solution involved placing the cylindrical lens in front of the objective lens, between the ring and objective. While this fixes the optical aberration, it is inconvenient to have an additional lens in this position, especially when it must be accurately located. Additionally, an infinity-

corrected microscope system is used in this project, introducing a tube lens in addition to the sole objective lens that was used by Zhang et al. (a finite-correction optical system). This meant the equations they derived for placement of the lens could not be used for this system and a new analysis was required.

$$S = M_{a3}M_{tube}M_{a2}M_{obj}M_{a1}M_rM_g \quad (14)$$

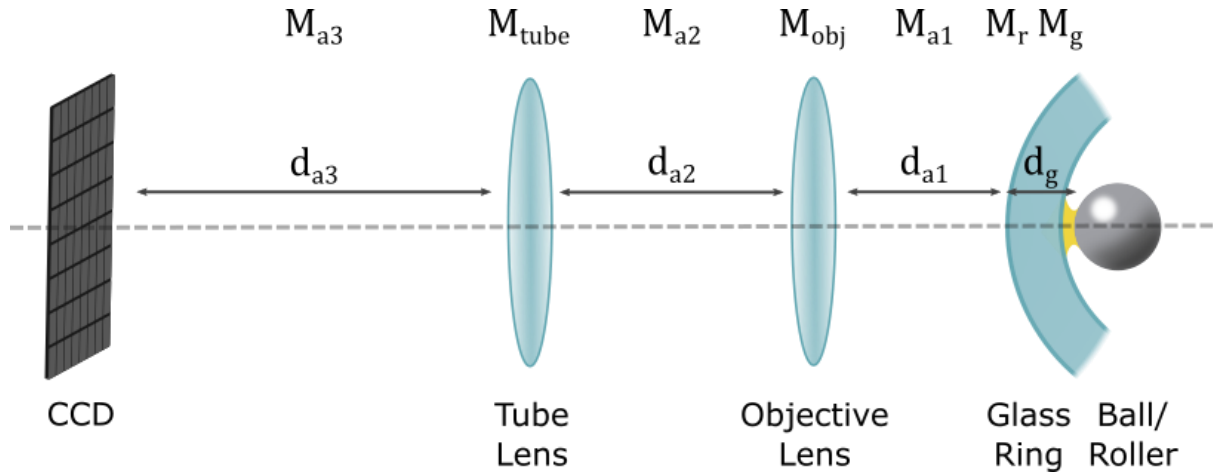


Figure 6.8: Diagram of the uncorrected optical system, showing each component and the corresponding OTMs. The optical transfer matrix (OTM) of an optical system describes the change in angle and position of a ray entering and exiting the system. It can be derived by multiplication of the subcomponents of the system such as lenses and optical media. S , the OTM of the uncorrected system, is represented in Eq. 14 and the subcomponents shown in Figure 6.8. M_{a1} , M_{a2} and M_{a3} represent the OTMs of the air distances between glass ring and objective, objective and tube lens, and tube lens and CCD respectively. When passing through an optical media the angle of a ray is unchanged and the OTM is simply:

$$M_a = \begin{bmatrix} 1 & d_a & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & d_a \\ 0 & 0 & 0 & 1 \end{bmatrix} \quad (15)$$

where d_a is the distance travelled. In most cases a 2D 2 x 2 matrix suffices for this type of analysis as the optic components are rotationally symmetric but in this case x and y must be treated separately. M_{tube} and M_{obj} represent the OTMs of the tube and objective lenses respectively. Each should be accurately represented by three matrices, the air-glass interface

at one surface, the glass medium itself and the glass-air interface at the second surface. The OTM of a curved change of media (in one direction) is:

$$M_{\Delta} = \begin{bmatrix} 1 & 0 \\ \frac{n_2 - n_1}{n_1 R} & \frac{n_2}{n_1} \end{bmatrix} \quad (16)$$

where n_1 and n_2 are the refractive indices of the first and second media and R is the radius of curvature of the first medium. If the lens is sufficiently thin it is possible to treat both the tube and objective lenses as simple thin lenses (though this is not very accurate for the objective which is comprised of many lenses). In this case, the d_a value of the second matrix (the glass medium) is zero and the OTM of all three simplifies to:

$$M_{lens} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ -\frac{1}{f_{lens}} & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & -\frac{1}{f_{lens}} & 1 \end{bmatrix} \quad (8)$$

where f_{lens} is the focal length of the lens. M_r represents the optical transfer matrix of the glass-air interface at the surface of the ring. As this component differs in the x and y axes, it is more complex than eq. 17 as the entire matrix must be used:

$$M_r = \begin{bmatrix} 1 & 0 & 0 & 0 \\ \frac{n_1 - n_2}{n_2 R} & \frac{n_1}{n_2} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & \frac{n_1}{n_2} \end{bmatrix} \quad (9)$$

In this case, $M_{r,43}$ tends to zero as the radius in that direction is infinite. Finally, M_g is the OTM of the glass ring itself which is of the form in eq. 15. As the refractive indices of glass and grease or oil are approximately equal, no refraction occurs at that boundary.

In order to achieve focus, the elements S_{12} and S_{34} of the overall OTM must equal zero. This is equivalent to stating that the final position of the ray is independent of its original angle in x or y, only its position. After substituting the real parameters of the system into these two equations, it is clear that they cannot simultaneously be satisfied as they require different values of d_{a3} and so an additional lens must be introduced. The OTM of the suitable lens, a

plano-concave cylindrical lens, can take the thin lens form, with magnification only in one dimension:

$$M_c = \begin{bmatrix} 1 & 0 & 0 & 0 \\ -\frac{1}{f_c} & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \quad (10)$$

Considering the difficulty in placing an additional lens in front of the objective, an alternative placement was considered. Ideally the lens could be situated behind the objective in the body of the microscope where it is trivial to introduce a lens, either between objective and tube lens or between the tube lens and CCD. The existing distance values cannot be changed in order to maintain focus so the lens must fit within an existing space. The parameters of the system are shown in Table 6.2.

n_1	n_2	f_{tube}	f_{obj}	d_{a1}	d_{a2}	d_{a3}	d_g	R
		(mm)	(mm)	(mm)	(mm)	(mm)	(mm)	(mm)
1.5	1	80	19	14.3	110	80	7	42

Table 6.2: Parameters of the optical system.

Both positions were tried, with various distances and f_c values trialed using MATLAB to allow easy modification of the system. When positioning the lens as shown in Figure 6.9: the corrected optical system, including a cylindrical lens between the CCD and tube lens. the equation for the OTM is:

$$C = M_{a5}M_cM_{a4}M_{tube}M_{a2}M_{obj}M_{a1}M_rM_g \quad (20)$$

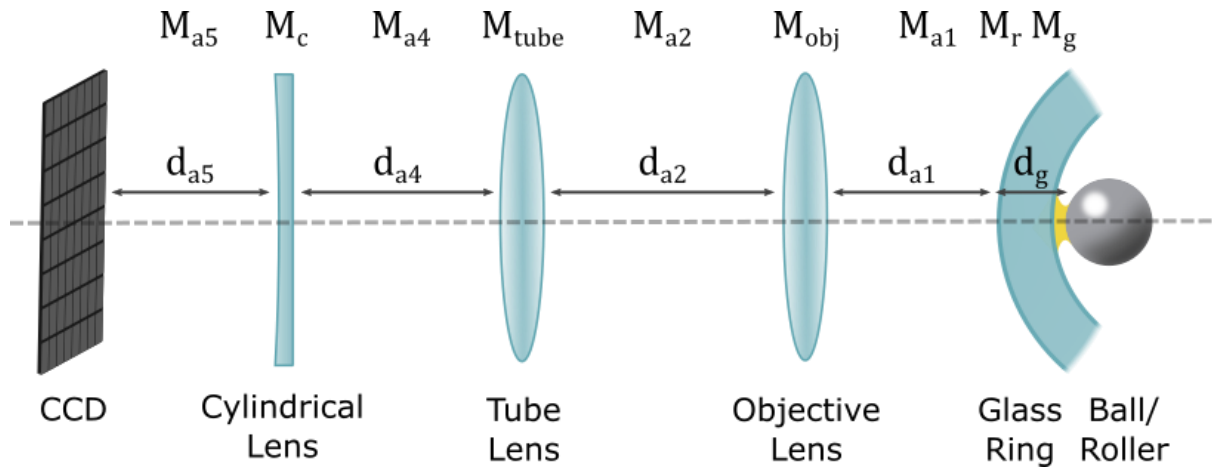


Figure 6.9: the corrected optical system, including a cylindrical lens between the CCD and tube lens.

The equation $C_{34} = 0$ can be solved using an f_c value of -400 mm for a d_{a4} value of 33 mm. This was deemed acceptable as it allowed a minimum of 33 mm of adjustment so that any errors in the optical analysis could be accounted for. The lens was placed in this position and then manually adjusted to achieve perfect focus. Figure 6.10 shows the original image with focus in only one dimension and the effect of the additional lens, bringing the entire image into focus at once.

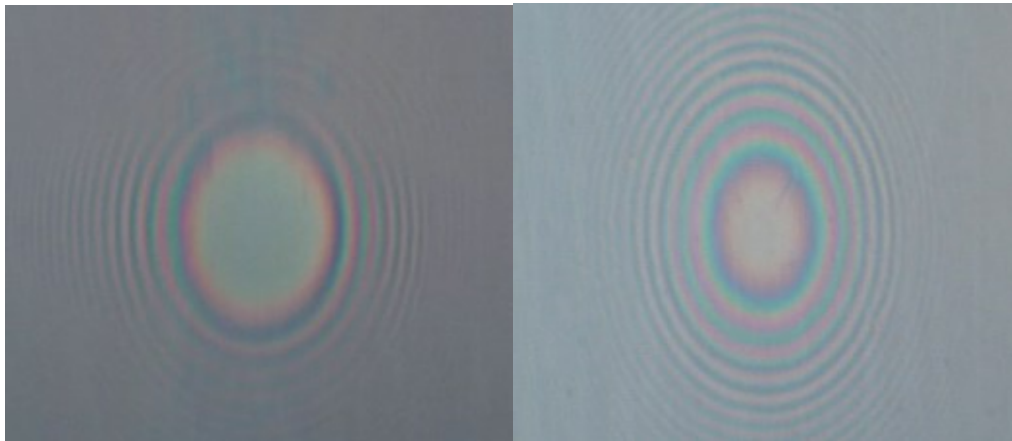


Figure 6.10: The uncorrected (left) and corrected (right) contact of a ball on the ring. Note that, due to the poor initial quality of the coating, the image contrast is poor.

6.3 SOFTWARE

MATLAB app designer was used to develop control and measurement software for the rig, and was planned to interface with both the motor controller and framegrabber to both control speed and record images. Unfortunately, the MATLAB app designer software was deemed too slow to rapidly record and save images and video files and so a program to do so was

developed using the Spera LT SDK, a software library provided by the framegrabber manufacturer, Teledyne Dalsa. This was written in C# and was significantly faster than the MATLAB alternative. The user interface of this program is shown in Figure 6.11. As MATLAB is able to easily interface with the Arduino and manage the speed control reliably, it was kept in use for that task.

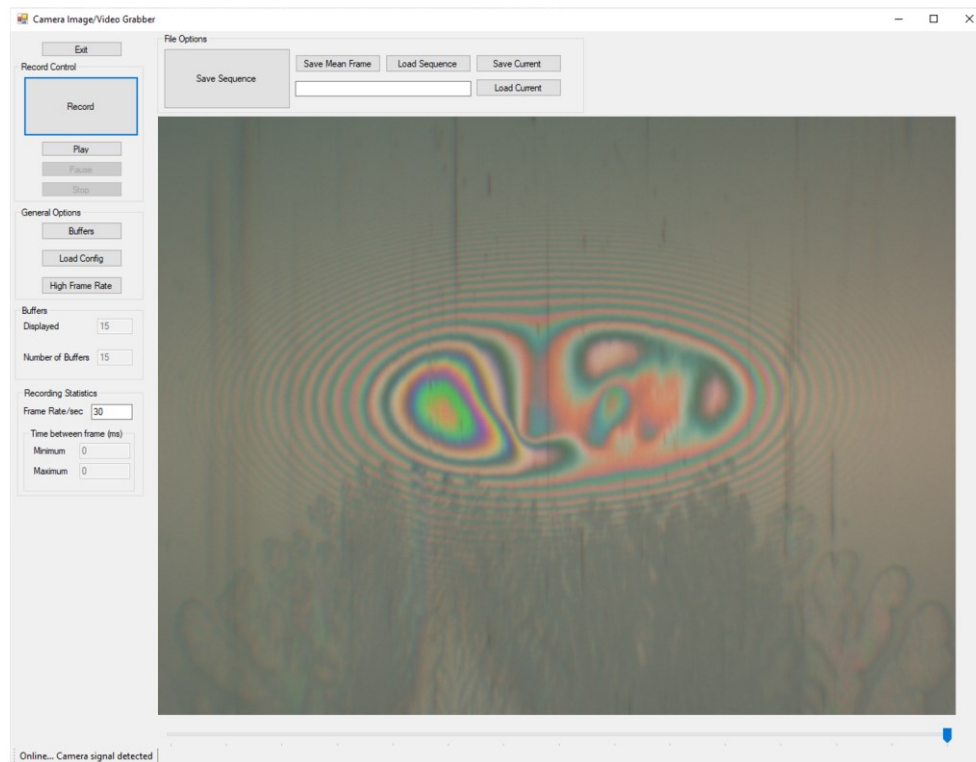


Figure 6.11: The image capture program in use. A specified number of frames are captured at a specified framerate and saved as a video file. Alternatively, those captured frames can be averaged and saved as a bitmap file.

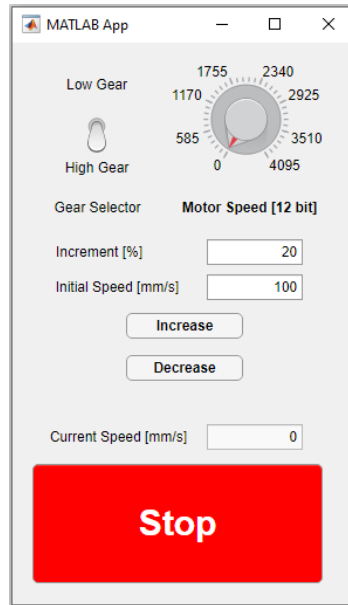


Figure 6.12: MATLAB speed control interface.

6.4 ANALYSIS

The recorded video files are post-processed using MATLAB to extract film thickness data for each frame. A SLIM-style process is used, where the RGB values of individual pixels are compared to a calibration curve, allowing the film thickness to be extracted as the value for which the error is minimum.

6.4.1 Calibration Curve

The accuracy of the calibration curve is vital for accurate calculation of film thickness and so the method of generating the curve must be considered. It is ideal to produce the curve immediately before testing as this prevents error due to changes in illumination or coating thickness since the time of calibration curve generation. Calibration curve generation in this work was performed using the Newton's rings beside the contact. As the radius of curvature of the barrel roller is very large in one direction, this produces a gradually increasing film beside the contact and the angle of the metal surface is low, hence the reflected intensity is reduced by only a small amount. In practice this means that the RGB values of areas beside the contact correspond closely to those within the contact, when film thickness matches.

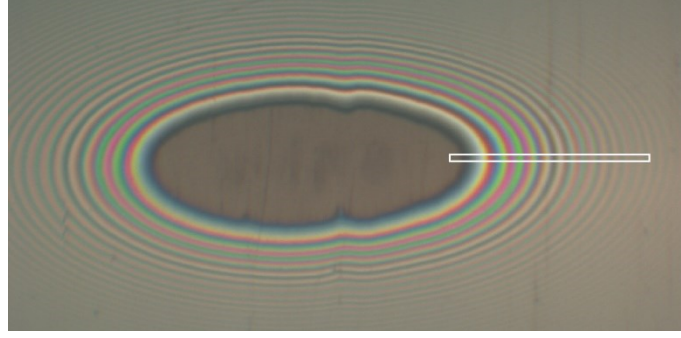


Figure 6.13: Example of the stationary image used for calibration, with the white-bordered region indicating where pixel values are extracted.

Figure 6.13 shows a typical image used for calibration prior to testing. The roller is loaded against the ring with lubricant present. This ensures the refractive index of the optical media is the same as in testing. The edge of the contact is manually selected and the intensities of the red, green and blue channels are extracted. The resulting curves represent intensity against pixel position. By imaging a graticule the size of the image, the position step per pixel can be measured and the intensity against distance from contact can be found. This must be transformed into intensity against gap height to be used for analysis which requires a relationship between distance from the contact and film thickness. This relationship can be derived using Hertzian contact mechanics as was performed by Molimard et al. [237] and Guegan et al. [238] or derived from the known interference behaviour of monochromatic light as used by Hartl et al. [239] and it is this method that was used in this work.

$$h_c = \left(N + \frac{\phi}{2\pi} \right) \frac{\lambda}{2n} \quad (21)$$

Equation 21 describes the film thickness, h_c , at which the constructive maxima appear, where N is the order number, ϕ is the phase change upon reflection, λ is the centre wavelength of the light and n is the refractive index of the optical medium. If the centre wavelengths of the RGB LED bands and the refractive index of the lubricant are known, it is possible to calculate the film thickness at which all the maxima appear and fit that to the intensities measured in the calibration image. This effectively accounts for the curvature of the barrel roller.

An additional consideration using this method is the phase change on reflection, ϕ . When the incident light reflects off the steel and chromium surfaces it undergoes a phase change which, for the chromium layer, is dependent on its thickness. The difference in these phase

changes results in a phase difference when the film thickness is zero. As a result, there is an interference at zero film thickness and consequently the contact is darker than a full reflection would be, as shown in Figure 6.13. This effectively shifts the interference fringes to a slightly lower film thickness and must be accounted for in order to accurately determine film thickness. Measuring the phase change on reflection can be done by simply measuring the light intensity within the contact at zero film thickness and comparing this to the first order minima and maxima which are at known phase positions.

6.4.2 Solving for Film Thickness

Once the calibration curve is generated it is possible to determine film thickness for any pixel by comparing the three values to the three calibration curves. Theoretically, the pixel colour values will match perfectly to a single value of film thickness, but in practice it is the value with least error that is deemed to be the correct value. Many problems could cause the measured RGB values to deviate from theoretical: a scratch or change in surface reflectivity, thickener that may be less transparent than oil or movement of the contact over the exposure time. These small deviations can result in erroneous solutions presented by simple algorithms designed to produce a value for each pixel individually. It is clear from Figure 6.7 that multiple film thickness values can have very similar RGB values.

The knowledge that adjacent pixels are unlikely to be severely discontinuous can enable a much more robust solution for automatically calculating film thickness. Even when thickener lumps enter the contact the film thickness surface is bumpy but smooth on the small scale. This means that the solution for a given region of pixels, e.g. a 100x100 square at the centre of the contact, can be iterated while minimising these discontinuities. Once a solution with no significant discontinuities is found, it is far less likely that an erroneous fringe order has been chosen. This is particularly true of regions with curved contact surfaces, i.e. a range of film thickness values are present.

Before finding the film thickness it is first necessary to locate the centre of the contact as this is where the RGB data must be taken from, if central film thickness is the goal. This is made more difficult as a consequence of attempting to reduce the slip at the contact. The friction of the carriage that supports the rolling element must be minimised in order to reduce the extent

of sliding. If the friction is too high the roller will not turn at all, and a pure sliding contact will result. One way to limit this is to not use any system of axial constraint and this results in the contact moving within the frame, generally limited to approximately one contact width or 0.5mm. The contact centre must therefore be identified at theoretically any point of the image.

The centre location was performed by a method of pattern recognition. This process can be explained simply as identifying the regions of the image where fringes of a certain size (in terms of pixels) are vertical and horizontal. This allows identification of the fringes outside the contact above and below, and left and right of the contact. Their row and column location then provides the contact centre.

This method employs the Gabor wavelet, a complex wavelet [240] (real part shown in Figure 6.14A). It is particularly suited for accurately locating image regions of similar ‘texture’ to the wavelet. The result of filtering an image is shown in Figure 6.14B and this data is then summed along the horizontal direction. The maximum value of the result (indicated by yellow colour) will indicate the centre row of the contact. This process is repeated in the vertical direction to find the centre column.

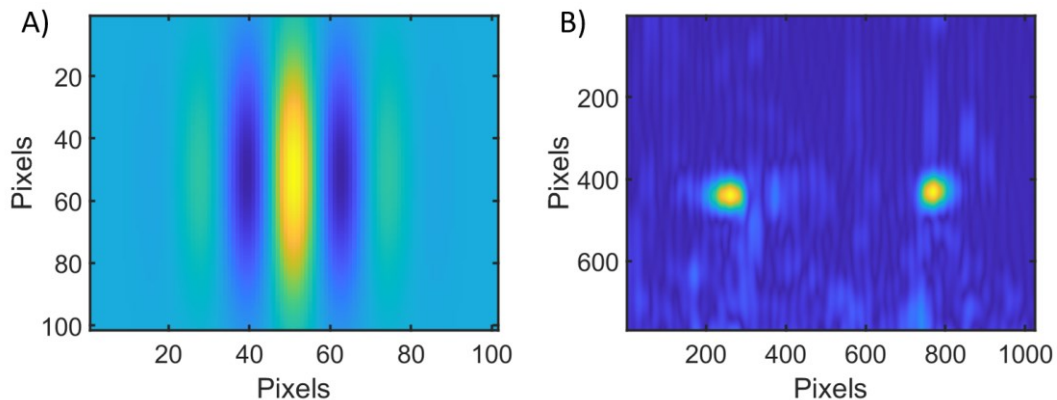


Figure 6.14: A) The real part of the Gabor wavelet. B) The result of filtering a typical image with the wavelet.

6.5 OPTICAL COATING DEVICE

A crucial element in the measurement of film thickness, if it employs thin-film interferometry, is the semi-reflective coating. The coating acts to divide incoming light into two beams which

then interfere with one another constructively and destructively. This produces the colourful images from which film thickness values can be extracted.

An extremely thin (typically less than 25 nm) layer of chromium is typically used for this purpose. While chromium does not have superior reflectivity, it is oxidation resistant, durable and adheres very well to the glass substrate. Fu et al. performed an analysis of EHD interferometry and calculated a reflectance of 19.8% and a transmission of 46.1% resulted in the maximum contrast between dark and bright fringes [241] which is therefore optimum for interferometry. They found that this corresponded to a Cr film thickness of 6-12 nm but also reported that films of around 20 nm are often used, likely due to variability in the refractive index of the deposited chromium, dependent on the deposition technique used.

Thin-film deposition techniques are divided into physical and chemical, and typically only the physical techniques are used for EHD film thickness measurement. These techniques operate by vaporising the material to be deposited, which then condenses onto the substrate. The simplest of these techniques is termed resistive thermal evaporation. In this case the heat is delivered to the sample through Joule heating of a heating element, often tungsten, which itself does not produce significant vapour pressure at operating temperatures. Figure 6.15 shows the vapour pressure as a function of temperature for chromium and tungsten, showing that useful chromium deposition pressures are achieved at temperatures exceeding 1400 K while the tungsten vapour pressure remains low and as a result does not contaminate the deposited film. This technique must be performed in a high vacuum in order to prevent oxidation of the deposition material at such elevated temperatures.

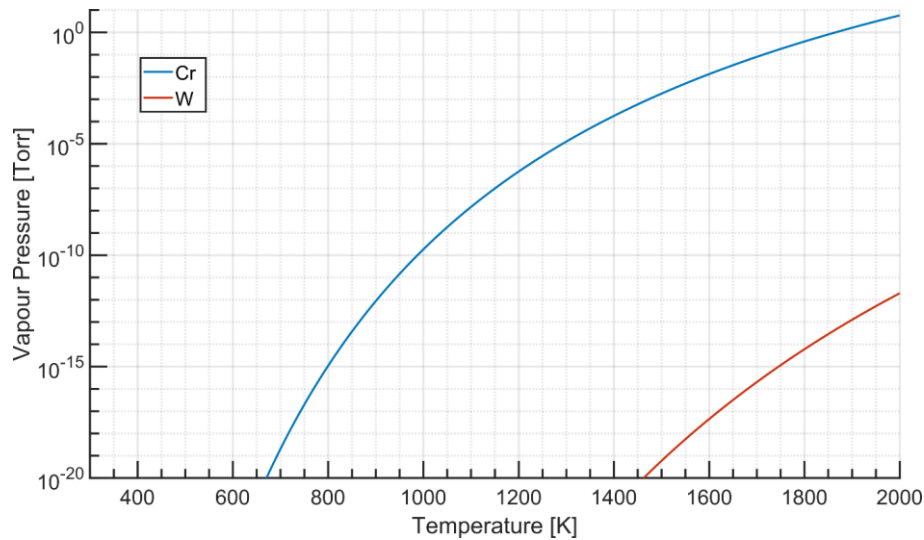


Figure 6.15: Vapour pressure of chromium and tungsten as a function of temperature. Fitted equations taken from [242].

As the coating process is performed under high vacuum the mean free path, the average distance a particle travels before it collides with another particle, is typically greater than a metre. This is beneficial in that it prevents collision with oxygen or nitrogen molecules that may react, but it also means that only surfaces in line-of-sight of the source are coated. For planar specimens such as those used in ball-on-disc testing this is not an issue, however if a ring is to be used then the internal surface must be coated which presents a problem as most coating systems are not designed for this task.

The majority of companies approached to perform coating for this project refused, however the single company that were willing to attempt it were unable to produce a usable specimen. As the fundamental mechanism of the coating process is extremely simple, it was deemed achievable to construct a bespoke coating rig for this purpose.

6.5.1 Design

The deposition of chromium is a common task for companies working in thin-film technology, however chromium is somewhat unusual in that it reaches a working vapour pressure well below its melting point of 2180 K. This presents difficulties in use, mainly that it is very difficult to heat the chromium granules under vacuum if there is minimal conduction from the tungsten vessel, only radiated heat. To solve this issue, chromium-coated tungsten rods are produced (sourced from Kurt J. Lesker Company) which may easily be heated by

high current passing through them and this heat is directly conducted to the chromium on the surface. Such rods are shown in Figure 6.16A. These rods are particularly suited to coating the internal surface of tubes. If the rod is aligned with the centre of the tube, a very even coating will be deposited.

The coating rig was built around this principle. A large borosilicate vacuum chamber contains a method of gripping and rotating a single ring axially, while a chromium-coated rod (filament) is inserted into its centre and heated, shown in Figure 6.16B. The coating thickness is controlled by setting a filament current and coating for a set time.

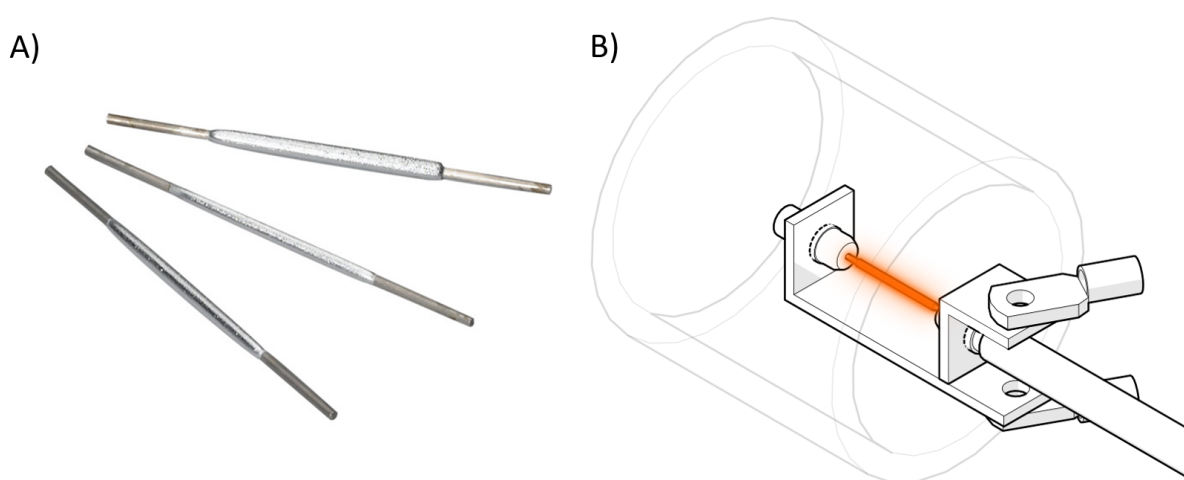


Figure 6.16: A) Chromium-coated tungsten rods. B) Diagram showing the filament assembly within the glass ring.

6.5.2 Chamber

The full coating rig is shown in Figure 6.17. A borosilicate tube of 180 mm internal diameter, 300 mm length and 10mm wall thickness was used as the main chamber. This allowed an excellent view into the chamber and glass is an appropriate material for high vacuum as it outgasses (emits vapour when under high vacuum) very little. In the interest of safety an excessively thick wall was chosen to reduce the risk of a catastrophic implosion. While the stresses exerted on such a vacuum chamber are significant, they are purely compressive and therefore the risk of material yield is very low. However, any accident in use may cause the glass to shatter and implode with significant energy, so it is necessary to reduce the risk of such a failure.

The chamber is capped by two acrylic endplates of 25 mm thickness. Viton rubber provides a seal at both ends. The endplates contain feedthroughs for the two shafts to support the ring and the filament assembly. Additional feedthroughs are used for passage of filament current and access for a vacuum gauge to measure pressure within the chamber.

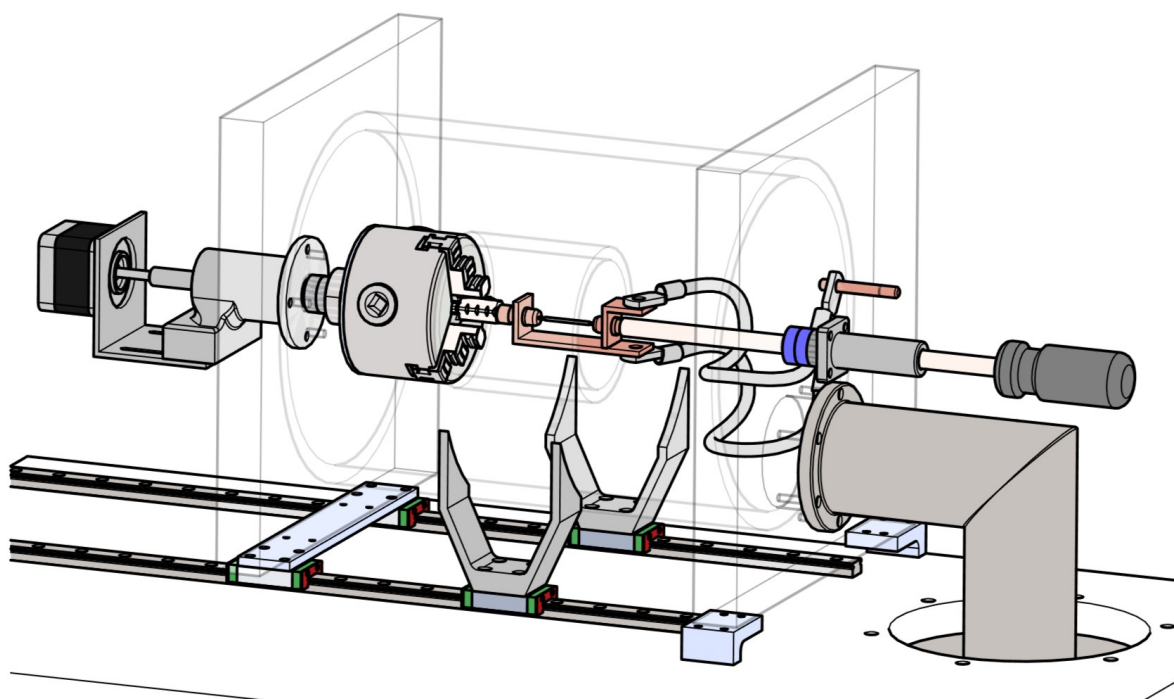


Figure 6.17: Illustration of the assembled coating rig. The acrylic endplates sit on either side of the glass chamber. One endplate and the chamber itself are mounted on linear rails to aid assembly and disassembly. The glass ring is held in a chuck and supported by a shaft passing through two seals. This shaft is driven by a stepper motor. At the other endplate the filament is supported, able to slide in and out of the centre of the glass ring. Wires carry the filament current to copper pins which are seated in the endplate. Also at this end a large stainless steel pipe connects the chamber to the vacuum pump.

Acrylic is an atypical choice for high vacuum systems, even amongst plastics which are seldom used in general, as it outgasses quite substantially for two reasons. Firstly, the simple outgassing of low-molecular weight molecules such as unreacted monomers, additives etc. Secondly, due to its polar structure it is hygroscopic, absorbing water from the air, and this will be released at a slow rate under vacuum. The second source can be mostly overcome by sealing and storing the system under vacuum, preventing reabsorption, while the first must be compensated for with a high pumping speed.

Such material choices were made due to the situation in autumn of 2020, when a solution to the coating problem was necessary, but manufacturing capability of the mechanical

engineering research workshop was reduced. This meant the necessary machining techniques such as boring flat-bottomed holes to seat bearings and seals would not be possible and therefore a more suitable material such as aluminium was not used. Such techniques were, however, achievable using acrylic with the tools available.

The shaft supporting the glass ring is mounted with a chuck on the chamber side, gripping the ring internally, and coupled to a stepper motor on the atmospheric side, allowing rotation of the ring at constant speed while coating. The shaft supporting the filament assembly is supported by a linear bearing which allows the filament to be brought into and out of the centre of the ring when desired. This can allow the filament to warm up outside the ring, expelling any surface contaminants.

6.5.3 Filament Assembly and Current Control

The chromium-coated rods are designed to operate at around 100-150 A, corresponding to a voltage drop of around 0.8 V and a power dissipation of around 100 W. To operate them, a very high-current, low-voltage source is required. For this purpose, a transformer was wound with ~350 turns on the primary coil and 3 turns of 25 mm² copper cable on the secondary, producing approximately 2 V when supplied with 230 V mains, current being limited to what the secondary winding will carry before overheating. Current control was performed with a TRIAC on the primary side of the coil, allowing a potentiometer knob to control the RMS voltage into the transformer.

This current is fed into the chamber through copper rods epoxied in place. The filament itself is gripped by a copper collet assembly on either end, originally designed for gripping TIG welding rods, which provides a low-resistance contact that is necessary when working with such low voltages and high currents. These assemblies are screwed into copper brackets that are supported by a shaft through insulated connections and the current is supplied via copper lugs connected to each copper bracket, shown in Figure 6.16B.

6.5.4 Vacuum Pump System

One of the simplest high vacuum pumps is the diffusion pump, a design that requires no moving parts and is able to achieve high pumping rates down to pressures as low as 10⁻⁸ Torr.

They operate through the action of momentum transfer, producing fast jets of vapour which collide with gas molecules and direct them out towards a second backing pump. This is achieved by heating of a silicone oil to $\sim 200\text{ }^{\circ}\text{C}$ and allowing the vapour to ascend a central tube and escape only through vanes directing it downwards. The hot vapour then condenses on the water-cooled walls of the pump chamber and flows back down to repeat the process. A diffusion pump with a maximum pumping speed of 150 L/s was used for this machine. A Leybold-Heraeus D2A dual-stage rotary vane pump with a pumping speed of 1 L/s was used as a backing pump and also as a 'roughing' pump, pumping down to <0.1 Torr above which the diffusion pump cannot be used due to potential oxidation of the pump fluid.

6.5.5 Outgassing

An MKS 901p vacuum gauge was used to measure vacuum pressure in this system. It contains both a diaphragm sensor for measuring low vacuum, and a Pirani gauge for measuring high vacuum pressure. The Pirani gauge operates by measuring the resistance of a constant-current heating element, assessing how effectively it is cooled by the surrounding gas. This method loses accuracy below 10^{-5} Torr beyond which there is little detectable change in cooling, and this is therefore the lower limit of the gauge. At this pressure the mean free path is calculated to be ~ 7 m, compared to the distance from source to substrate of 35 mm, and is therefore more than sufficient to perform coating.

As the machine was assembled, various leaks were identified, mostly due to aged O-rings which were easily replaced, and failed epoxy seals. The largest leaks were identified by audible hissing, while smaller ones were identified by application of isopropanol to the external surface. The isopropanol would flow into the chamber and visibly bubble and boil, as well as causing an indicated rise in pressure. Once an ultimate pressure of ~ 0.001 Torr had been achieved, it was difficult to tell if the main source of pressure was a small leak or outgassing and therefore where improvements could be made. One technique to diagnose this problem is to record the pressure rise over time. A constant pressure rise is indicative of a leak, while outgassing will tail off as the equilibrium pressure is reached. Figure 6.18 shows the results of an overnight recording of pressure rise. As the pressure begins to plateau above 1 Torr this suggests outgassing to be the cause. At this stage, the pressure difference across

any potential leak has only been reduced by $\sim 0.1\%$ therefore it is highly unlikely to be a change in leak rate.

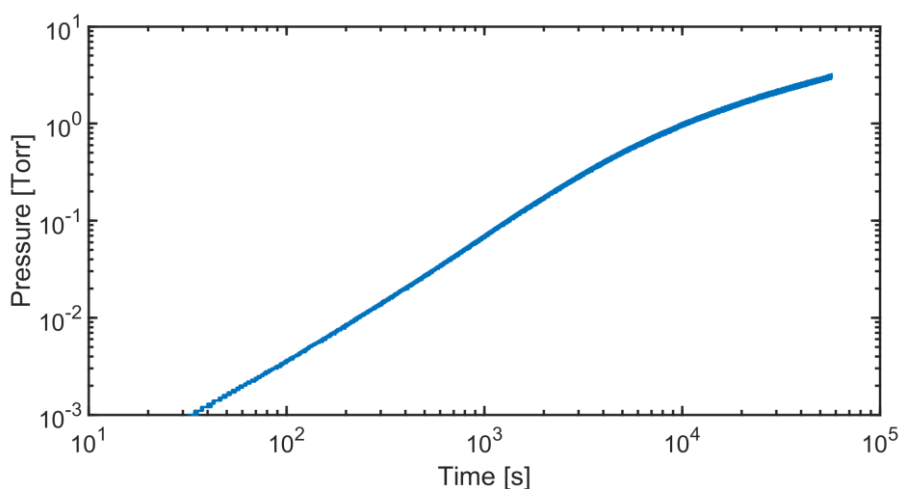


Figure 6.18: Pressure rise of the chamber over several hours, showing a levelling-off that is indicative of outgassing.

There were many potential sources of outgassing. The primary sources are likely to be materials that are heated and so the insulation of the high-current cables within the chamber were replaced as these warm considerably during use. The acrylic endplates are likely to be the largest source of outgassing due to their large surface area and so care was taken to maintain vacuum when possible and reduce the time that the internal surfaces of the acrylic were exposed to air. Cleanliness of the chamber is also important, all components exposed in the chamber were cleaned with isopropanol and warmed with a heat gun to evaporate volatiles from the surfaces prior to pumping down. These methods reduce the time taken to pump down to a set pressure, but the longer the pump down, the more outgassed mass is removed and so the limiting factor becomes how long can be spent pumping down. With all these techniques in place, a pressure below the lower limit of the Pirani gauge (10^{-5} Torr) was achieved within 2 hours.

6.5.6 Specimen Cleaning

As the specimens must endure extremely high surface stresses in operation, the deposited chromium film must be extremely well-adhered. In order for a deposited film to be adhere strongly to the substrate, the substrate must be extremely clean. All surfaces encountered in everyday life are coated with thin layers of organic, inorganic and microbial contaminants

that are difficult to remove with conventional cleaning methods. Typically, a plasma cleaning step is performed in-situ prior to thin-film coating which is able to clean the surface, leaving little to no residue and ‘activating’ the surface by oxidising surface atoms and leaving polar bonds [243]. This activation provides additional strength to film adhesion. The cleaning is performed by a variety of mechanisms, depending on the gas used. For air, the oxygen ions created by the plasma react with any organic matter, producing water and carbon dioxide which evaporate and can be pumped away. Inert gases will also clean surfaces by bombarding contaminants and breaking down molecules. The plasma is also emitting light in the ultraviolet spectrum, which is effective in breaking organic bonds, creating lower molecular-weight products.

For this system it was initially not deemed feasible to plasma clean in-situ and instead a cleaning procedure was developed utilising a separate plasma cleaner as a final step. The procedure included an initial clean with oxalic acid, intended to remove inorganic deposits such as limescale, which would not easily be removed during plasma cleaning. The cleaning procedure was as follows:

Cleaning Procedure
1. 30 mins in an ultrasonic bath in oxalic acid.
2. Rinse with deionised water.
3. 30 mins in an ultrasonic bath in Decon90 solution.
4. Rinse with deionised water.
5. 30 mins in an ultrasonic bath in isopropanol.
6. 30 mins in plasma cleaner using oxygen gas.

Table 6.3: Glass ring cleaning procedure prior to chromium-coating.

This procedure was unfortunately not sufficient to produce adequately adherent films. Adhesion is often tested in a simple manner with the ‘peel test’ by placing adhesive tape on the surface and peeling it off. The films readily resisted peeling off in this manner, however when testing in practice, they would delaminate under the high-pressure rolling contact conditions. The necessary adhesion was clearly significantly greater than typically required

for thin films. A number of modifications were made to the cleaning procedure in an effort to improve adhesion, such as longer cleaning times as well as covering the specimen in clean foil during transfer from the plasma cleaner to the rig. Heating the sample in an oven (wrapped in foil) prior to plasma cleaning was attempted to reduce condensation of contaminants from the atmosphere during transfer but no significant improvement was made. It appeared that upon exposure to atmospheric conditions (especially those of the tribology labs where organic solvents are commonly used) contamination occurred very rapidly. The only apparent solution was to perform plasma cleaning in-situ, as is done professionally.

6.5.7 RF Plasma Cleaning

There are many methods by which plasma can be produced, the most common for plasma cleaning being inductively-coupled and capacitively-coupled plasma. In this work, plasma was produced through inductive coupling. This technique is analogous to inductive heating, where a rapidly changing magnetic field induces eddy currents in a conductive material, heating it. As plasma is itself conductive, energy is transferred from an induction coil into the plasma. More technically, ions and electrons within the plasma are accelerated by the inductive electric field, itself a product of the rapidly changing magnetic field. Under atmospheric pressure the distance a charged particle is able to accelerate before colliding and dissipating its energy is typically too small to ionise the other particle. This prevents a cascade effect that will ignite plasma throughout the chamber. At approximately 0.1 Torr, particles are able to become sufficiently energetic to initiate such an 'electron avalanche'. Once pressure is brought significantly below this level, there are too few particles to sustain plasma and it is no longer possible to ignite.

Radio-frequency (RF) current is used in this process with various ISM (industrial, scientific and medical) bands in use: 40 kHz, 13.56 MHz and 2.45 GHz most commonly. These bands are designated for such purposes and emissions at these frequencies are not controlled. It should be noted, however, that despite the high powers used, solenoids are relatively poor emissive antennas, emitting a minimal amount of RF energy. The higher the frequency, the lower the energy required to generate the plasma, however the 'skin-effect' becomes stronger at higher

frequencies, resulting in the majority of the energy being dissipated in the surface of the plasma.

A Comdel CX-5000 RF source was used to generate current at 13.56 MHz, capable of delivering up to 3.5 kW of power, far greater than was required for this purpose. Typically, plasma cleaners use up to 100 W, with higher powers potentially eroding surfaces and increasing roughness. A 10 mm diameter copper tube was wound into a helix with 4 turns and placed around the vacuum chamber as the solenoid/antenna.

Connecting the RF source directly to the coil will result in very poor power transfer due to a mismatch of impedances. For a DC case, the maximum power transfer theorem states that the maximum power will be delivered into the load when the load resistance equals the source resistance. This is also the case for the complex impedances the source (RF generator) and load (induction coil) have when operating at RF frequencies. Technically, the load impedance must equal the complex conjugate of the source, however the sources are typically designed to have zero reactance. While the source resistance is a designated 50 Ω , the induction coil will have an unknown impedance at the operating frequency and in fact will vary as the plasma density within the coil varies. Not only is the power transfer very poor, but a significant proportion of the forward power is reflected by the load and dissipates within the source, potentially damaging it by overheating. As the RF source in this case is designed to dissipate far more power than was being delivered, this was not a concern, however the impedances must still be matched in order to deliver sufficient power forward.

An MFJ-949D antenna tuner was used for the purpose of impedance matching, connected between the source and load, and providing an adjustable impedance that transforms the source impedance to that of the load. This is done with adjustable inductance and capacitance settings, acting to store energy rather than dissipate it, and thus is considered lossless.

With the network appropriately tuned, plasma can be ignited at a low power of ~50 W and increased to the desired level. Figure 6.19 shows the RF generating setup in A), including the source, matching network and a spectral analyser used to monitor intensity of RF emissions. The display of the RF source indicates that the desired setpoint is 50 W and 44 W is being

delivered forward, with just 1 W reflected back due to an appropriate impedance matching. B) shows the plasma in use, a bright purple colour due the presence of nitrogen in the air.

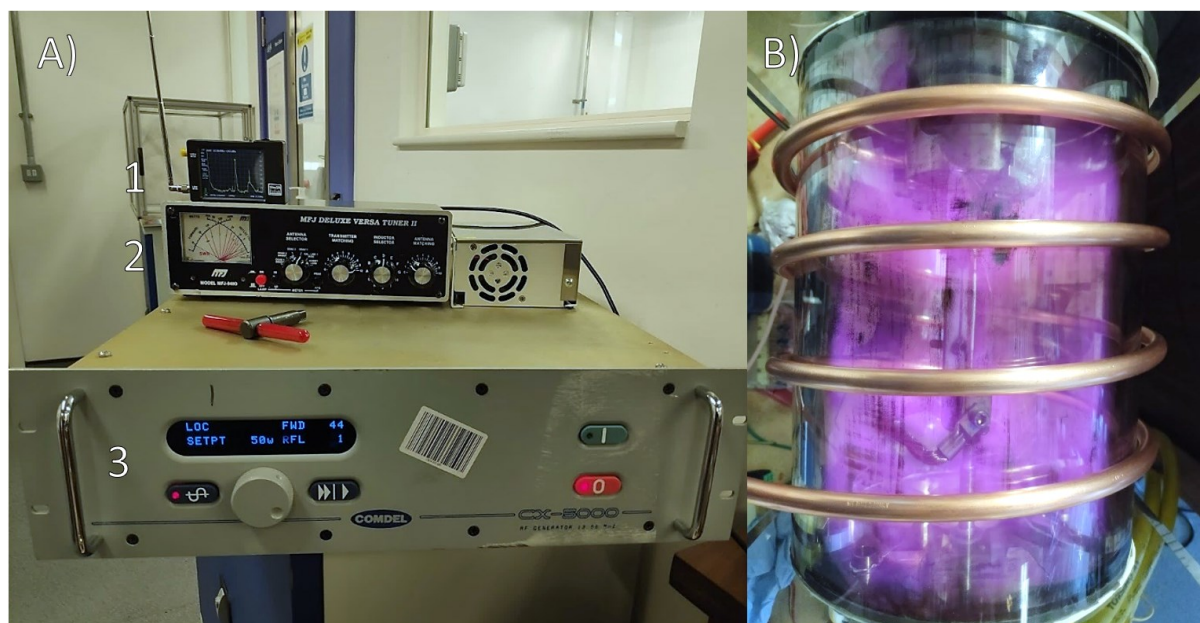


Figure 6.19: A) RF source (3), matching network (2) and spectral analyser (1). B) View directly above the vacuum chamber during plasma generation.

6.5.8 Coating

The same cleaning procedure was used as in Table 6.3, without the final plasma cleaning step prior to transferral of the specimen to the chamber. This ideally leaves only organic material on the surface. After pumping down using only the rotary vane pump to around 0.1 Torr, the plasma is ignited and left on for around 30 minutes to ensure surfaces are clean and the volatile gas products are removed. Once this is complete, the diffusion pump is turned on. A pressure below the limit of the Pirani gauge is soon reached, in fact aided by the plasma cleaning step. The plasma cleans all surfaces within the chamber, removing any contaminants that may outgas at very low pressures.

After the lower limit of the gauge has been reached and maintained for half an hour to ensure the pressure is stable and low, the coating process can begin. Initially the current is set to ~50 A to warm the filament and assembly and slowly increased to the starting current of 70 A. At this point the filament is inserted into the rotating specimen, beginning to deposit a chromium layer very slowly. Optimum adhesion is achieved when there is an intermediate transition layer of chromium oxide between the glass structure and the metallic chromium [244]. For

this reason, coating was started at this low level, allowing a greater proportion of the deposited film to oxidise compared to a higher deposition rate. This continued for 2 minutes before the filament was withdrawn. The current was then increased to 80 A, the filament allowed to settle at the resulting temperature and then reinserted. Coating continued for another 5 minutes at which point the desired thickness was achieved. These values of time and current were determined by trial and error, attempting to match the resulting appearance of semi-reflective films to known specimens.

A white-light interferometer was used to assess the thickness of the resulting films by imaging the border between the coated surface and an area where the coating had been gently removed with 4000 grit sandpaper. The resulting step change was measured as 11.8 nm, matching well the predicted values of 6-12 nm given by Fu et al. [241] that are required for optimum fringe contrast.

6.6 CONCLUSION

This chapter has described the design and, where of relevance, the manufacture of the single-contact bearing rig, as well as the coating rig required to produce test specimens. Successful development of this rig enabled further work to explore how this test system compares to existing systems, and what benefits in understanding grease lubrication are offered.

7 SINGLE-CONTACT BEARING RIG RESULTS

The preliminary results taken using the SCBR are shown in this chapter, including the validation of the system by comparing to the expected film-thickness versus speed behaviour predicted by empirical formulae for base oils. The starved film thickness results using greases are analysed and compared to the ball-on-disc EHD system and to results from real bearings, aiming to show that the SCBR better-replicates the reflow mechanisms present in bearings.

The single-contact bearing rig was proposed as a solution to the fundamentally different geometries of the standard ball-on-disc grease testing machines, and that of the bearings which are intended to be better understood by these tests. One issue with the ball-on-disc geometry is the additional centrifugal force that the lubricant experiences, significant at high speed. When attempting to understand starvation and reflow, this effect can dominate the true effects occurring in a bearing. The single-contact bearing rig does not introduce centrifugal force in the same way and therefore should be able to test up to very high speeds. In addition to the ring-shaped glass specimen, a barrel roller was selected as the rolling element. This creates a much wider contact than that of the ball-on-flat, better emulating the conformal contacts of a bearing, and forms large areas beside the contact where the glass and rolling element are separated by only a small distance. The latter characteristic of the contact has two effects, it is expected to increase capillary reflow as the capillary driving pressure is inversely proportional to surface separation [245], as well as provide a large area of high-shear, which is likely to increase the levels of shear degradation experienced by the lubricant.

With successful construction of the single-contact bearing rig and coating of the custom cylindrical glass specimens complete, there was insufficient time to perform a comprehensive range of tests with the new rig. Instead, it was only possible to test a select few greases in their fresh, sheared and thermally aged states. This would allow the results to be compared to the EHD results and provide some form of qualification, though it was predicted the behaviour may be quite different in these two test geometries. It would also allow observation of the effect of degradation on starvation, as this test rig is inherently likely to induce some level of starvation. The ball-on-disc setup and the barrel-on-ring setup can be compared in

the way they respond to shear and thermal degradation of lubricant. The same greases tested in Chapters 4 and 5 are used here, including the sheared and thermally aged samples.

One of the disadvantages of this rig is that the specimens and lubricant are not temperature-controlled and therefore testing must be performed at room temperature which was measured to be 25°C. Bearings generally operate at a higher temperature than this, either due to hotter ambient conditions such as those in electric motors [24], or self-heating from frictional losses. This would provide an obstacle to maintaining fully-flooded inlet conditions due to the higher lubricant viscosities, however, in this case, we are interested in observing starvation. The high viscosities will also produce very thick films under fully-flooded conditions which are typically quite difficult to measure. As discussed in Chapter 6, the LED illumination of the contact was selected to allow distinct interferometric fringes even up to films of 2000 nm.

Each lubricant test began with a brief run-in step, running at 100 mm/s for 2 minutes in order to distribute the lubricant around the ring. Following this, a speed sweep began from 0.03 m/s to 9.5 m/s in logarithmically spaced points, with 15 images captured at each speed. The speed was then brought back to zero, and two more speed sweeps were taken immediately without resupplying any lubricant. The maximum speed reached varied as the chromium layer was at risk of abrasion under starvation at high speeds and caution was taken to prevent this.

7.1 BASE OIL FILM THICKNESS

The first test performed with this rig used the base oil of the CaX 100 and CaXB 100 greases, having a kinematic viscosity of 100 cSt at 40°C. This test served as a form of validation, allowing comparison to the predicted film thickness according to the Chittenden equation that applies to elliptical contacts such as the one formed between a barrel roller and the glass ring in this test rig [246]. It should be noted, however, that under the expected semi-starved conditions of this system, agreement with these equations is likely to be limited to the lowest speeds. As is discussed below, further analyses can be applied as an attempt to compensate for the effects of inlet shear-heating and starvation on film thickness.

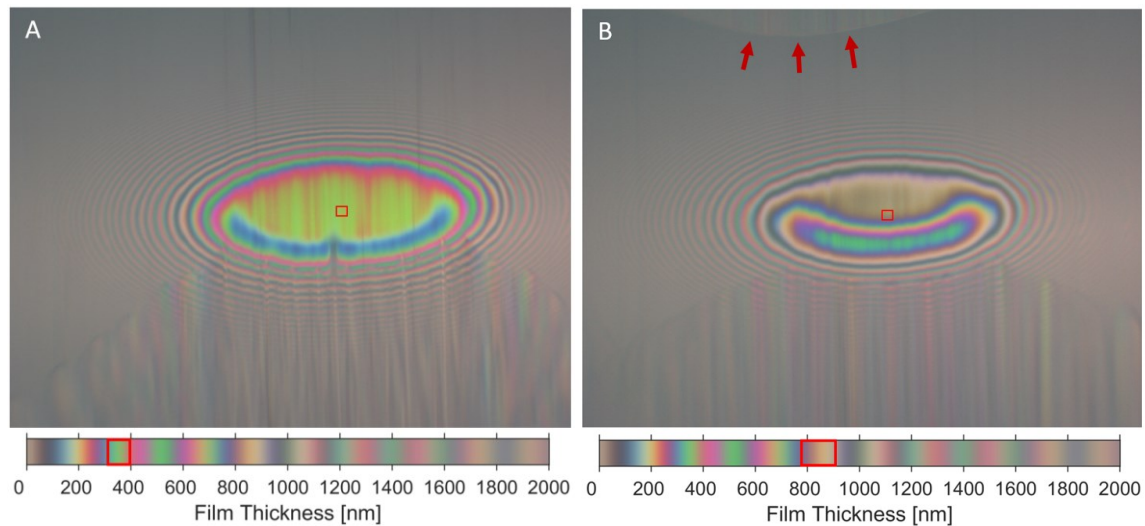


Figure 7.1: A) Example image of the oil-lubricated contact at 0.16 m/s, showing the centre of the contact and the matching region of the calibration that corresponds to this film thickness. B) Example image taken at 0.97 m/s, showing a film shape indicative of a relatively high slide-roll ratio, and an inlet meniscus that is nearing the contact, indicated with red arrows.

Example images that were used to calculate film thickness are shown in Figure 7.1A) and B), and Figure 7.3. The corresponding ring speeds are 0.16, 0.97 and 3.49 m/s. The low-speed contact appears quite standard, however, the contact at 0.97 m/s begins to show a film shape that is indicative of a relatively high slide-roll ratio (SRR). While the MTM testing in previous chapters was conducted with a SRR of 5%, approximating that of a bearing which is generally between 3-5% [170], and the EHD testing was ostensibly under pure rolling conditions, the roller in this case may be slowed by friction in the supporting carriage. In the work by Zhang et al., in which a similar ball-on-ring system is developed and tested with PAO oil, they observe a significant increase in SRR as the speed of the ring is increased, tending to a value of 1.75 [233], shown in Figure 7.2.

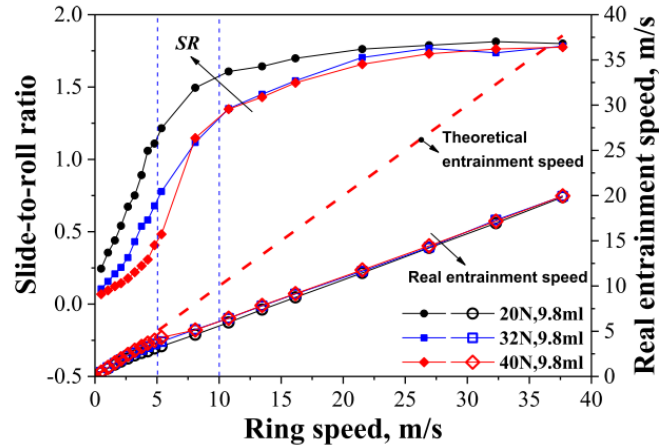


Figure 7.2: Slide-roll ratio and real entrainment speed against speed of the rotating ring in the work by Zhang et al.. Reprinted from “Experimental study of EHL film thickness behaviour at high speed in ball-on-ring contacts” [233] with permission from Elsevier.

In this work it is apparent from the contact film thickness profile, in which the contact minima merges with the flatter central region more gradually, that a similar effect is occurring. This is in contrast to low SRR film shapes which feature a flat central region and sharp decrease to the film thickness minima, even up to high speed. Measured results are therefore plotted against ring speed as opposed to assumed entrainment speed.

It is not possible to measure the speed of the rolling element in the SCBR, though the use of a magnetised rolling element and hall sensor as used by Hili et al. [247] and Zhang et al. [233] is a simple and easy-to-implement solution to this problem. Given the similarities of the system used in this work and that of Zhang et al., a crude estimate of SRR can be obtained with a linear fit from 0.05 at 0.03 m/s to 1.5 at 10 m/s to match their findings. Where a predicted film thickness is plotted, it is corrected for this SRR and is plotted against the ring speed, rather than entrainment speed.

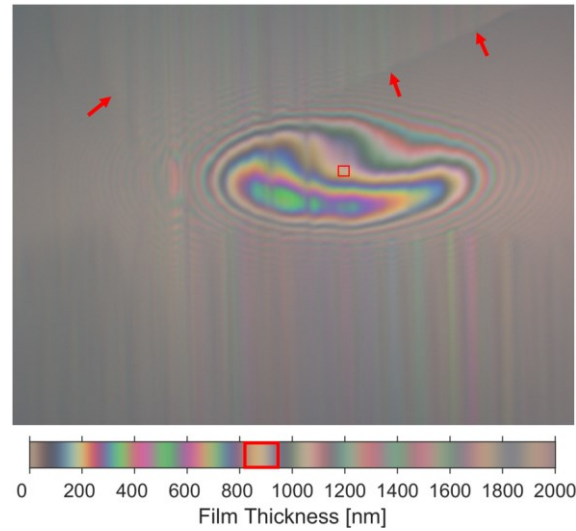


Figure 7.3: Example image of the oil-lubricated contact at 3.49 m/s, showing the inlet meniscus reaching the left edge of the contact, causing a severe drop in film thickness on that side. Arrows highlight the meniscus which is less clear to observe due to motion blur at this high speed.

The high-speed image in Figure 7.3 shows the clear effect of starvation as the inlet meniscus has reached the contact on one side, significantly reducing film thickness. This is generally a chaotic occurrence, leading to high variations in film thickness.

The film thickness results for the base oil are shown in Figure 7.4, each run plotted separately, and example images shown for the indicated speeds. As with the film thickness results in Chapter 5, the solid lines represent the mean values from all 15 frames at each speed, while the shaded region represents the 99% confidence interval. The Chittenden film thickness prediction is shown in black, corrected for assumed SRR. While the first run appears to undergo a brief starvation around 0.8 m/s, it recovers at higher speed and the subsequent runs vary only in the film thickness limit reached at high speed. This plateau of film thickness begins at approximately 1 m/s, reaching a constant value of ~ 1000 nm, however the deviation from the predicted base oil film thickness begins at a much lower speed. Agreement with the Chittenden prediction is very good at the lowest speed, but begins to deviate at 0.1 m/s, assuming a straight power-law relationship with speed in this log-log plot, but at a significantly lower speed exponent. The Chittenden equation predicts $h_c \propto U^{0.68}$ but the exponent in the region from 0.1 to 1 m/s is 0.58 for this test. This is quite a significant deviation from values reported in the literature as standard variation for fully flooded film thickness: 0.62 – 0.77 [248]. Paouris et al. observed values as low as 0.57 when measuring film thickness

under the influence of inlet shear heating and starvation [249]. It is clear that starvation is occurring in this work and, given the low test temperature, high speed and SRR, it is to be expected that inlet shear heating is occurring also.

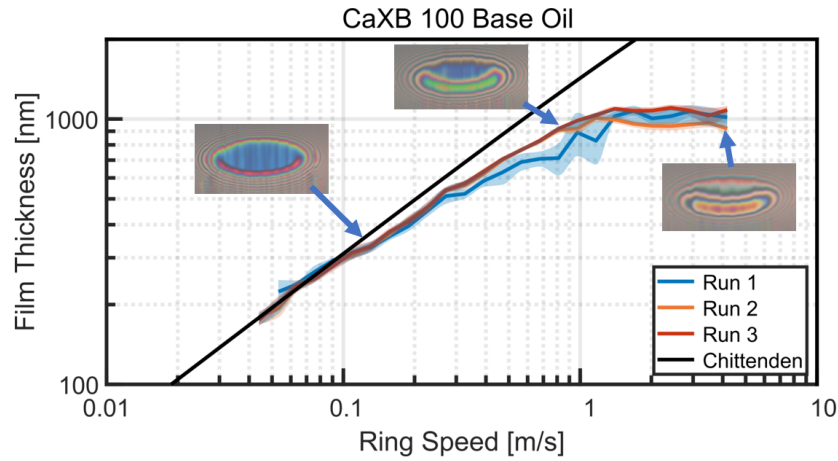


Figure 7.4: Measured film thickness of the CaXB 100 base oil, with example contact images at the indicated speeds. Results compared to predicted values from the equation developed by Chittenden et al. [246].

In order to estimate the impact of these effects on film thickness further analysis was performed, firstly by applying the “thermal reduction factor” Φ_T developed by Gupta et al. [250], which has been widely used in a multitude of papers [47], [233], [247], [249], [251], [252]. It is defined as:

$$\Phi_T = \frac{1 - 13.2 \left(\frac{p_0}{E'} \right) L^{0.42}}{1 + 0.213(1 + 2.23SRR^{0.83})L^{0.64}} \quad (22)$$

where p_0 is the maximum contact pressure, E' is the reduced Young’s modulus and L is the thermal loading parameter:

$$L = -\frac{\partial \eta}{\partial T} \frac{U^2}{K_f} \quad (23)$$

Here, η is the dynamic viscosity of the lubricant, U is the entrainment speed and K_f is the thermal conductivity of the lubricant. Clearly the thermal loading parameter is strongly dependent on the entrainment speed, but also of importance is the derivative of viscosity with temperature. The Vogel model of viscosity variation with temperature was fitted to the measured viscosity for the CaXB 100 oil and is shown in Figure 7.5, demonstrating a large

increase in $-\frac{\partial\eta}{\partial T}$ at the test temperature of 25°C, compared to the test temperatures of previous work, 40°C or 80°C.

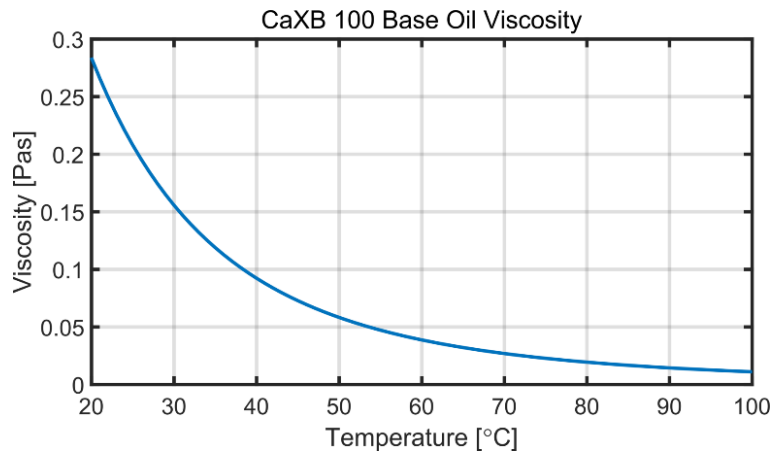


Figure 7.5: Viscosity of the CaXB 100 oil as a function of temperature, according to the Vogel model.

This leads to quite a significant thermal reduction factor at high speeds in these conditions. The measured film thickness (runs 2 and 3 combined) are shown in Figure 7.6, along with the film thickness prediction corrected for inlet shear heating. Despite the significant effects of shear heating at the highest speeds, it is clearly not sufficient to explain the observed film thickness results.

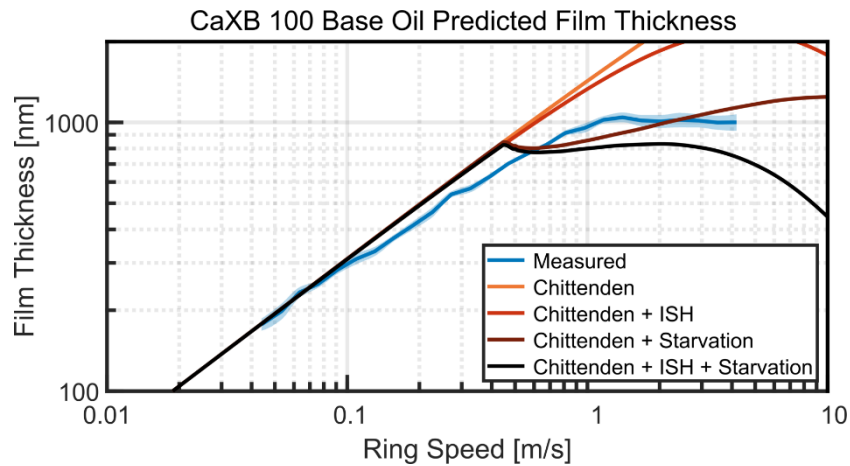


Figure 7.6: Comparison of measured and predicted film thickness for the CaXB 100 oil. The Chittenden prediction is shown corrected only for the SRR, as well as corrected for inlet shear heating (ISH) with the Gupta thermal reduction factor, and starvation with the Zaretsky model.

Also shown in Figure 7.6 are predictions corrected for the effects of starvation. A review of the starved EHD film thickness models is provided in the literature review in Chapter 2, and it is concluded that there is great difficulty in developing accurate models without knowing

detailed information about the inlet meniscus position or the thickness of the lubricant film in the track. The Zaretsky model of starvation was developed using first-order approximations to provide an estimate of the effect of starvation on bearing film thickness using just the material parameter $\bar{G}$ and the speed parameter $\bar{U}$ [141]. It was applied by Paouris et al. in their analysis of film thickness and friction under conditions of starvation and inlet shear heating with reasonable accuracy [249].

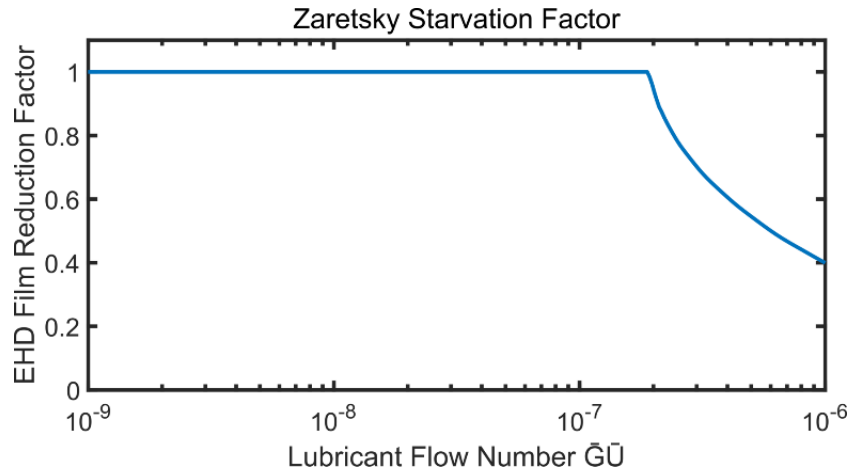


Figure 7.7: Zaretsky film reduction factor as a function of lubricant flow number which increases with entrainment speed. For low speeds the value is 1, but at a flow number value of 2×10^{-7} the factor abruptly decreases.

Figure 7.7 shows the film reduction factor due to starvation according to Zaretsky, fixed at a value of 1 at low speeds but sharply reducing film thickness at high speed where $\bar{G}\bar{U}$ is greater than 2×10^{-7} . The behaviour above this value has been extracted from the plot in [141]. As seen in Figure 7.6, the Chittenden prediction is sharply decreased above the critical value of speed, ~ 0.5 m/s in this case. The rate of film thickness increase is high enough to mean that, despite the Zaretsky correction, the film thickness begins to increase even after starvation has begun. When both inlet shear heating and starvation effects are combined there is a film thickness plateau predicted from around 0.6 – 3 m/s. The starved predictions both predict a lower film thickness observed than was measured by experiment, however. The other failure of these models is in the low-speed behaviour, where a change in the film thickness gradient was observed through experimentation, but not predicted by either of the models used here, which only begin to show large effects at high speed. It should also be noted that while the effects of inlet shear heating and starvation are directly combined here, they are in fact highly

interdependent. Under starvation the volume of lubricant being sheared will be far smaller, reducing the shear heating effect, and under shear heating the viscosity of the lubricant will fall, reducing starvation [249]. Therefore, a direct combination is likely to underestimate film thickness as observed here.

This attempt to account for the effects of sliding, inlet shear heating and starvation has brought the film thickness prediction closer to that observed in experiment but relies on an assumed SRR. It is possible that a more detailed starvation analysis and a more appropriate combination of the shear heating and starvation effects might yield a closer film thickness prediction but in an ideal case this would be possible with information available a priori, rather than inlet meniscus position for example. By extending the problem to non-Newtonian greases the matter is further complicated, now requiring such detailed information about the rheology of the degraded grease that prediction is currently not feasible.

7.2 GREASE FILM THICKNESS IN STARVED CONDITIONS

7.2.1 CaXB 100

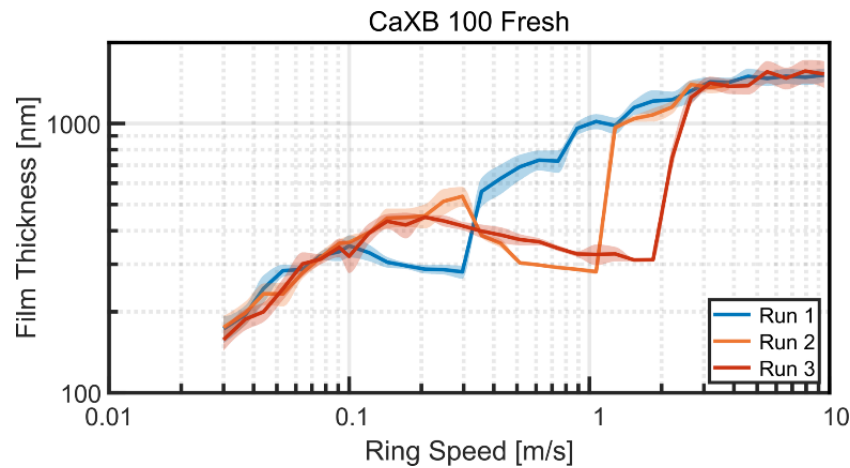


Figure 7.8: Film thickness results for the fresh CaXB 100 grease, showing three runs.

The film thickness results for the CaXB 100 grease are shown in Figure 7.8, displaying measurements for three speed sweeps as with the base oil. While the general behaviour is similar to that of the base oil, all three runs display significant periods of starvation. The first run starves at just 0.1 m/s but quickly recovers after a brief decay of film thickness with speed. In the second run a higher speed is reached before starvation, but the drop in film thickness

is much greater, falling to around 300 nm as in the first run. In this run, film thickness recovers only at 1 m/s. The third run reaches a higher speed than the first run before starving but this period of starvation lasts much longer, with film thickness reducing until a speed of 2 m/s is reached. Once this speed is reached, the film thickness continues to increase, plateauing much more gradually than the base oil and reaching a much higher film thickness. Apart from at the highest speeds, the film thickness of the grease is very similar to that of the base oil, ignoring regions of starvation.

Despite the brief run-in before the first run, the effect of running time is clearly present, with the last run displaying the most significant starvation behaviour in the medium speed range. What is unexpected is the recovery of film thickness at higher speeds which was also observed in the ball-on-disc testing. In that case it was assumed to be a consequence of the high centrifugal force acting on the lubricant, however in the case of the SCBR there is no such force to cause bulk transport of the lubricant on the ring. Centrifugal force will exert a 'flattening' force on lubricant beside the track, acting to aid a similar effect caused by surface tension and hence increase the rate of spread of thick films which could contribute to reflow, however this is an effect that would also be observed in any radial bearing. The majority of film thickness testing performed on bearings involves testing at constant speed for a period of time and there is little research demonstrating behaviour in similar speed sweeps. Baly performed speed sweeps on bearings with three greases and observed intermittent film thickness increases as speed increased, with one grease undergoing a prolonged period of increasing film thickness as speed increased [18]. Longer term tests using the SCBR would be worthwhile and allow comparison to the plentiful research on constant speed bearing tests.

An alternative explanation for this spontaneous resupply at high speeds is the effect of lateral motion of the roller. In order to limit the resistance of the roller's rotation, no mechanism for axial location of the roller was used. This was necessary to limit the already high SRR, but allowed significant motion of the roller, particularly at high speed. It has been found that lateral vibration of a rolling contact can increase grease film thickness at high speeds [253], which could also explain the increase in film thickness. It is not clear how this relates to real

bearings, which contain rolling elements constrained by a cage that will allow a small amount of motion, and therefore may also benefit in a small way from such a process.

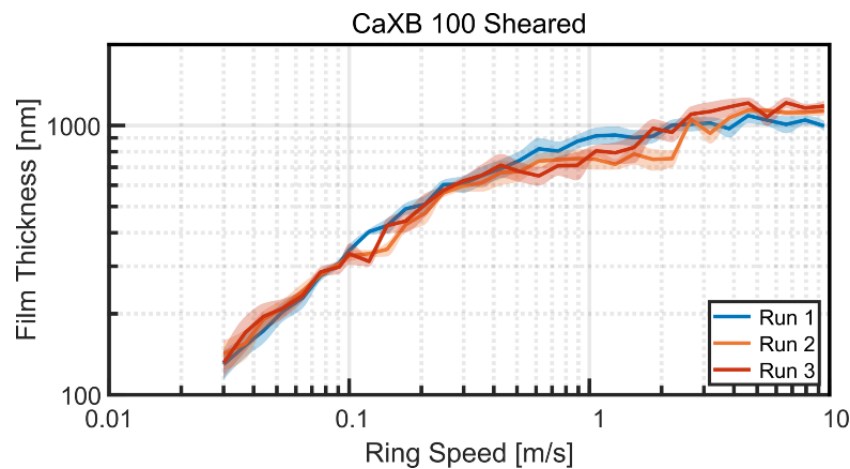


Figure 7.9: Film thickness results for the sheared CaXB 100 grease sample, showing three runs.

Shearing the CaXB 100 grease for 168 hours in the roll stability tester has significantly changed the measured film thickness, shown in Figure 7.9. Up to around 0.2 m/s, when starvation began in the fresh grease, the behaviour is similar, however, the sheared sample does not appear to display significant starvation. Only a small decrease in film thickness is observed around 1 m/s in the second and third runs. In contrast to the linear increase in film thickness of the fresh grease and base oil up to the plateau, this sample appears to reduce the rate of increase and transition to the plateau region more gradually, perhaps due to a more consistent and increasing level of starvation. Also notable is the lower maximum film thickness reached at high speed which is consistently lower for the sheared grease, in fact matching closely that observed from the base oil testing. This suggests that, despite the common assumption that high-speed film thickness is base oil-dominated, the integrity of the thickener contributes to film thickness at these high speeds, increasing by ~25%. There is little difference in the variance of the film thickness as the films are generally too thick to observe the thickener lumps that are likely to be larger in the fresh grease. During starvation in the fresh grease, however, the variance can be extremely low, which suggests a consistent rate of reflow.

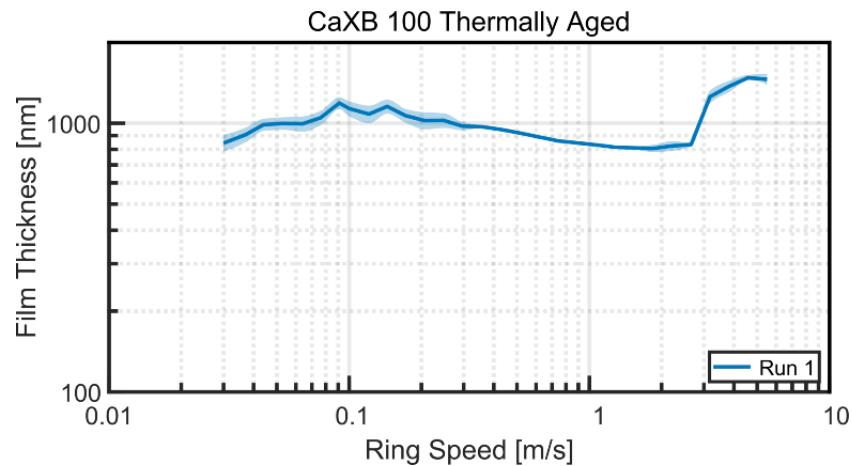


Figure 7.10: Film thickness results for the thermally aged CaXB 100 grease sample, showing just one run.

Due to the complete loss of consistency and extremely high viscosity of the thermally aged CaXB 100 sample it was only tested for one run as the other samples were considered more important for the time-pressured testing. It is clear from the high film thickness at just 0.03 m/s that the viscosity is extremely high. Very little film thickness increase is observed before starvation begins to limit film thickness. Interestingly, despite the extremely high viscosity and obvious starvation, the starved film thickness remains very high.

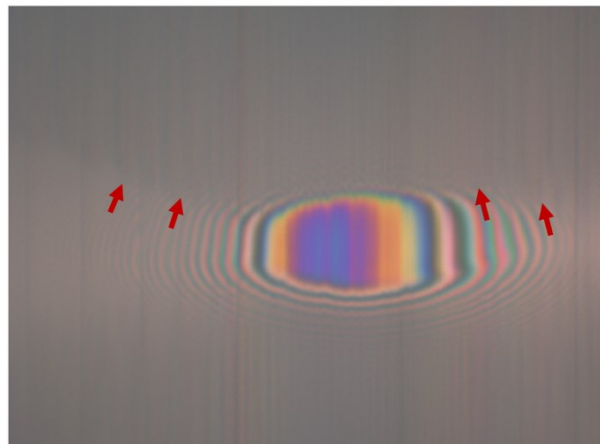


Figure 7.11: Image of the thermally aged CaXB 100 sample rolling contact at 1.84 m/s, showing severe starvation, yet relatively thick films due to sufficient lubricant on the track. The meniscus is shown approximately by the red arrows, though the image blur makes this observation difficult.

As observed in the contact image in Figure 7.11, at a ring speed of 1.84 m/s, the film thickness is high (around 800 nm) despite the inlet meniscus reaching the contact on the left-hand side. The contact film at that point is therefore produced solely by lubricant remaining on the track. This is a transient phenomenon however, and this supply of lubricant decays over time and number of overrollings [140], [254], [255]. Were this test extended for repeat runs, the film

thickness would be expected to reduce as observed in the CaXB 100 fresh sample. Evidently the reflow rate of the sheared CaXB 100 sample was sufficient to maintain film thickness during the test.

7.2.2 Li 100

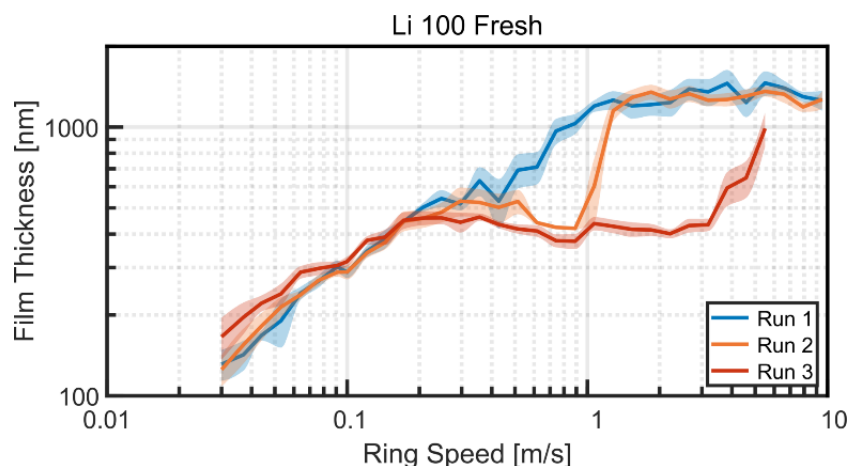


Figure 7.12: Film thickness results for the fresh Li 100 grease, showing three runs.

The SCBR film thickness results for the Li 100 fresh grease sample are shown in Figure 7.12. Noting that the base oil viscosity of this grease is 100 cSt at 40°C, it is possible to compare it generally to the results for the CaXB 100 base oil. The first run is fairly similar to this base oil but shows larger variance across the entire speed range as well as generally higher film thickness. Only during a period of temporary starvation from 0.3 – 0.7 m/s is film thickness lower than the base oil. At the highest speed, where film thickness becomes mostly constant, the achieved film thickness is significantly higher than the ~1000 nm achieved by the base oil.

For the second run, the behaviour is similar until the point when starvation began in the first run, however now a much more significant reduction in film thickness is observed and film thickness begins to decrease with speed. At 1 m/s a complete recovery occurs, and film thickness returns to the value seen in the first run. The third run begins to starve at a slightly lower speed and maintains a lower film thickness in the 0.3 – 1 m/s region. At 1 m/s a small increase in film thickness is seen, however the complete recovery seen in the second run does not occur. A more gradual recovery is seen at 4 m/s, appearing to approach the value of the previous runs, but at this point the test was stopped out of concern for the semi-reflective coating. Looking at the very lowest speeds, there is a small increase in film thickness in the

third run that could be attributed to thickener deposition, however, due to the low test temperature of 25°C the V-shaped curve seen in previous testing has been shifted to lower speeds. This means the thickener effect will be relatively small, if present at all.

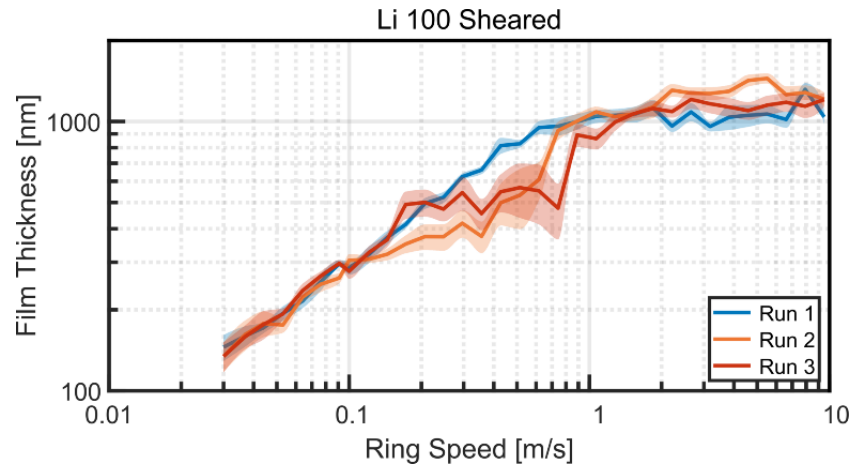


Figure 7.13: Film thickness results for the sheared Li 100 grease sample, showing three runs.

Shearing of the Li 100 grease sample, film thickness shown in Figure 7.13, has improved the starvation response as in the CaXB 100 grease, but not to the same extent. The first run is entirely unstarved, and in fact shows a gradient of 0.64 which matches the Chittenden prediction of 0.68 more closely than the base oil value of 0.58. The subsequent runs do undergo starvation in the mid-speed region, however, but to a much lower degree than the fresh grease and recovery occurs at a lower speed. Another difference between the starvation behaviour compared to fresh is the variance of the starved film thickness. The very high variance here indicates a film that is intermittently recovering due to increased reflow, compared to the fresh grease which reached a relatively stable point of starvation.

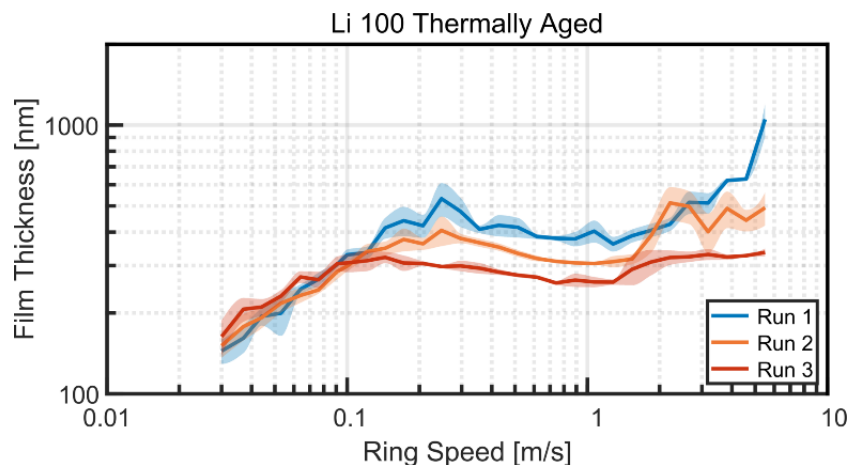


Figure 7.14: Film thickness results for the thermally aged Li 100 grease sample, showing three runs.

The thermally aged Li 100 sample in Figure 7.14 demonstrates much more severe starvation than previously observed. Even at high speed in the first run the film thickness does not recover completely. Subsequent runs demonstrate progressively lower film thickness and initiate starvation at a lower speed. The last two runs show relatively stable film thickness in the mid-speed region, evidently achieving a stable reflow. Clearly, thermal aging has lowered starved film thickness compared to fresh, while shear degradation has increased it.

7.2.3 PU 220

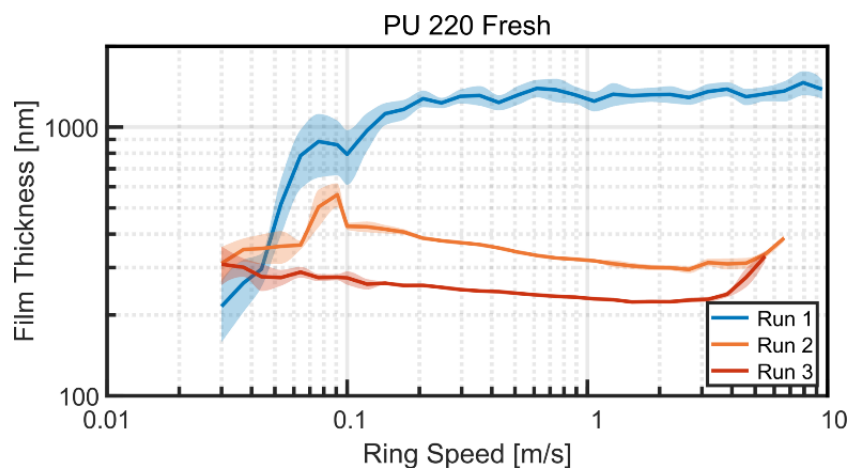


Figure 7.15: Film thickness results for the fresh PU 220 grease, showing three runs.

Results for the higher viscosity PU 220 fresh grease are shown in Figure 7.15. The first run displays extremely thick films even under 0.1 m/s, caused by entrainment of thickener lumps which boost film thickness enormously, as shown in Figure 7.16. At a speed of just 0.2 m/s a plateau is reached, not increasing in film thickness despite more than an order of magnitude

increase in speed. After this initial run, the behaviour is changed drastically. Starvation begins at 0.1 m/s for the second run and the third run begins in a starved state. A slight increase in film thickness at the highest speeds is seen for these runs but for the most part they exhibit very stable, decreasing film thickness.



Figure 7.16: Image of the rolling contact at a ring speed of 0.076 m/s, lubricated by the PU 220 grease.

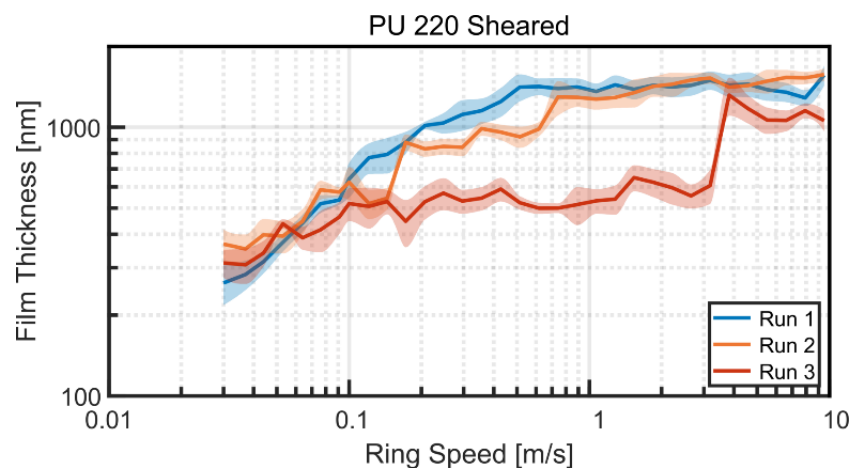


Figure 7.17: Film thickness results for the sheared PU 220 grease sample, showing three runs.

The sheared PU 220 film thickness results in Figure 7.17 show a large increase in film thickness in the mid-speed range, undergoing starvation in the third run but recovering at higher speed and not reaching such low values of film thickness. During starvation in the second and third runs, the variance indicates a greater variability in the lubricant reflow, intermittently resupplying and increasing film thickness. At the lowest speed in the first run no thickener lumps are observed and the film thickness is much lower, behaving much more like a high-

viscosity base oil. In both the fresh and sheared samples an increase in film thickness around 0.03 m/s after the first run might indicate the deposition of highly viscous thickener layer, as observed in the bearing raceways in Chapter 4.

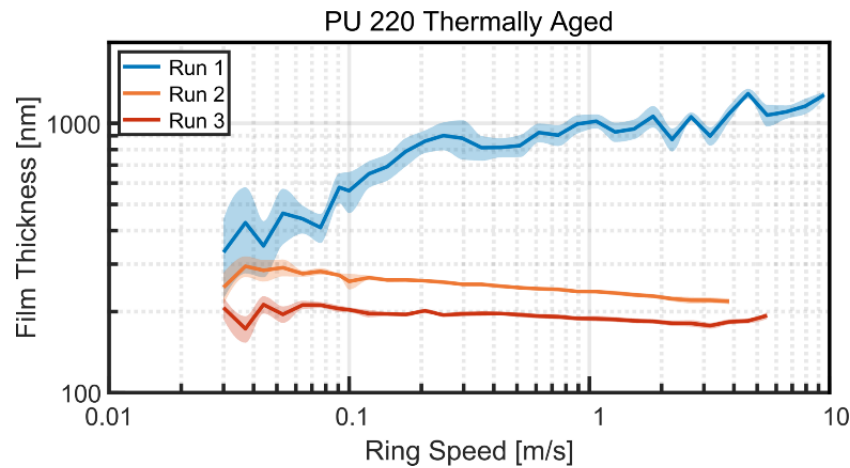


Figure 7.18: Film thickness results for the thermally aged PU 220 grease sample, showing three runs.

Figure 7.18 shows the film thickness of the thermally aged PU 220 sample. Compared to the fresh grease, the first run shows different behaviour at low speed. High film thickness is seen in the thermally aged sample at speeds of ~ 0.04 m/s, with no boost over the sheared grease film thickness around 0.08 m/s. This is reversed in the fresh sample, suggesting the way thickener lumps are entrained has changed, possibly as a result of change of the size of the lump, or a change in lubricant viscosity which lowers the speed at which the thickener effect is seen. The first run appears to slightly starve after 0.3 m/s and displays lower film thickness than fresh or sheared grease from that point on. The second and third runs are then severely starved, again, showing very low variance in film thickness, indicating a stable state of reflow has been achieved. The third run shows an almost-constant film thickness of around 200 nm, suggesting that the reflow is increasing with speed in a way that almost perfectly counteracts the reduced time for reflow that follows increasing speed. Even in this final run, there is an indication of increasing film thickness at the highest speed. As with the two previous greases, thermal aging has been shown to reduce the ability of a grease to resist starvation, while shear degradation has increased this ability.

7.3 REPLENISHMENT ANALYSIS

In comparing the performance of the barrel-on-ring SCBR, ball-on-disc EHD and real bearings, it is useful to account for the widely differing speeds, as well as viscosities at the test temperature. Degree of starvation has been directly associated with the entrainment velocity and viscosity [256] and further work has developed this relationship. Cann et al. assessed starved oil film thickness in a ball-on-disc rig as a function of an SD (starvation degree) parameter, including the track width, the surface tension of the oil and the film thickness of lubricant adjacent to the track [257]. Recent work by Cen and Lugt [258] analysed film thickness in a bearing with a range of greases and used a simpler parameter – the product of speed, viscosity and contact half-width. Using this parameter, they found that film thickness decayed in a power-law that could be described by:

$$\frac{h_g}{h_{ff}} = \left(\frac{s}{u\eta b} \right)^d \quad (24)$$

where h_g is the film thickness of the grease, h_{ff} is the fully flooded film thickness at that speed, s is a fitting parameter indicating the onset of starvation, $u\eta b$ is the starvation parameter, consisting of u the entrainment speed, η the base oil dynamic viscosity and b the contact half-width. The final variable, d , is another fitting parameter, representing the decay rate of film thickness. Using this equation, Cen et al. found a good fit to their bearing results using $s = 1.27 \times 10^{-4}$ and $d = 0.791$. With these parameters, this equation then represents the onset and decay of film thickness in greased bearings. In the same work, the authors modified the equation found in [257], describing the decay of base oil film thickness in a ball-on-disc system, and determined values of $s = 1.8 \times 10^{-6}$ and $d = 1.671$, representing starvation at a much earlier $u\eta b$ value, as well as a more sudden decay. This implies a much more severe condition in ball-on-disc rigs, where replenishment is insufficient to provide full films beyond low speeds.

By applying the same equation to the ball-on-disc results in this work, shown earlier in Chapter 5, a comparison can be directly made between grease performance in ball-on-disc and bearing conditions. Figure 7.19 shows a comparison between the two fits described above, and a fit based on the grease-lubricated EHD rig data from section 5.2.2, ‘EHD – Film

Thickness Under Starved Conditions’ on page 174. Also shown are the data points used to achieve the fit.

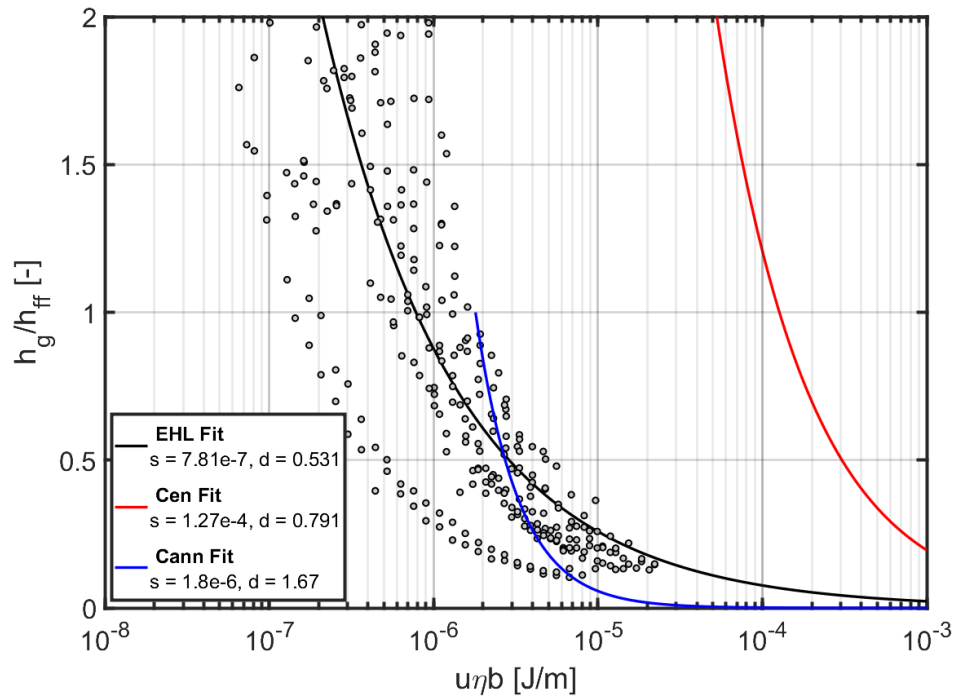


Figure 7.19: Plot showing the relationship between relative grease film thickness and the starvation factor. Three fits are shown: the Cen fit in red which was based on data from a greased bearing [258], the Cann fit in blue which is a modification of the paper’s original fit and is based on starvation in an oil-lubricated ball-on-disc rig [257], and the current work in black which is based on grease-lubricated ball-on-disc data.

The data includes only fresh greases, rather than the degraded samples. When high-speed recovery occurred, this deviated greatly from the trend and so those data points were excluded. The CaXB 100 sample was excluded entirely as it underwent starvation, or $\frac{h_g}{h_{ff}} \ll 1$, immediately, and then began a steady recovery which deviated from the trend seen in the other data. A non-linear least squares regression method was used to fit the equation to the cleaned dataset. Bisquare weighting was applied to minimise the effect of mild outliers.

The plot shows a significant difference between the starvation behaviour of greased bearings (Cen fit), and oil-lubricated ball-on-disc tests (Cann fit), exemplified by the different fitting parameters. The s value for bearings is almost 100x higher, meaning that starvation initiates in the ball-on-disc device, but not in bearings, at a notionally similar replenishment rate. This implies that the replenishment of the ball-on-disc system is, in fact, impeded in comparison to bearings. The fit from this work is quite different to that of oil lubrication, despite being

measured on the same rig. Grease appears to initiate starvation at a lower $un\eta b$ value (roughly half of the oil s value), but decays in film thickness at a much lower rate ($d = 0.531$ compared to 1.67), much more like the behaviour of grease-lubricated bearings. It is clear that there are some outliers, two runs evidently beginning starvation at a low speed. These two runs are from the PU220 grease. Starvation is chaotic in nature and such outlying behaviour is expected.

Comparing the greased ball-on-disc fit to the bearing fit, the decay behaviour is relatively similar, but the onset of starvation occurs at a far lower starvation parameter. The results of Jacod et al. [223] and Cen et al. [258] both suggest that the bulk of reflow in bearings occurs in the vicinity of the contact and not in the time between overrollings. Effective simulation of bearing reflow should, therefore, be possible with a single-contact system, however ball-on-disc testing clearly causes starvation at a much lower $un\eta b$ value which implies that reflow mechanisms differ strongly. The difference could simply be an offset in the starvation parameter, which would mean ball-on-disc results are applicable to bearings, but it is more likely that the difference is due to a different balance of reflow mechanisms and therefore results cannot be assumed to be valid for the bearing case. By bringing the single-contact system closer to that of the bearing, the s value should increase, and emulate bearing contacts more accurately.

The SCBR results have been analysed in the same way as those of the EHD rig. The fresh grease results are plotted in Figure 7.20. In this case, only the last run of each of the three fresh grease samples was analysed. This compares more accurately with the EHD results, which had a far longer run-in and did not show such significant development of starvation with each successive run.

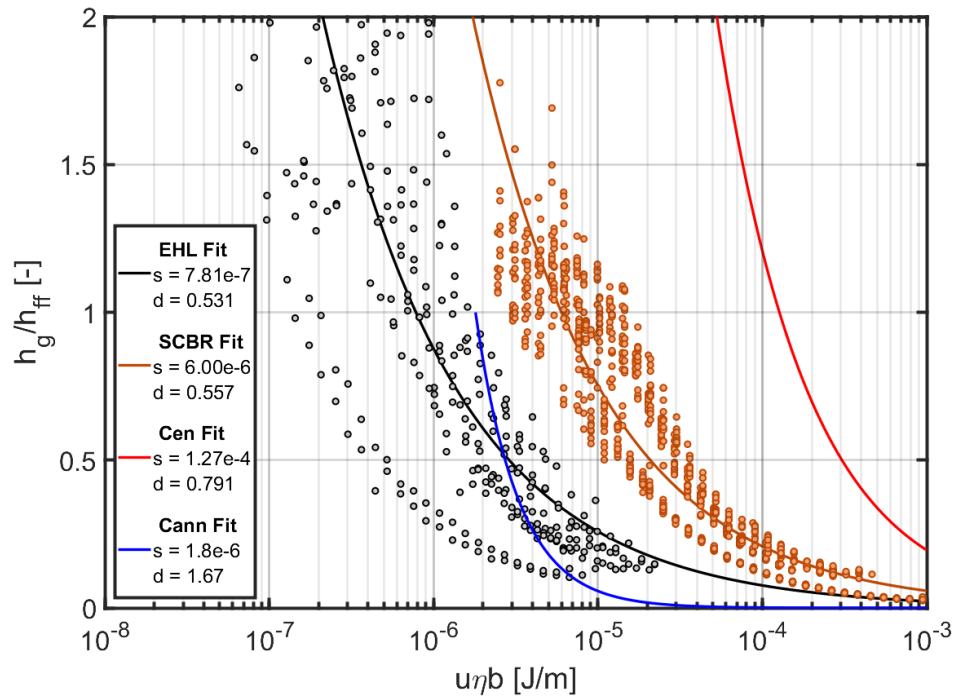


Figure 7.20: Plot showing the relationship between relative grease film thickness and the starvation factor. In addition to the greased bearing, oil-lubricated ball-on-disc and grease-lubricated ball-on-disc results, the grease-lubricated SCBR results are shown in orange.

The SCBR results show a generally tighter grouping than those of from the EHD rig, though the PU 220 results clearly initiate starvation at a much lower starvation parameter and give a distinctly lower relative film thickness throughout the test. The fit, however, shows that starvation begins at a much higher value, an almost 10x higher starvation parameter. The decay rate is similar, but slightly closer to that of the bearing fit. The SCBR evidently allows replenishment to occur at a greater rate than the EHD rig, allowing thick films even at cool temperatures and high speeds, which would cause extreme starvation in the ball-on-disc system. Most importantly, the behaviour is much closer to that of bearings, which suggests that the reflow mechanisms are more closely related and the predictions from this test rig are likely to be more accurate than those of a ball-on-disc system. The Cen fit begins starvation at a $u\eta b$ value more than 20x higher than the SCBR fit, meaning there is still significant improvement before a single-contact rig can be claimed to accurately emulate bearing lubricant reflow. The changes introduced in the SCBR may help inform how such a rig might be developed.

The two differences in geometry that are likely to aid/not inhibit reflow are the ring, which eliminates centrifugal force as an influence on lubricant motion, and instead applies it as a force which acts to smooth the lubricant in the rolling track, as would happen in a DGBB. The second change is the use of a barrel roller rather than a ball, and may be a more important influence on the reflow in the contact vicinity, providing narrow gaps beside the contact along which capillary forces can cause lubricant reflow. Despite this change, the size of such gaps is significantly narrower in bearings, which are, as a rule, highly conformal contacts. In order to further improve this, a roller with a larger radius could be used. That solution would retain the relatively simple manufacturing of the rings, but an alternative which would more accurately match bearing geometry would be to include a groove within the ring and roll a ball or barrel roller within it. This would also allow centrifugal force to accelerate lubricant back into the centre of the groove. Only a shallower roller would be required, according to the findings of Jacod et al. [223] and Cen et al. [258] that reflow is predominantly based on mechanisms surrounding the contact. Despite this, work has shown that the cage can strongly influence grease film thickness in ball-on-disc rigs [133] as well as influence the size of oil reservoir in an oil-lubricated model bearing [259]. A design featuring a cage surrounding a barrel roller with a large radius would appear to be a good compromise between accuracy of bearing emulation and ease of manufacture.

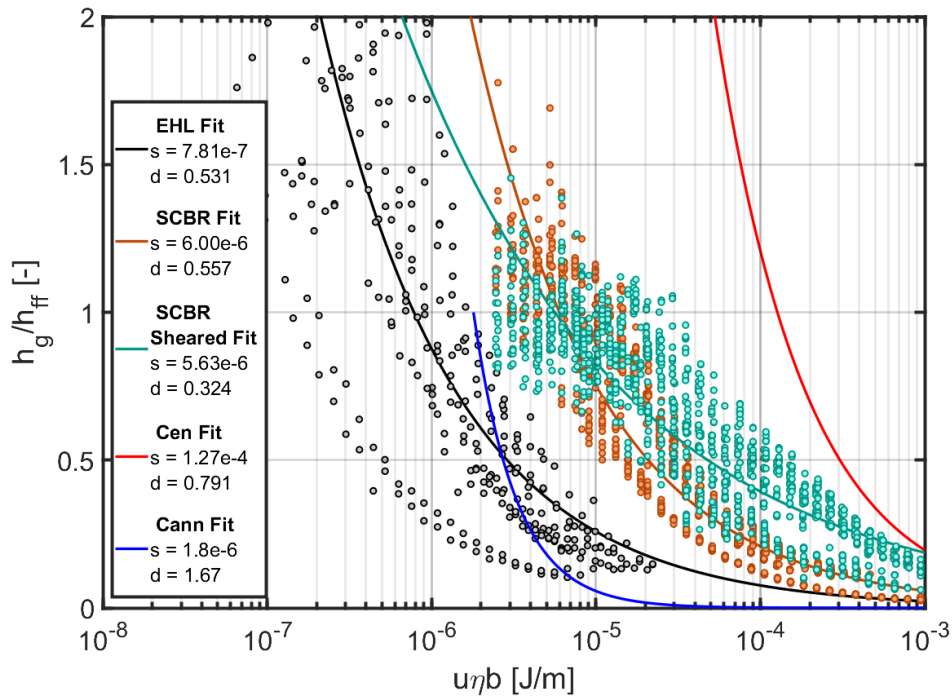


Figure 7.21: Plot showing the relationship between relative grease film thickness and the starvation factor. In this plot the shear-degraded film thickness results taken using the SCBR are also shown.

The effect of shear degradation on these results was not to smoothly alter the data to a higher onset of starvation, but instead, the reduced thickener effect led to a constant relative film thickness of approximately 1 for low $u\eta b$ values, shown in Figure 7.21. This meant that the fit is now quite poor, the equation above now failing to accurately describe the trend. The measured film thickness maintains a significant fraction of the fully flooded value, approaching the relative film thickness measured in bearings at very high $u\eta b$ values. The decay behaviour is quite different, however, reducing relative film thickness at a much lower rate. In fact, due to the poor fit, the s value is even lower than the fresh grease case, despite the true onset of starvation having shifted slightly to a higher $u\eta b$ value. In comparison, the sheared grease performance in the EHD rig was not significantly different to the fresh grease, hardly altering the fitted equation. This is likely to be because the narrow contact vicinity of the SCBR enables lubricant with lower yield stress to reflow via capillary action to a greater extent than the EHD contact allows.

This analysis has not included the effect of SRR, which has led to lower-than-assumed entrainment speeds and will have shifted the data points in the figures above to lower $u\eta b$

values, at most, halving the value, which is a modest change on the log-axis plots. This would also affect the predicted film thicknesses and hence the relative film thickness, acting to increase the values. This is only likely to have influenced the values above a $u\eta b$ value of $\sim 5 \times 10^{-4}$. The effect of inlet shear heating was also not accounted for. As the model contains both speed and viscosity terms, inlet shear heating is unavoidable at high $u\eta b$ values, and was not considered separately in the analysis by Cen and Lugt [258], therefore the model, based on real data, is likely to already account for this effect. As with the SRR, only the highest $u\eta b$ values are affected.

In order to compare these results with the literature, only the last run was used, however it is likely that the measured film thicknesses would continue to change upon further time under rolling. The greased bearing data was taken after 15 hours of running in, which will have significantly sheared the active lubricant. The use of a pre-sheared lubricant may make a better comparison, achieving almost the same film thicknesses at the very highest $u\eta b$ values.

7.4 DISCUSSION

The limited results presented here have demonstrated clearly the effects of degradation on film thickness. Shear degradation has significantly increased film thickness under starved conditions compared to fresh grease and thermal degradation has had the opposite effect. In comparison to starved testing using the EHD ball-on-disc rig in Chapter 5, these effects are much more significant and (excluding the CaXB 100 thermally aged grease which underwent complete loss of consistency) there were no exceptions to the trend. The effect of shear degradation agrees well with results measuring film thickness of shear degraded grease in bearings [14]. The implication is that the barrel-on-ring setup is a better model of a bearing in terms of the resupply of shear-degraded lubricant, which has been shown to constitute the active lubricant of real bearings in Chapter 4.

The test temperature was too low to allow the thickener effect to be observed – the oil viscosities were so high that EHD film thickness dominated even at low speeds. This prevents a comparison with the observed reduction in thickener effect due to shearing in the ball-on-disc testing in Chapter 5, and the opposite effect due to thermal degradation. The low

viscosities also had the effect of reducing the possible rate of lubricant reflow. This did not, however, manifest as significantly greater starvation. In fact, despite the low temperatures, the barrel-on-ring rig appears to innately experience lower starvation than the ball-on-disc rig at what can be considered equally challenging conditions to maintain lubricant reflow. This was shown to compare positively with bearings, which are able to operate at far higher entrainment speeds for far longer without risking catastrophic starvation due to innate resupply. It may be that the conformal contact of a barrel-on-ring allows capillary reflow at a much higher rate due to the thinner gap beside the contact. An additional effect that may compound the difference is that this thin area will shear lubricant much more effectively than the area beside a ball-on-disc contact would, meaning the run-in phase may be producing a quantity of shear-degraded active lubricant which reflows more easily than fresh. The effect of improved capillary reflow would also contribute to the greater observed impact of starvation-resistance imparted by shear degradation.

The progressive decrease of film thickness in sequential runs shows that a steady-state situation has not been reached, though it is interesting to note that the sheared greases do not decrease to such an extent, suggesting a steady-state can be reached sooner with these lubricants. This testing would have benefitted from a longer run-in period in order to exclude the effect of time.

The inability to measure SRR meant that the film thickness values from the rig are associated only with the ring speed, and not the true entrainment speed which is likely to be much lower, given the significant sliding observed in the contacts. While it would be ideal to minimise this sliding to a value more representative of bearings, characterising it using a magnetised roller and a hall sensor is a simple addition which would provide more accurate information. Driving the roller with an independent drive system would be ideal to vary the SRR as desired, but adds significant complexity to the system.

An additional shortcoming of the rig in its current form is that, despite the validation tests showing an excellent agreement with the Chittenden film thickness prediction at low speeds, demonstrating that the rig behaves as expected in principle, deviation at higher speeds is in large part due to inlet shear heating as well as starvation. Starvation is the primary

phenomenon under study and this effect obscures the results. The cause of the high inlet shear heating is both the low test temperature and the high sliding. The latter can be improved as described above, but a necessary addition for this rig to be of high utility is a means of temperature control, allowing tests at higher temperatures.

The sudden increase of film thickness at high speeds, as observed in the ball-on-disc testing, is thought to originate from a different cause in this case, being a result of the free axial movement of the barrel roller. This is not representative of bearings, at least to the extent observed, and so should be limited to allow realistic testing at high speeds. It is, of course, possible that this is not the cause, and so eliminating it would help to discern what the true cause might be. Any additional constraint is likely to increase friction and raise the SRR even further, so the only conceivable way to limit axial movement is to drive the barrel roller independently. This would then solve two of the main problems with the rig as it stands.

Further improvements to the emulation of a bearing could include the addition of a cage element to the system. Work has demonstrated that the cage can play a large role in lubrication of a bearing, acting to redistribute the grease, as well as produce a shear-degraded lubricant which is able to reflow more easily [133]. A barrel roller with a larger radius could further reduce the gap adjacent to the contact and increase capillary reflow, which might bring the starvation behaviour even closer to that of a bearing.

7.5 CONCLUSIONS

This chapter has presented the validation of a novel film thickness test rig, and the film thickness results of a range of greases using this system. The work presented in this chapter has demonstrated that the change of test geometry from ball-on-disc to barrel-on-ring has positive effects in emulating the lubricating behaviour of greased bearings. Starvation is better resisted in such a configuration, appearing to improve the innate resupply mechanisms such as capillary reflow. It has also been shown that shear degrading grease has a greater effect in resisting starvation in this system when compared to ball-on-disc results, appearing to match the lubrication mechanism of bearings, in which an active, shear degraded lubricant reflows to resupply the contact. By better emulating the lubrication process, the predictive

power of model testing is greatly improved. A range of improvements to the rig have also been described, which would further emulate bearing contacts, as well as eliminate confounding influences on the results.

8 DISCUSSION AND CONCLUSIONS

This chapter reviews the results shown in previous chapters and extends the individual discussions from each chapter, bringing them together into an overall set of ideas, and exploring how they relate to the initial aims and their significance. The limitations of the work are discussed, and improvements and potential avenues of further research are suggested.

8.1 UNDERSTANDING GREASE LUBRICATION OF BEARINGS

Chapter 4 contains the following, summarised, findings:

Thermal and Shear Degradation in Bearings

- The distribution of grease around R0F+ bearings supports previous findings, with relatively unsheared grease at the shields and sides of the race and highly sheared, generally base oil-rich lubricant in the raceway. Thickener-rich grease was attached to the cage.
- Changes observed in the IR spectra of the bearing grease samples was hypothesised to be markers of shear degradation influencing thickener interactions.
- Bench shearing methods were able to reproduce these IR changes, generally to a lower extent. A method involving intense crushing of the grease was the most effective in matching the IR spectra from bearing raceways.

Main conclusions: The active lubricant in greased bearings is highly degraded, oil-rich grease. IR markers may be able to assess the extent of shear degradation.

8.1.1 Discussion

It was vital to first assess the condition of lubricant in bearings operating under normal conditions, within the main phase of life. Only by understanding the properties of this lubricant could they be replicated in an accurate tribological bench test.

The observational findings of this study confirmed earlier work analysing bearings, the best example being Cann's investigation of R2F bearings, which were similarly under typical running conditions [180]. The active lubricant that covered the raceway was oil-rich, widely considered to be the result of oil-bleed from bulk grease sitting elsewhere in the bearing [13]. It is this lubricant that is displaced by the passing ball, but is able to reflow to provide adequate lubrication over the life of the bearing. Whether passive oil-bleed, perhaps aided by centrifugal forces, is the only supply of the oil to form the active lubricant is questionable. It appears more likely that intense shear degradation of the thickener, which was observed both in the shield grease and particularly in the raceway lubricant, directly increases bleed rate by reducing the ability of the thickener to retain oil [130]. The highly degraded lubricant is also likely to reflow itself, carrying thickener particles into the raceway. This is supported by the consistent presence of thickener in the raceway lubricant.

A diagram of grease lubrication of bearings is shown in Figure 8.1. This was influenced primarily by the literature, including the feed-loss models of Baker [122], Wikström et al. [120] as well as other work analysing grease and oil starvation and reflow [119], [124], [223], [258]. The results of Chapter 4 were also considered and influenced the combination of key findings in the literature.

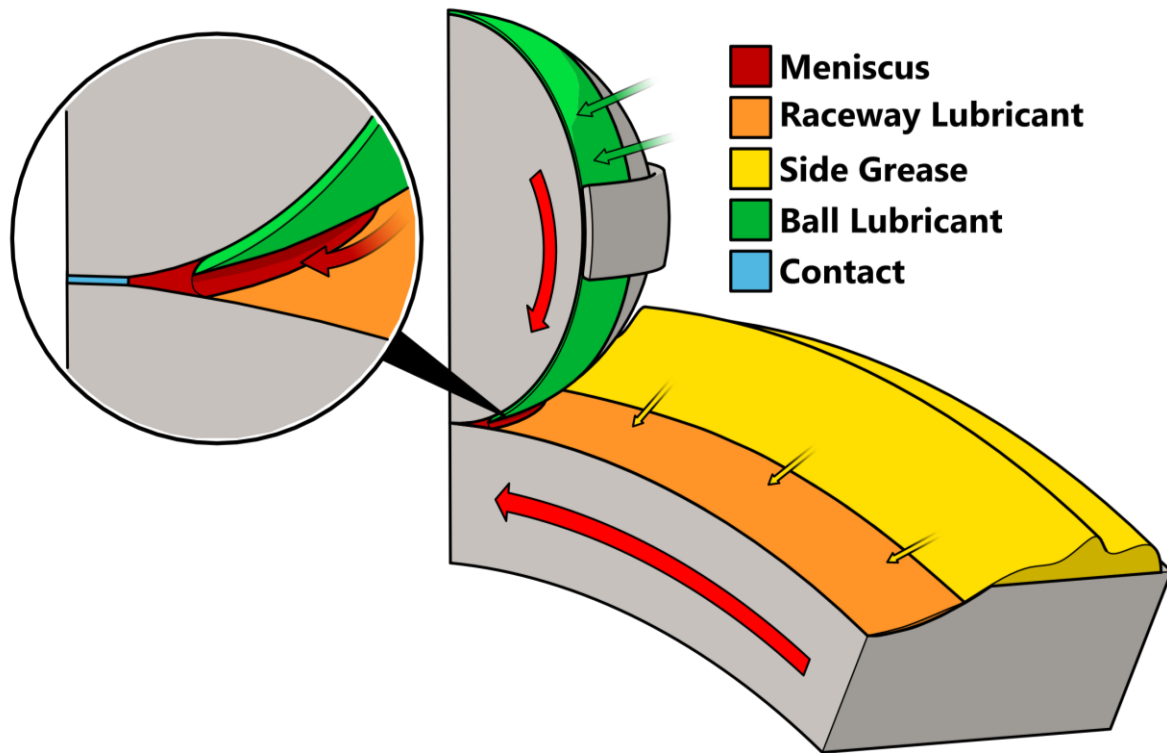


Figure 8.1: Diagram showing the greased lubrication of a bearing. Grease at the sides releases oil and/or reflows upon high levels of shear degradation. The raceway lubricant and ball lubricant are thin layers, consisting of oil and very highly sheared thickener. This can be described as the ‘active’ lubricant. Yellow arrows indicate oil bleed and flow of the side grease into the active lubricant. Green arrows represent the redistributing effect of the cage. The red arrow indicates the capillary reflow that occurs at the inlet meniscus.

The side grease is relatively unsheared, having been worked during the churning phase, increasing oil bleed rate, but maintaining solid behaviour. Within the track and between the ball and cage a high shear rate produces highly degraded lubricant, which both bleeds oil at a high rate, and is able to reflow more easily due to reduced yield stress. Churning and these shearing processes can be thought of as ‘conditioning’ of the active lubricant, creating a lubricant with high oil-content and low yield stress. The active lubricant coats the balls and raceway in thin films. It is displaced by the passing balls, but the cage can act to redistribute the lubricant, and it can reflow under ‘out-of-contact’ processes into the contact path. This could be through various means, including centrifugal force and surface tension. Evidence suggests that the primary processes of reflow occur ‘in-contact’ instead, most likely through capillary flow or ball spin [18], [223], [258]. Nonetheless, the ability of the active lubricant to reflow dominates the quantity of lubricant able to reflow at the meniscus. There is evidence of thickener-rich layers being deposited on the metal surfaces in ball-on-disc testing [124],

[181], and polyurea greases have been observed to deposit thickener layers in bearings in the IR analysis in chapter 4 and in one other example in the literature [260].

The ongoing mechanisms are also shown in Figure 8.2, described in terms of three bearing locations: the side grease, which constitutes the majority of grease in the bearings; the active lubricant, which coats the raceway and balls, and is the contributor to separating lubricant films; and the contact itself, supplied by the inlet meniscus. The three main loss mechanisms of leakage, volatile loss and oxidation all occur primarily from the shield grease. Conditioning of the grease allows the active lubricant to form in the raceway through oil bleed, centrifugal force and other mechanisms. This lubricant flows to the meniscus by capillary reflow, is entrained, displaced and reflows again, forming the main cycle of grease lubrication. As degradation in the form of conditioning increases the supply processes indicated by the green arrows, degradation also contributes to the loss mechanisms indicated by red arrows.

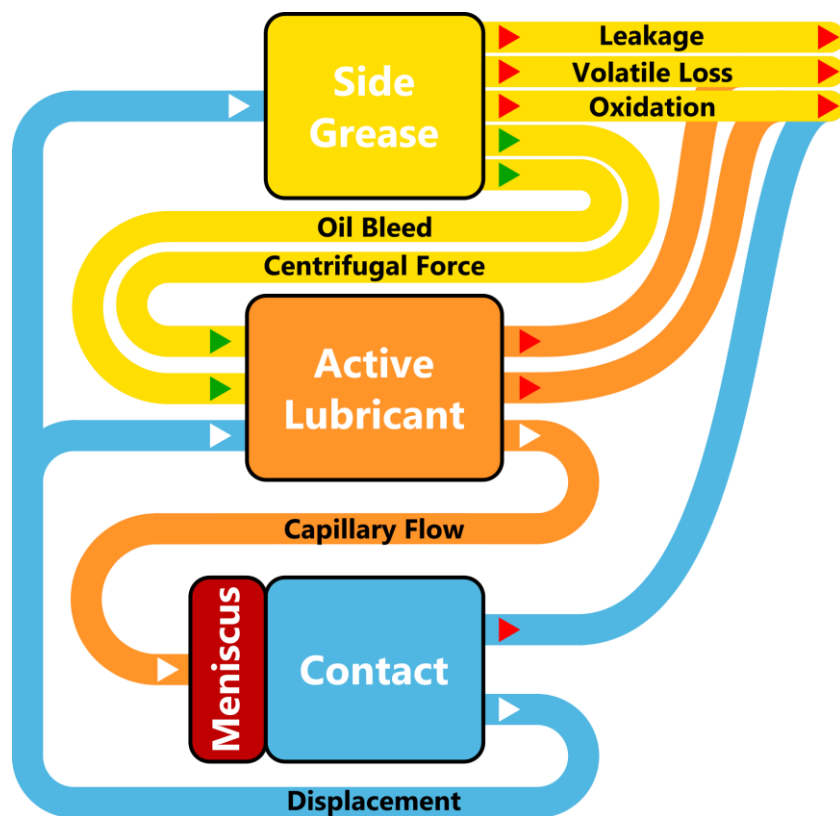


Figure 8.2: Diagram showing transport and loss mechanisms within bearings. Green arrows indicate production of the active lubricant, aided by conditioning, while red arrows indicate loss mechanisms.

This model of grease lubrication shows clearly that the transformation of fresh grease in the bearing into the active lubricant is critical to lubrication performance. If this occurs too

slowly, the contact can starve. The very mechanisms that serve to increase resupply will also contribute to loss, and so, if these occur too rapidly, the bearing can fail prematurely through inadequate lubrication.

There are two separate goals that a perfect model test would achieve: firstly, it must emulate the main cycle of lubrication in which degraded active lubricant reflows to the contact, allowing the properties of this lubricant to control tribological performance, rather than force fresh grease into the contact; secondly, it must emulate the mechanisms that generate this lubricant, as the ability of a grease to do this at the appropriate rate can dictate life of the bearing.

8.2 EVALUATING WEAKNESSES OF EXISTING TRIBOLOGICAL TESTS

Having clarified the salient aspects of grease lubrication, and before a superior test can be developed, it was first necessary to explore the existing tribological tests used to analyse grease. The ways in which they are able, and unable, to reproduce greased bearing lubrication must be well-understood. It should also be questioned if the changes made to the active lubricant are of relevance to tribological performance.

A summary of the results of Chapter 5 are provided below:

Effects of Shear and Thermal Degradation on Grease Rheology and Lubrication Properties

- Bench-top shear and thermal degradation were both found to affect the rheology of the test greases. Thermal aging caused an increase in yield stress, while shear degradation reduced it. This is thought to be due to volatile loss and thickener restructuring in the first case, and destruction of thickener particles in the second case.
- The ‘thickener effect’ of high film thickness at low speeds is diminished after shear degradation, while thermal aging increases it. Fully-flooded friction was increased by both shear degradation and thermal aging, with shear degradation mainly affecting low speed.

- Starved film thickness generally increased after shear degradation and reduced after thermal aging, though these effects were not definitive. The ball-on-disc EHD rig readily starved without the use of a grease scoop.
- IR measurements of the rolled tracks showed that only long-term MTM tests were able to produce measurable shear degradation of the lubricant and not to the same extent as found in bearings.
- Thickener-rich films were observed in the MTM rolled tracks, contrasting with bearing films which were oil-rich. The polyurea grease was an exception and did show thickener-rich films in the bearing.

Main conclusions: Shear and thermally degraded grease (the former closely representing the active lubricant in bearings) behaves very differently to fresh grease. Testing of fresh grease does not represent true bearing tribological performance and fails to replicate these changes in typical testing.

8.2.1 Discussion

Artificially aging grease through shear degradation had been validated in the previous chapter as producing similar effects, in terms of thickener intermolecular interactions, as found in the active lubricant from bearings. This enabled an investigation of how the active lubricant in bearings might differ from the fresh grease that is normally tested in bench film thickness and friction tests. The effect of reduced thickener content was ignored in this work, but is an area that should also be explored.

Ball-on-disc testing of friction and film thickness has been widely used to assess grease performance, consistently exhibiting the ‘thickener effect’, in which thickener particles are entrained at low speed and provide increased film thickness over the base oil alone [16], [85], [220], [221]. The corresponding decrease in friction at low speed has been known as the ‘inverse-Stribeck’ effect [209]. There is evidence that thickener-rich films can be deposited on the rolled track in ball-on-disc tests [126], [181]. All of these effects were observed in this work, when using fresh greases.

There is a large body of work in the literature studying the rheological and structural changes induced by shear and thermal degradation, as discussed in section 4.1. There is relatively little work on the effects of degradation on film thickness in ball-on-disc testing, however. Examples include Hurley's work on thermally aged greases [192], showing an initial increase in film thickness with aging, but a decrease upon further aging and Cen's work on shear-degraded grease [52] which showed a reduction in the thickener effect.

Shear degradation has been shown in this work to greatly reduce the thickener effect, and consequently increase friction at low speeds. As the active lubricant in bearings is both shear degraded and oil-rich, the thickener effect may be very small. Evidence for deposition of thickener-rich films for the polyurea grease was found in Chapter 4, but not for other greases. As the measurement technique provides no information about thickener concentration as a function of depth, there remains a possibility that a thickener-rich layer forms on the metal surfaces in bearings also. It is therefore important that a lubricant as close in properties to the active lubricant in bearings is used in model testing. Bearing lubricant films and the rolled tracks of the MTM were compared in a novel way and it was demonstrated that shear degradation does not occur at a sufficient rate in such systems to produce a sufficient volume of degraded active lubricant within reasonable test times. The testing of 'pre-conditioned' grease should be encouraged in order to mitigate this issue and improve applicability of these tests.

As bearings generally operate under some level of starvation [13], it may be more important to consider starved behaviour. A comparison between a ball-on-disc system and bearings has been made, finding that the general starvation curve was similar between the two, though the speed of starvation onset was very different [18]. Testing of starvation on such model systems was found to be very difficult in this work, with starvation occurring at relatively low speeds and centrifugal effects causing a sudden, unrealistic, rise in film thickness. Cen and Lugt's paper comparing the starvation of bearings and the ball-on-disc EHD rig [258] found quite different behaviour, with the ball-on-disc rig reducing in film thickness in a much more sudden way, and evidently experiencing a much-reduced rate of lubricant reflow. While shear degradation has been shown to significantly increase starved film thickness in bearings

[14], it did not produce a significant increase in starved film thickness for the ball-on-disc system in this work. These findings suggest that the replenishment mechanisms are very different between bearings and ball-on-disc systems, possibly so different that important effects such as shear degradation are not modelled sufficiently. This is despite evidence suggesting that, as replenishment is a local phenomenon, it should be possible to reproduce multi-contact bearing reflow mechanisms in a single-contact machine [18], [223], [258].

While the use of ball-on-disc model tests has led to many advancements in the field of grease tribology, there are many reasons to think that this form of testing can be improved. An improved model test could retain the benefits of detailed understanding of lubricant performance, while enhancing applicability to the end use-case, a feature that can be called into question in current systems.

8.3 AN IMPROVED MODEL TEST

The results from Chapter 7, in which the newly developed single-contact bearing rig was tested, are summarised below:

Single-Contact Bearing Rig Results

- Testing of base oil produced film thicknesses that matched the Chittenden prediction at low speed, validating the rig, while higher speeds were influenced by shear heating and starvation.
- Much higher speeds were achievable on the SCBR than the EHD rig without the centrifugal force influencing reflow.
- Film thickness underwent an unexpected rise at very high speeds, believed to be due to the unconstrained roller achieving resupply by vibrating laterally and introducing fresh lubricant.
- The barrel-on-ring system is inherently more starvation-resistant than the ball-on-disc system if the results are compared according to a ‘starvation parameter’ and is more bearing-like in that regard. This is believed to be due to improved capillary reflow and removal of the centrifugal force effect.

- The effects of thermal and shear degradation on starved film thickness were pronounced and more differentiated than on the ball-on-disc rig. Thermal degradation reduced film thickness while shear degradation greatly increased it.

Main conclusions: A barrel-on-ring system is able to better-emulate starved lubrication in bearings than a ball-on-disc system. Highly conformal contacts should be studied to match those of a bearing. Shear degradation should be an integral part of any test aimed at representing bearing performance.

8.3.1 Discussion

The final aim of this PhD work was defined as: “the development of a new test rig to bring bench model testing of grease even closer to a true bearing emulation” and this chapter directly addressed that aim. The results summarised above show that a new rig has been developed which produces valid results, can operate at realistic speeds and provides a replenishment mechanism that behaves more like that of bearings than the existing ball-on-disc test systems. In these aspects, the specified aim has been met, bringing together the work of the previous two results chapters. There remain many aspects of bearing lubrication that were not adequately replicated and these are discussed in the final section.

Due to the more favourable capillary reflow conditions, the effects of thermal and shear degradation were significantly more pronounced using the SCBR than the ball-on-disc system, further emphasising the findings of the previous chapter: that the degradation of the active lubricant is likely to have strong influences on tribological performance.

There exists only one comparable single-contact rolling element-on-ring rig in the literature, developed by researchers at the Beijing Institute of Technology [232] and used to measure oil film thickness under very high-speed conditions [233] and investigate oil slip under these high speeds [234]. No research investigating the behaviour of grease in single-contact-on-ring rigs, or barrel-on-ring systems in general has been found. Starvation has also been neglected as a topic of research in any ring system. This work is, therefore, novel in applying the barrel-on-ring geometry to starved grease lubrication. Having demonstrated a step forward in improving the applicability of grease model tests, hopefully the findings will be

put into practice by researchers and lubricant engineers looking to understand grease performance in bearings. The more conformal contact produced by a barrel roller compared to a ball is believed to be critical in improving the capillary reflow that is vital in starved lubrication. Rig design should consider this and, ideally, replicate the raceway groove of a bearing. Using a barrel roller is likely to be an easier solution. An additional benefit that a conformal contact vicinity provides is higher shear rates for the surrounding lubricant. If a model test is to also simulate lubricant conditioning, it must subject relatively large volumes of lubricant to high shear rates. Alternatively, preconditioning of lubricant by using the roll stability tester, for example, would also achieve the goal of testing lubricant that represents the active lubricant of bearings.

One unexpected finding from this work was that, despite designing to avoid the sudden resupply observed in ball-on-disc testing which was believed to be due to centrifugal force, a similar rise in film thickness was observed at high speed. Lateral vibration as a potential explanation has been discussed, perhaps acting in a similar way to ball spin in bearings, which is thought to introduce lubricant and replenish under starved conditions [261], [262]. It is also possible that a critical speed is reached where centrifugal force acting on the lubricant in the rolled track is sufficient to cause flattening of the outlet ‘side bands’ which would normally happen purely by surface tension forces [256].

Limitations in the design of the rig were noted during this initial testing, and the testing using the SCBR was also constrained due to the limited time available. There are, therefore, many possible improvements and significant test work that could go further in understanding grease lubrication, and replicating bearing lubrication in model tests.

8.4 CONCLUSIONS

The main aim of this work was to understand the salient aspects of grease lubrication of bearings that would influence the effectiveness of model testing and apply them in the design of a novel, improved test rig. Such a system would provide a cost-effective means of developing improved grease formulations and allow engineers to predict early in a formulation’s development cycle how it might perform in a bearing. It would also give

researchers insight into the fundamental mechanisms occurring in grease lubrication, while remaining applicable to the real-world application. If incremental improvements to greases can be made in properties such as friction or working life, the gains will be significant, due to the abundance of greased bearings in operation. In practice, this aim has led to three objectives:

- To understand how grease degrades in real bearings.
- To understand how this degradation affects the results of model tests, in comparison to fresh grease.
- To design and develop a novel test rig which addresses issues identified with standard tests, and produces more applicable results.

These objectives have largely been met. A study of bearings operating under typical conditions has shown that the majority of the grease is distributed away from the rolled track at the shields and raceway shoulders. A small amount of oil-rich 'active' lubricant remains in the track, containing heavily shear-degraded thickener. Even grease that remains on the shields shows evidence of shear degradation, which may increase the rate of oil bleed.

By reproducing similar shear degradation of grease in bulk, it was possible to assess the effects of such degradation on rheological and tribological performance. Shear degradation was found to reduce yield stress, while thermal aging increased it. Shear degradation greatly reduced the high film thicknesses seen at low speed with fresh grease. A consequent increase of friction at low speed was observed. Thermal aging had the opposite effect, tending to increase film thickness at low speed. Friction was increased across the speed range for thermally-aged greases. Testing under starved supply with standard ball-on-disc test systems was found to be difficult, with starvation occurring at low speeds, and film thickness suddenly rising unexpectedly at high speeds. This effect is believed to be inherent to the ball-on-disc system, as centrifugal force may produce bulk transport of lubricant at high speeds. Degradation of grease had subtle effects on starved film thickness using the ball-on-disc system, with shear degradation increasing starved film thickness, while thermal aging reduced it.

A new test rig was developed, featuring a barrel-shaped roller contacting the inner surface of a glass ring. The design and development of this rig was challenging due to the enclosed geometry, but initial results show that it is effective in improving lubricant replenishment under the same apparent starvation conditions. This brings it closer in behaviour to a bearing, and allows study of starvation at realistic speeds. The effects of shear and thermal degradation on starved film thickness are much more pronounced in this system compared to a ball-on-disc system, probably because replenishment via capillary reflow is a dominating factor in starved film thickness, as is the case in bearings.

Several limitations of the new test rig have been identified, requiring work to develop the rig with the addition of features such as temperature control, slide-roll-ratio measurement, slide-roll-ratio control and traction measurement. Test work beyond the initial experiments described in this thesis has been outlined, seeking to determine if the rig can 'condition' fresh grease into a mobile 'active' lubricant in the same way that occurs in bearings. This ability would bring the test even closer to a perfect emulation of real bearings.

8.5 FUTURE WORK

There are few analyses of the active lubricant of bearings, which is unfortunate because it is vital to understand the properties of this lubricant, both to understand grease lubrication in bearings, but also to optimise grease formulation. Further work in characterising this lubricant for a wider range of greases would be useful. The change in properties that occurs prior and during bearing failure is also of great importance and a set of tests of advancing speed or temperature might help understand in what way the active lubricant fails to provide lubrication.

The IR markers identified in this work were specific to the grease types studied and required shear degraded examples to use as a comparison when analysing the state of degradation of other samples. Ideally, the changes could be associated strongly with a thickener type and therefore if such changes are identified, the worker can conclude that some level of shear degradation had occurred. A wide range of grease thickeners could be subjected to intense shear degradation using a ball homogeniser or other system, and thereby characterise the

degradation of many grease types. A theoretical analysis of how changing thickener interactions could affect the IR absorption bands would provide an explanation for the changes, rather than the empirical assumptions provided in this work.

Testing of degraded grease, in particular shear-degraded and oil-rich grease, should be more common, given this is typically the lubricant involved in bearing lubrication. The role of the remaining thickener molecules is of interest and work could be done to investigate whether it serves a role in surface protection, acting like a high-concentration additive. Many friction modifiers are remarkably similar in structure to thickener molecules and given they are likely to be free and in solution, they may be able to adsorb on the metal surfaces, providing low friction or surface protection. The thickener-rich films observed in ball-on-disc testing may exist in bearings also. Measuring IR spectra of residual films only provides the sum total through the thickness of the film. It is possible a thin, thickener-rich layer exists at the surface on top of which lies a highly oil-rich lubricant.

One ideal property of model grease tests would be the ability to shear degrade and ‘condition’ the fresh grease to form an active lubricant which then preferentially reflows and supplies the contact. This was believed to be improved in some way in the SCBR but was not proven. By running for longer than the two minute run-in used in this testing, there may be sufficient time for such degradation to occur. A test to prove this could involve running for half an hour at a high speed, then stopping and sampling the lubricant in the rolled track in order to perform IR transmission spectroscopy. It would not be possible to analyse it in-situ as was done for bearings and the MTM rig, without permanent damage to the ring specimens. If the shear markers that were observed in the bearing were also observed in the SCBR rolled track, this would indicate a critical aspect of bearing lubrication had been reproduced.

Using longer run-ins in general would be worthwhile, as the film thickness had evidently not settled to a stable value in the testing in Chapter 7. If shear degradation occurs, this stable value might increase, otherwise it is likely to fall until reflow matches displacement in the standard feed-loss model of starvation.

There are many possible improvements that could be made to the SCBR. Testing at room temperature exacerbates starvation due to relatively high viscosities, which may be desirable,

but the ability to bring test temperatures closer to realistic values would be better. A heating and cooling system could be added, enabling such tests, as well as low-temperature tests, which could investigate conditions of extremely low replenishment rate.

The addition of a cage around the barrel roller would include a potentially vital mode of reflow as bearing cages have been shown to increase starved grease film thickness in a ball-on-disc machine [133] and is believed to be critical to the formation of the active lubricant in bearings [180].

One major problem in interpreting data from the SCBR is the unknown slide-roll ratio. At high speeds this is likely to be very high, based on the results from a similar rig [233], and can lead to both erroneous assumptions about the entrainment speed, and inaccurate estimates of shear heating. The authors of the cited work used a simple system where the roller was magnetised, and a Hall sensor was used to measure the oscillating magnetic field, directly linked to the rotational speed of the roller. Such a technique was originally used by Hili et al. [247], and would be simple to include on the SCBR.

In order to assess behaviour under specified SRR, given that the high loads of bearings usually limit the SRR even at high speeds, the roller could be driven by an independent motor. Doing this would also enable a force sensor to be included and provide traction measurements at a range of speeds and SRRs, giving film thickness and friction information with one test.

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