Tribological evaluation of environmentally friendly MoS_2 based solid film lubricants for gas turbine engines

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This is to certify that the thesis prepared

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Abstract

Tribological Evaluation of environmentally friendly MoS_2 based solid film lubricants for gas turbine engines

Parikshit Tonge

Solid lubricants such as MoS_2 have been widely used in the aerospace industry with the primary purpose to lower the friction and wear of the tribological interfaces. Pure MoS_2 generally performs better (i.e., in terms of low friction and low wear) in vacuum conditions compared to humid environments as the premature failure of the lubricant can be attributed to undesirable interfacial processes as well as the formation of oxides such as MoO_3. To overcome these limitations as well as increase the endurance life of these lubricants in ambient conditions, they are generally doped with different elements or compounds. For instance, Pb based and Sb_2O_3 compounds have been used as dopants with MoS_2 to improve the tribological performance of the lubricant. However, due to the recent environmental concerns and targets to eliminate non-green lubricants, there is a strong desire to eliminate Pb based compounds due to its toxic nature. In addition, bonded MoS_2 based solid lubricants contain a binder system and various carriers to bind and deposit the lubricating solid (i.e., pigment) and the dopant with the substrate. Currently, the carriers are mainly composed of the organic solvents and thus, are responsible for the release of volatile organic compounds (VOCs) during the curing process. The release of the VOCs can be harmful for the ecosystem due to its toxicity and carcinogenicity. Hence, to eliminate these organic solvents, alternatives are preferred which are generally aqueous solvents.

The main purpose of this research is to provide a better understanding of the influence of the toxic elements on the interfacial processes of MoS_2 based solid lubricants. This thesis is composed of two research studies where we critically evaluate the tribological performance of 'non-green' and 'green lubricants' in order to fully capture the influence of the various elements on the interfacial phenomenon. In the first study, the baseline 'non-green lubricant' was doped with Pb based compound and Sb_2O_3 and in the 'green lubricant', the Pb based compound was removed and was replaced by higher percentage of Sb_2O_3. In the second study, the bonded MoS_2 based solid lubricants were doped with Sb_2O_3, with one of the lubricants containing solvent-based carrier and the other lubricant with water-based carrier.

In both the studies, the tribological evaluation was performed using ball-on-disc tribometer with various normal loads. Subsequently, the ex-situ analysis was done using Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Micro-Raman Spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR) to understand the chemical composition and to analyze the interfacial processes at different normal loads. It was observed that the non-green lubricant performed better in terms of tribological behavior (i.e., low friction and low wear) when compared with the green lubricant. The improved tribological properties were attributed due to the formation of dense and uniform tribofilm and transfer film with the basal planes oriented in the parallel direction. Furthermore, it was observed that the solvent-based lubricant had performed better tribologically (i.e., low friction and low wear). The increased coefficient of friction and reduced wear resistance of the water-based lubricant was attributed to the increased cohesiveness within the lubricant. The findings of the interfacial phenomenon have provided vital information for developing green alternatives that may have the ability to replace toxic compounds in the future for sustainable ecosystem.

Résumé

Évaluation tribologique de lubrifiants à film solides écologiques à base de MoS_2 pour moteurs à turbine à gaz

Parikshit Tonge

Les lubrifiants solides tels que le MoS_2 ont été largement utilisés dans l'industrie aérospatiale dans le but principal de réduire le frottement et l'usure des interfaces tribologiques. Le MoS_2 pur fonctionne généralement mieux (de faible frottement et faible usure) dans des conditions de vide par rapport aux environnements humides, car la défaillance prématurée du lubrifiant peut être attribuée à des processus interfaciaux indésirables ainsi qu'à la formation d'oxydes tels que MoO_3. Pour surmonter ces limitations ainsi que pour augmenter la durée de vie de ces lubrifiants dans des conditions ambiantes, ils sont généralement dopés avec différents éléments ou composés. Par exemple, des composés à base de Pb et de Sb_2O_3 ont été utilisés comme dopants avec du MoS_2 pour améliorer les performances tribologiques du lubrifiant. Cependant, en raison des récentes préoccupations environnementales et des objectifs d'élimination des lubrifiants non verts, il existe un fort désir d'éliminer les composés à base de plomb en raison de leur nature toxique. De plus, les lubrifiants solides à base de MoS_2 lié contiennent un système de liant et divers supports pour lier et déposer le lubrifiant solide (le pigment) et le dopant avec le substrat. De nos jours, les supports sont principalement composés de solvants organiques et sont donc responsables de la libération de composés organiques volatils (COV) pendant le processus de durcissement. La libération de COV peut être nocive pour l'écosystème en raison de sa toxicité et de sa cancérogénicité. Ainsi, pour éliminer ces solvants organiques, on privilégie des alternatives qui sont généralement des solvants aqueux

L'objectif principal de cette recherche est de fournir une meilleure compréhension de l'influence des éléments toxiques sur les processus interfaciaux des lubrifiants solides à base de MoS_2. Cette thèse est composée de deux études de recherche qui a pour but d'évaluer de manière critique les performances tribologiques des lubrifiants 'non verts' et 'verts' afin de saisir pleinement l'influence des différents éléments sur le phénomène interfacial. Dans la première étude, le 'lubrifiant non vert' de base a été dopé avec un composé à base de Pb et du Sb_2O_3 tandis que dans le 'lubrifiant vert', le composé à base de Pb a été supprimé et remplacé par un pourcentage plus élevé de Sb_2O_3. Dans la deuxième étude, les lubrifiants solides à base

de MoS_2 liés ont été dopés avec du Sb_2O_3, l'un des lubrifiants contenant un support à base de solvant et l'autre lubrifiant avec un support à base d'eau.

Dans les deux études, l'évaluation tribologique a été réalisée à l'aide d'un tribomètre à bille sur disque avec diverses charges normales. Par la suite, l'analyse ex-situ a été effectuée à l'aide du microscope électronique à balayage (MEB), de la microscopie à force atomique (AFM), de la spectroscopie micro-Raman et de la spectroscopie infrarouge à transformée de Fourier (FTIR) afin de comprendre la composition chimique et analyser les processus interfaciaux à différentes conditions normales. Il a été observé que le lubrifiant non vert a obtenu de meilleurs résultats en termes de comportement tribologique (un faible frottement et faible usure) par rapport au lubrifiant vert. Les propriétés tribologiques améliorées ont été attribuées en raison de la formation d'un tribofilm et d'un film de transfert denses et uniformes avec les plans basaux orientés dans la direction parallèle. De plus, il a été observé que le lubrifiant à base de solvant avait de meilleures performances tribologiques (un faible frottement et faible usure). L'augmentation du coefficient de frottement et la réduction de la résistance à l'usure du lubrifiant à base d'eau ont été attribuées à la cohésion accrue entre le lubrifiant et la surface d'appui. Les découvertes du phénomène interfacial ont fourni des informations vitales pour développer des alternatives vertes qui pourraient avoir la capacité de remplacer les composés toxiques à l'avenir pour un écosystème durable.

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Finally, I would like to thank my friends and my parents for their blessings, continuous love and encouragement throughout my career.

Dedicated to

My beloved parents

"Wisdom is not a product of schooling but of the lifelong attempt to acquire it."

- Albert Einstein

Contribution of Authors

This thesis is mainly based on the peer-reviewed and under-development articles. All the articles are produced in collaboration with different people having me as a principal author and my supervisor, Prof. Pantcho Stoyanov as a co-author. Majority of the experimental work was performed by the principal author and the supervisor has assisted in data analysis and the manuscript preparation. I would like to acknowledge the contributions of the co-authors for the articles produced and the following summarize the contributions of each author:

- Chapter 3: Tonge, P.; Roy, A.; Patel, P.; Beall, C.J.; Stoyanov, P. Tribological Evaluation of Lead-Free MoS_2-based Solid Film Lubricants as Environmentally Friendly Replacements for Aerospace Applications. Lubricants 2022, 10, 7. https://doi.org/10.3390/lubricants10010007
    - Tonge P was responsible for the tribological tests, the data analysis and writing of the original manuscript draft. Roy, A was responsible for data analysis and critical review. Patel, P was responsible for data analysis and critical review. Beall C.J was responsible for providing the deposited samples for experimental work and critical review. Stoyanov, P was responsible for supervision, data analysis, conceptualization, and modification in the original manuscript
- Chapter 4: Tonge, P.; Roy, A.; Patel, P.; Beall, C.J.; Stoyanov, P. Influence of Sb_2O_3 and the Binder System on the Tribological Characteristics of MoS_2-based Solid Film Lubricants. *To be Submitted*
    - Tonge P was responsible for the tribological tests, the data analysis and writing of the original manuscript draft. Roy, A was responsible for data analysis and critical review. Patel, P was responsible for data analysis and critical review. Beall C.J was responsible for providing the deposited samples for experimental work and critical review. Stoyanov, P was responsible for supervision, data analysis, conceptualization, and modification in the original manuscript

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Abbreviations

COF – Coefficient of Friction

SEM – Scanning Electron Microscope

EDS – Electron Dispersive Spectroscopy

AFM – Atomic Force Microscopy

FTIR – Fourier Transform Infrared Spectroscopy

FDC – Force Displacement Curve

VAM – Velocity Accommodation Mode

Organization of thesis

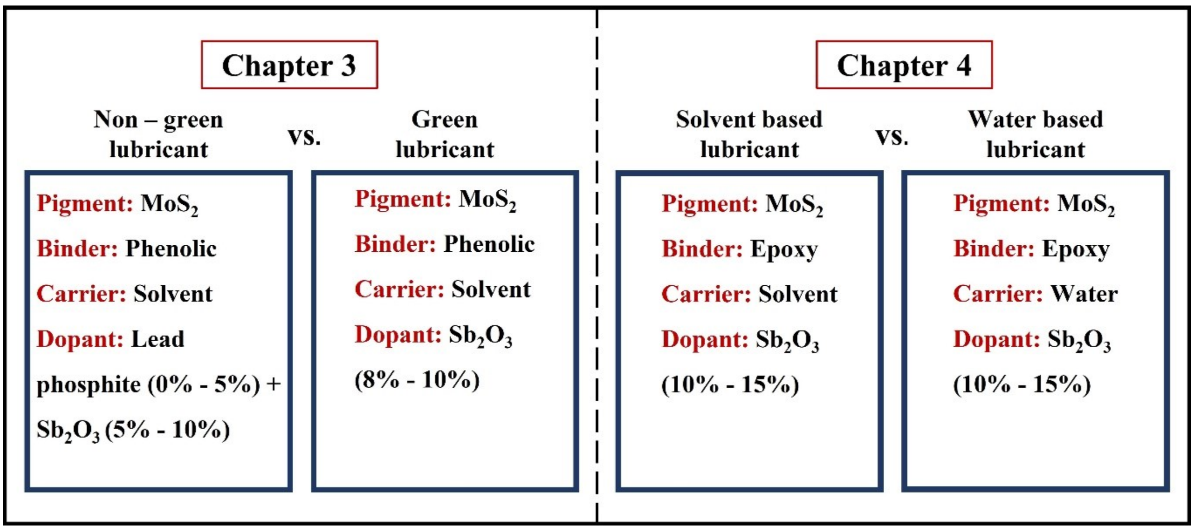
i. Chapter 1 presents the introduction along with the motivation and scope of the thesis

ii. Chapter 2 provides a background information related to Tribology. Additionally, literature review on MoS_2 based solid lubricants is presented.

iii. Chapter 3 presents the tribological study between non-green lubricant (with Pb based compound) and green lubricant (without Pb based compound). The tribological testing was performed at different contact pressures and in this study, the friction behavior of both the solid lubricants were identified in terms of the Hertzian elastic sliding component.

iv. Chapter 4 presents the tribological study between solvent based lubricant and water based lubricant. The Tribological testing was performed at different contact conditions and the coefficient of friction results in this study were correlated with the phenomenon of interfacial shear stress.

v. Chapter 5 concludes the thesis with overall major conclusions and the future work on MoS_2 based solid lubricants.



Chapter

1. INTRODUCTION & SCOPE

In this chapter…

The basic introduction along with the motivation and the scope of the thesis is presented.

1.1. Introduction

The history of lubrication systems dates back to approximately two thousand years ago. A lubricant is a substance that helps in reducing friction and wear of the contact surfaces during the relative motion [1]. In early 20^{th} century, the most commonly used lubricants were mineral oils, vegetable oils and greases. However, due to the recent technological advancements, lubricants can be applied in any phase such as solid, liquid and gas [1,2]. Among these, the usage of solid lubricants in the aerospace industry have increased in recent years due to their stability in extreme environments. Some of the common solid lubricants used in the aerospace industry are MoS_2, Graphite, hBN [3–5]. However, MoS_2 based solid lubricants are most frequently used in extreme environments especially in gas turbine engines. These lubricants help in reducing the friction and increasing the wear resistance of the component [5]. The main drawback of using MoS_2 as solid lubricant is that it is very sensitive to the environmental conditions. It is known that pure MoS_2 performs better (i.e., low friction and low wear) in vacuum conditions, however, in humid conditions, they experience premature failure due to the formation of oxides such as MoO_3 [6–8]. To overcome these limitations, MoS_2 solid lubricants are generally doped with different elements or compounds such as Au, Ag, Pb, Ti, Sb_2O_3, PbO, WS_2 etc. [5,8–10]. Additionally, some of the most common techniques used for the deposition of MoS_2 are sputtering, spray deposition and burnishing [11]. Specifically in spray deposition technique, a bonded MoS_2 solid lubricant contains a lubricating solid which is known as a 'pigment', a binding agent which is used to bind the pigment and the dopant with the metal substrate and the carrier solvents which helps in dissolving these formulated ingredients. The pigment primarily helps in providing low friction and wear during the sliding motion [12].

Pb based compounds have commonly been used in aerospace industry for quite some time [13], in particularly as doping elements to MoS_2-based lubricants. Pb is a soft metallic element that has excellent seizure and corrosion resistance properties and has lower friction characteristics [13,14]. However, due to the toxic nature of Pb, there is a strong desire to replace Pb based compounds with 'green' alternatives. Likewise, a bonded MoS_2 based solid lubricant may contain organic solvents or aqueous solvents that can be used as carriers. Organic solvents are occasionally preferred as they have good corrosion resistant properties, and they have excellent dissolving capabilities. However, they can be harmful to the environment due to their release of volatile organic compounds (VOCs) during the curing process [15,16].

Consequently, there exists a strong desire to replace the organic solvents with more eco-friendly alternatives such as aqueous solvents. Moreover, it remains unclear how the addition of Pb based compounds or the type of binder and the carrier systems affects the tribological behavior of the bonded MoS_2 based solid lubricants.

1.2. Scope of the thesis

The primary objective of this thesis is to develop and critically evaluate next generation 'green' solid lubricants for extreme environments as well as to provide a better understanding of the interfacial processes. The following short term objective (SO) have been identified:

SO1 → To develop a methodology and procedure for evaluating green solid lubricants

SO2 → To identify the influence of the increase in Sb_2O_3 content within bonded MoS_2 based solid lubricants on the tribological performance

SO3 → To identify the influence of Pb-based compounds on the interfacial processes of the bonded MoS_2 based solid lubricants

SO4 → To provide a better understanding of the influence of the carrier solvents on the interfacial processes of these lubricants

1.3. Final remarks

All the manuscripts in this master's thesis have already been published or under internal review. The chapter 3 and chapter 4 includes an experimental procedure section, which might be similar and contain the information that may overlap within the manuscripts.

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Chapter

2. BACKGROUND INFORMATION AND LITERATURE REVIEW

In this chapter…

A brief introduction to tribology, friction, wear and lubrication and solid lubrication especially with MoS_2 is presented. Additionally, literature review on MoS_2 such as friction and lubrication mechanisms along with the information on spray bonded MoS_2 is presented.

2.1. What is Tribology

Tribology is a derived from a Greek word named "Tribos" which means rubbing or sliding. Tribology is relatively new branch of science which deals with friction, wear and lubrication of interacting surfaces in relative motion. Surface interactions in the tribological interface can be very complex and their understanding requires a lot of disciplines such as physics, chemistry, fluid mechanics, thermodynamics, heat transfer, material science etc. [1,2]. Wear in general is usually caused in between high friction surfaces and it causes loss in mechanical efficiency. To increase this efficiency, lubricants are employed which effectively reduces the wear and friction between two bodies.

The tribological interactions can occur at numerous levels, but usually can be divided into macrotribology and micro/nanotribology. The main difference is that in macrotribology, the tests are conducted at heavier loads and therefore the wear is unavoidable and is generally in higher amounts. On the other hand, nanotribology, the tests are conducted at lighter loads and the wear is generally in the nanolayers [1].

2.2. Friction behavior

Friction is resistance to motion of one object moving relative to another during sliding, that is experienced when one object moves tangentially over another. The resistive tangential force which acts directly opposite to the direction of motion is called frictional force.

Two basic laws of friction are generally obeyed over a wide range of applications. These are known as Amonton's laws off friction. The first law states that the frictional force (F) is proportional to normal load (W). In this, the coefficient of friction is independent of Normal load. It is represented by

$$\mu = \frac{F}{W}.$$

The second law states that the frictional force is independent of the apparent area of contact which means that the coefficient of friction is same regardless of the size of the bodies. Usually, the frictional force is divided into two components and is represented as [1,3]

$$F = F_a + F_p,$$

where F_a is the friction force due to adhesion and F_p is the friction force due to plastic deformation

2.3. Wear

Wear is the removal of the surface or damage of the material during the sliding or rolling motion. The environment in which the sliding or rolling motion occurs has a huge impact on the wear removal rate. There are different types of wear classified based on the type in which the material is removed, and these are classified as wear mechanisms [1,2,4]. The most common types of wear mechanisms are

- **i.** Adhesive wear
- **ii.** Abrasive wear
- **iii.** Fatigue wear
- **iv.** Tribochemical wear

Apart from these basic wear mechanisms, many more different types of wear mechanisms have been proposed such as corrosive wear, oxidative wear, erosive wear etc.

As mentioned earlier, the wear of the material mostly depends on the type of the environment used for sliding motion, and the amount of wear of the material is shown in the form of wear rate. Generally, the wear rate is given by [4].

$$K = \frac{V}{W * S},$$

where V is worn volume, W is normal load applied during sliding and S is distance moved

2.4. Lubrication

To reduce the amount of wear and friction in the contact interfaces, a lubricant is introduced, and this process is known as lubrication. The lubricant can be of any form of material such as solid, liquid or gas. They are usually in form of nano layers that impart low shear strength during the sliding motion. The type of lubricant imposed between the two contacting surfaces depends on the type of application. However, if the lubrication is due to gas or liquid, it is generally termed as "hydrodynamic lubrication" and if the lubrication is due to solids, then it is termed as "solid lubrication" [2,4].

2.5. Solid Lubrication

Solid lubricants are materials that are in solid state and help in reducing the friction and wear between two contacts during relative motion. The low friction and wear is achieved when these solid state materials have low shear strength between the contact interfaces during the relative motion [2,4–7]. A solid lubricant can be used in the form of thin film or a powder, a coating or they can also be dispersed in liquids. Solid lubricants are mainly used where the liquid lubricants are not feasible to use. They are used in extreme environments such as high-vacuum environments where a liquid lubricant would evaporate easily. At higher temperatures, liquid lubricants would decompose or oxidize and at cryogenic temperatures, the liquid lubricants are highly viscous, and they may even solidify, hence, solid lubricants are employed that can operate at a range of temperatures (-280°C - 400°C)[6]. Additionally, solid lubricants are more effective at higher loads and higher speeds, they have high thermal stability and also, they have better corrosion resistant properties [4].

Generally, solid lubricants are classified into 3 types. a) Inorganic lubricants with lamellar structure (examples: MoS_2, Graphite, HBN etc.), b) Soft metals (examples: Pb, Ag, Au, Sn, Bi etc.) and c) Organic lubricants with chain structure of the polymeric molecules (example: Polytetrafluoroethylene-PTFE)[4]. Usually, materials with lamellar structure have great potential to be used as solid lubricants due to the fact that the lamellae can slide over one another at relatively low shear stress. Among those mentioned above, MoS_2 is widely used as a solid lubricant as it can operate at a wide range of temperatures and also at various ambient conditions based on the applications.

2.6. MoS_2 as Solid lubricant

MoS_2 has been widely used as solid lubricant for over 70 years. Due to its crystal structure, it can provide low friction and low wear during the sliding motion. Pure MoS_2 performs better in vacuum conditions, hence they are widely used in spacecrafts and satellites. The following sections discusses about the crystal structure, the mechanisms behind low friction and wear and effect of dopants on MoS_2 based solid lubricants.

2.6.1. Crystal Structure of MoS_2

The molecular structure of the Molybdenum disulphide (MoS_2) has 1 atom of Molybdenum with 2 atoms of Sulfur. It has a layered structure which is hexagonally packed with 3 individual planes of Mo-S stacked upon each other. There is a strong covalent bond between the Mo-S atoms and weak van der Waals forces between the layers of the atoms [4,5,8]. The crystal structure of MoS_2 is shown in the figure 2.1.

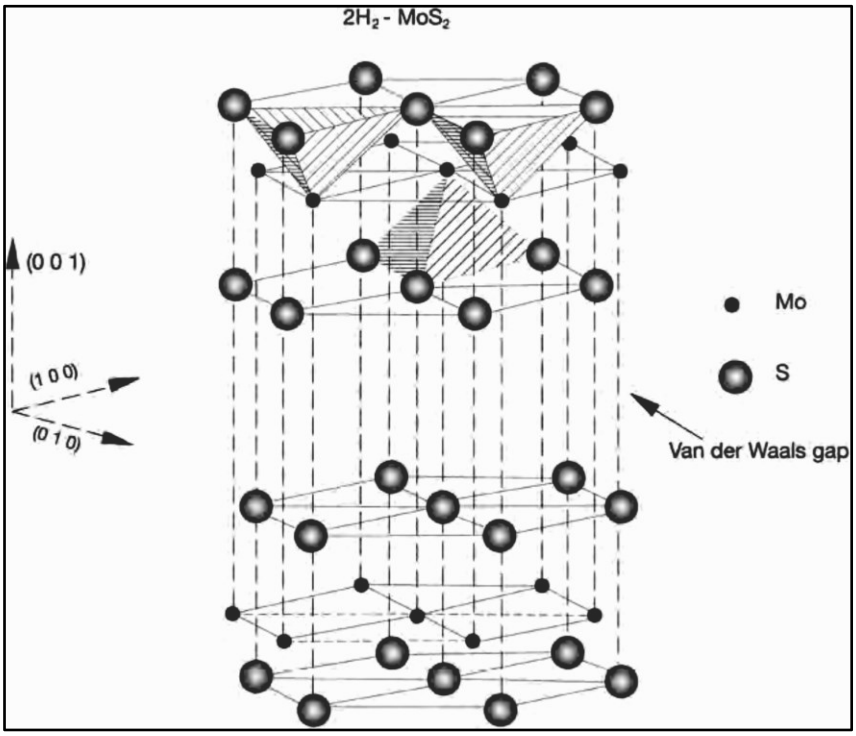

Figure 2.1 The layered hexagonal crystal structure of MoS_2 [4]

MoS_2 exhibits anisotropy, thus having low shear strength which is the reason for exhibiting low coefficient of friction. However, the COF of MoS_2 depends on several environmental factors such as pressure, temperature, humidity etc. [4,5]. For example, the MoS_2 with non-aligned orientation and in the presence of humidity and low pressure, the COF was measured to be as high as 0.3 [9]. On the other hand, in a controlled ultra-high vacuum conditions at a pressure of $50 * 10^{-9}$ Pa, the coefficient of friction was measured to be as low as 0.001 at a contact pressure of 0.4 GPa which is generally known as the superlubricity of MoS_2 [10]. However, the tribological properties of MoS_2 also greatly depends on the type of deposition technique. Generally, MoS_2 is applied to the surface by much traditional methods like powder or grease, spray bonding, burnishing, sputtering techniques such as PVD, CVD etc.

The MoS_2 films when formed with the process of burnishing can produce a coating thickness in between 1 µm and 5 µm. This deposition technique is inexpensive and easy to apply but can produce non-uniform thickness with poor adhesion to the substrate [4,9,11]. The bonded MoS_2 based solid lubricants can be produced either by dip spin process or by spraying. Likewise, this technique is inexpensive and easy to apply and can produce the coating thickness in between 5 µm and 25 µm [11,12]. However, thin film coatings cannot be produced with spraying and the films can be relatively abrasive in nature. Thus, the static coefficient of friction is higher. However, once the sliding motion begins, the random MoS_2 crystallites will orient themselves in the parallel direction to the substrate having lower coefficients of friction [4,9]. The PVD deposition technique, on the other hand, can produce thin film coatings which ranges from monolayer to micron level. This technique is expensive and requires vacuum as a medium to deposit, however, highly dense coatings can be produced with uniform hardness as well as excellent adhesion to the substrate [4,5,11].

2.6.2. Spray bonded MoS_2 based solid lubricants

A bonded MoS_2 based solid lubricant mainly consists of the lubricating solid (i.e., pigment) and a binder material. The pigment generally helps in lowering the friction and wear and is usually dispersed in the binder material. A binder material helps in providing the adhesion to the substrate [13]. A typical application process of the bonded MoS_2 based solid lubricant can be found elsewhere [14]. Bonded MoS_2 films generally have lower friction and wear, hence, they are used in wide range of applications such as aircrafts, satellites, nuclear power plants where the operations are performed at extreme environments [15]. The major factors that affect the performance of the bonded MoS_2 based solid lubricant films are [15]

i. Substrate conditions: Material of the substrate, hardness, surface roughness and the pretreatment process
ii. Film conditions: binder material, binder to lubricating ratio, film thickness and curing conditions
iii. Operating conditions: temperature, humidity, vacuum, sliding speed, normal load, presence of contaminants etc.

In bonded MoS_2 based solid lubricants, the binder material and binder-to-lubricant ratio are considered as important conditions as they can significantly influence the tribological properties [15,16]. Although, many binder materials are available in the market, the thermoplastic and thermosetting resin binders are most commonly employed for aerospace applications. The resin binders can be heat-cured or air-cured materials [13]. For resin-binders, the appropriate binder-to-lubricant ratio is 1:1 to 1:4 with 1:2 used typically [16]. As mentioned earlier, higher lubricant amount provides low coefficient of friction and higher binder amount provides increased wear resistance, better corrosion, and high hardness but with higher coefficients of friction. Moreover, an appropriate surface pre-treatment is essential for the bonded MoS_2 based solid lubricants, or else, the lubricant can get peeled off easily [13,16,17]. Usually, depending on the substrate, the pre-treatment process is employed. However, the most common pre-treatment process is grit-blasting which is performed to increase the surface adhesion. The grit-blasting is commonly done using alumina or steel grits [16].

Generally, the MoS_2 based solid lubricants are heat-cured films, although the air-cured films are used depending on application. The process of curing is usually performed at 200°C for 1 hr. The heat-cured resin bonded films often exhibit higher wear during the initial sliding motion as the loose particles are detached from the surface of the film. However, as the run-in process continues, the films appear more burnished due to the possible orientation of MoS_2 crystallites with the basal planes parallel to the substrate providing low coefficient of friction and low wear [13,16]. The schematic cross-section of the bonded MoS_2 film is shown in the Figure 2.2.

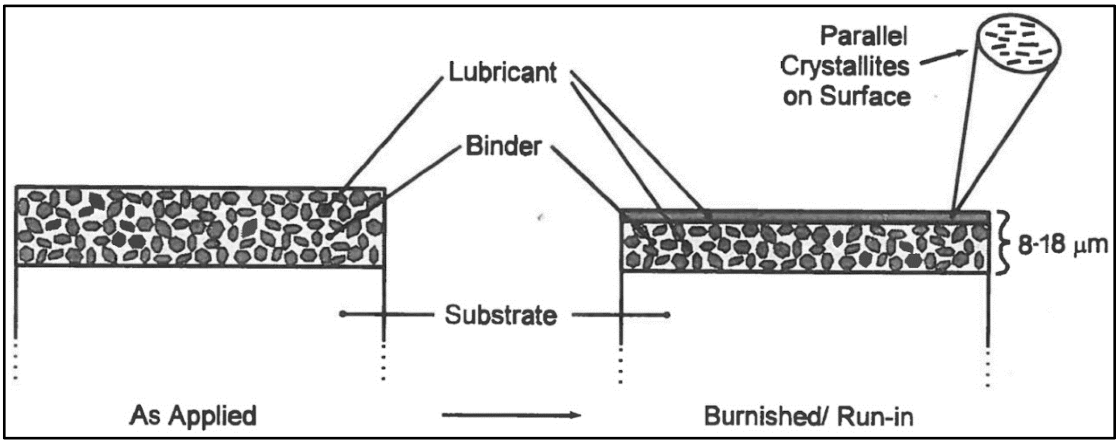

Figure 2.2 Schematic cross section of a typical bonded MoS_2 film [16]

Phenolics and the epoxy resins are the most common types of binder materials used in the heat-cured resin bonded solid lubricant films. Phenolics have good surface adhesion but require high temperature curing cycle whereas epoxy resins have good solvent resistance and good adhesion properties but are softer than phenolics [13,15,16]. The heat-cured resin bonded films are preferable over air-cured films because of higher load carrying capability and longer wear life [13].

2.6.3. Transfer mechanism in MoS_2

In dry sliding contact conditions, transfer of material from one surface to another is a common phenomenon[9]. The transfer layer formation is a process that starts with surface deformation, surface cracking, wear debris generation, particle agglomeration and then transfer layer formation. The Figure 2.3 shows the formation of transfer layer [4]

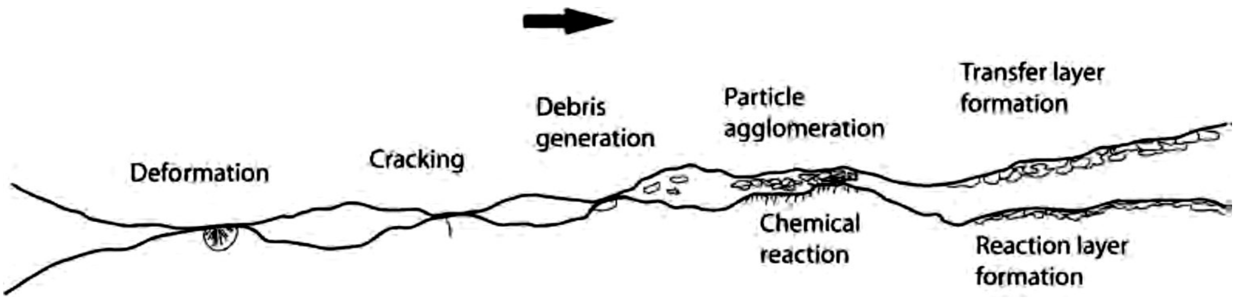

Figure 2.3 Process for the formation of transfer layer [4]

It is generally said that low friction and high endurance are incoherent with each other because soft films can be worn out very easily, but studies have proven that during sliding contact, there could be the formation of “third bodies” which can be beneficial in providing low friction and long wear life[18]. Based on the observation on the sliding contacts Singer [18] proposed a three-stage model for the formation of transfer layers. First, a thin layer is detached from the surface during sliding and gets transferred to the counterface. During the process, both the surface layer and the transfer layer react with surroundings to form new compounds. As the process continues, the transfer film thickens, it gets expelled from the contact area and can form wear debris. This process is repeated as the sliding continues and a layer-by-layer build up takes place.

One of the important findings regarding the transfer layer of the MoS_2 was during the sliding contact, the MoS_2 coating itself developed into a basally oriented texture [19,20]. This was also proved by Singer et. al.[20]where he performed an experiment on a four ball tester with MoS_2 coated steel substrate against uncoated sliders of steel, co-bonded WC and Sapphire. He observed a very interesting phenomenon of the wear scars on the uncoated sliders and revealed three noticeable areas around the contact. The first area was a circular contact zone which was covered with a transfer layer which is similar to the phenomenon discussed above. The second area was the entrance to the contact zone which had a compact debris that seemed gray and smooth. Finally, the third area was the loose, powdery debris which is present away from the contact area. The schematic is present in the Figure 2.4.

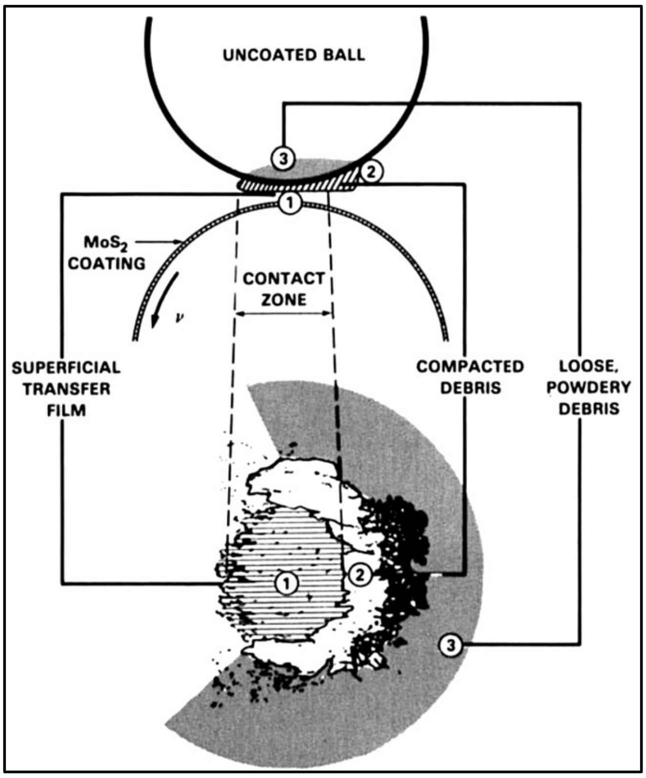

Figure 2.4 Schematic of debris observed on wear test balls [20]

Since the sliding contact during the lubrication process occurs between the basally oriented MoS_2 transfer layer and the wear track, these orientations are responsible for low shear eventually for low friction.

Now, the MoS_2 transfer layer which is formed during the process is not the only compound responsible for providing lubrication, there is a possibility of forming various transfer layers that contains MoO_3 as well as the oxides of the other compounds. By the existing evidence, we can say that these oxides may or may not be responsible for providing better lubrication[20]. These transfer layers are known as the tribochemical reaction layers where a thin oxide layer of usually 1-10 nm thick is formed on the surfaces. As discussed above, some oxides such as copper oxide is sheared more easily eventually providing better lubrication[4].

2.6.4. Friction mechanism is MoS_2

Generally, a three-stage mechanism of sliding MoS_2 is shown by Bartz and Xu [4] which consists of running-in stage, steady state stage and the failure stage as shown in the Figure 2.5.

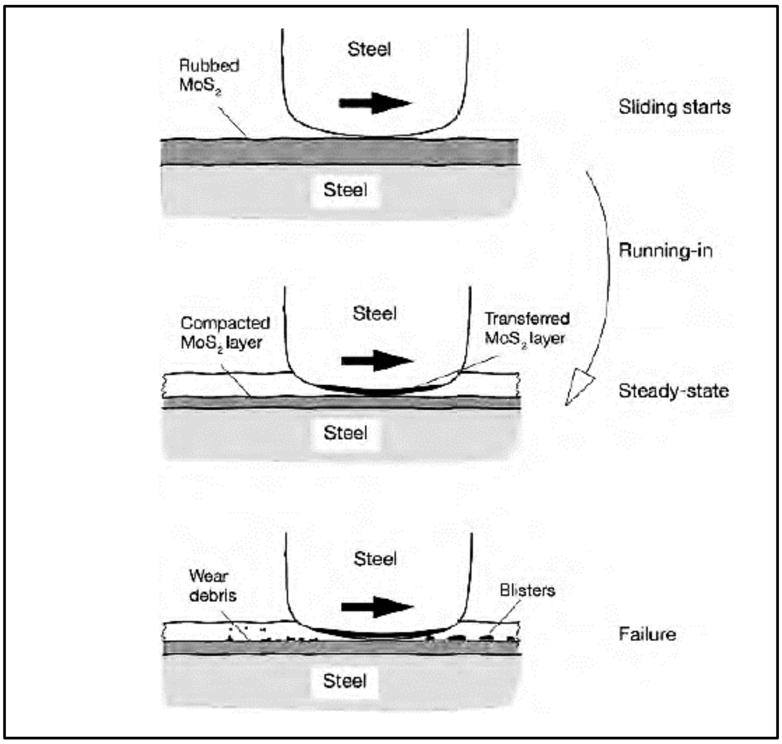

Figure 2.5 The different contact mechanisms of a steel pin during the sliding motion of MoS_2 [4]

- **i.** Initially, during the running-in stage, the sliding MoS_2 film under the influence of normal load and tangential shear, becomes compressed to some extent than the original thickness and form a transfer film on the counterface. In this process, the basal planes gets exposed and reorient themselves parallel to the sliding direction. The frictional heating may come into effect and there may be the formation of MoO3 at the interface.
- **ii.** After few thousand cycles, the compression of film is ceased and therefore attains the steady state stage. In this stage, the coefficient of friction of the film is lowest and wear rate of the MoS_2 film has the low. This completely depends on the normal load applied, the frequency of sliding, the sliding distance, temperature and humidity.
- **iii.** Finally, the failure of the MoS_2 films occur when the surface blisters and the wear fragments begin to appear. During sliding, the wear fragments, under the influence of normal load, become more brittle, ultimately forming a loose powdery debris. According to Gardos [21], the oxidation of MoS_2 films with the layers and the frictional heating at the interfacial region is the main cause of the blister formation eventually leading to failure of the MoS_2 films.

2.6.5. Lubrication mechanism

The mechanism behind the tribological behavior of MoS_2 based lubricant can be explained with the help of the formation of third bodies. This third body approach illustrates the process of the formation of tribofilm responsible for the steady state operation till the failure of the coating [22]. This theory can be better understood with the help of the tribological circuit as shown in the figure 2.6.

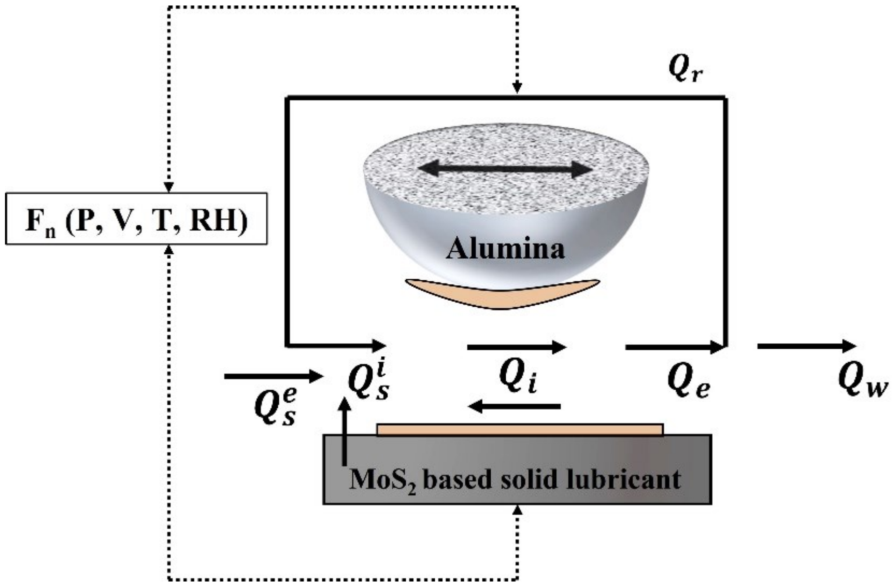

Figure 2.6.Tribological circuit showing the influence of third bodies across various flows [22, 23]

This circuit describes the tribological life of the contact material as it detaches, deforms, and gets ejected from the contact under the influence of normal load and the difference in the velocities. The tribological circuit describes the different flows by which the process of third bodies are created or ejected from the contact [11]. These third body particles during the sliding motion can experience fracture, shearing, rolling, elastic deformation or plastic deformation that represents various velocity accommodation modes. The internal source flow ($\boldsymbol{Q_s^i}$) represents the formation of natural third bodies due to adhesion, cracking etc. The external source flow ($\boldsymbol{Q_s^e}$) represents the formation of artificial third bodies from the external contaminants. $\boldsymbol{Q_i}$ represents the internal flow i.e., the flow of third bodies within the contact (trapped particles). $\boldsymbol{Q_e}$ represents the ejected flow external to the contact i.e., the flow of third bodies that are ejected from the contact. $\boldsymbol{Q_r}$ represents the recirculation flow where the ejected particles are re-introduced into the contact which again contributes to the velocity accommodation mode. Finally, $\boldsymbol{Q_w}$ represents the wear flow of the third bodies that are definitely ejected and do not participate in the re-circulation flow. They are generally the loose debris particles [11,22,23].

2.6.6. Effect of dopants

Pure MoS_2, due to their lamellar structure can itself be used as solid lubricant. The tribological properties of MoS_2 has shown to be working very well in the vacuum environments which has a gained a lot of importance in Aerospace industry [3,5]. However, pure MoS_2 when doped with other elements or compounds have shown excellent mechanical and tribological properties. MoS_2 can be doped with various metals such as Au, Ag, Ti, Pb, Ni, Cr, Cu etc. as well as various compounds like PbO, WS_2, Sb_2O_3 etc. It has been shown that at higher contact pressures, MoS_2 when co-sputtered with higher concentrations of Au has performed better in humid conditions [24]. Also, in dry air, small amounts of Au when added to MoS_2 improved the tribological performance(i.e., low friction and low wear) when compared with pure MoS_2 [25,26]. The addition of dopants has also made the MoS_2 films much harder and denser [26,27]. A study by Renevier et. al [27] has shown that small addition of Ti has made the MoS_2 films harder and also the wear endurance was increased. A similar study was also illustrated by Simmonds [28].

We know that the tribological performance(low friction and low wear) is superior with the crystalline MoS_2 i.e., when the basal plane orientation (0 0 2) is parallel to the substrate [29,30] and studies have shown that the crystallization of MoS_2 is possible at the sliding interface due to mechanical stresses [31,32]. In sputtered deposited MoS_2, during the initial sliding, high wear was observed due to crystallite breakage as a result of which subsurface crack evolution and the delamination of the flakes of MoS_2 were observed [32,33]. This phenomenon was restricted because of the addition of dopants especially with Pb-Mo-S coatings[32].

As mentioned earlier, pure MoS_2 performs exceptionally well in vacuum conditions rather than in humid conditions. Whenever pure MoS_2 comes in contact with oxygen or the humid environment, it oxidizes to form MoO_3 and H_2SO_4.

$$\boldsymbol{2MoS_2 + 9O_2 + 4H_2O \rightarrow 2MoO_3 + 4H_2SO_4} \text{ [34]}$$

MoO_3 particles are much abrasive in nature and shows higher interfacial shear strength which corresponds with higher frictional coefficients and reduced wear life. Consequently, they can damage the film microstructure eventually reducing the life of the overall coating [34–38].

However, the oxidation is prone only to the outermost layer of the film and this degree of surface oxidation is based on number of factors such as the film microstructure, temperature, humidity etc. Though the rate of oxidation usually increases with increase in absolute humidity [34]. This formation of MoO_3 can also be reduced when pure MoS_2 films are doped with the above-mentioned elements or compounds.

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Chapter

3. TRIBOLOGICAL EVALUATION OF LEAD-FREE MOS_2-BASED SOLID LUBRICANTS AS ENVIRONMENTALLY FRIENDLY REPLACEMENTS FOR AEROSPACE APPLICATIONS

In this chapter…

The tribological study between the non-green and green MoS_2 based solid lubricants is provided. The tribological testing and various characterization techniques were employed to understand the interfacial phenomenon of the solid lubricants.

3.1. Abstract

Solid lubricants, such as MoS_2 have been widely used in the aerospace industry with the primary purpose of reducing the friction and wear of tribological interfaces. MoS_2 based solid film lubricants are generally doped with other compounds, which can help overcome some of their limitations related to environmental conditions. For instance, compounds like Sb_2O_3 and Pb have been traditionally used to improve the endurance life of these lubricants. However, with the recent zest in transferring to eco-friendly lubricants, there is a strong push to eliminate Pb based compounds. The main purpose of this work is to better understand the influence of Pb based compounds on the tribological behavior of MoS_2 based solid film lubricants as well as to critically evaluate the performance of Pb free lubrication strategies. More specifically, the baseline 'non-green' lubricant was doped with Pb compound and Sb_2O_3 and the Pb compound in the 'Green' alternative lubricant was replaced by more Sb_2O_3. The wear test was done using a ball-on-disk tribometer for specific loads and for 5000 cycles. Ex-situ analysis was conducted using Scanning Electron Microscope (SEM), Atomic Force Microscopy (AFM), and micro-Raman to capture the interfacial processes of these lubricants at different loads. Overall, the non-green lubricant performed better in terms of the tribological behavior (i.e., lower friction and wear), which was attributed to the formation of a dense MoS_2-based tribo-/transfer-film with the basal planes oriented in the parallel direction to the sliding. The finding on the interfacial phenomena provided critical insights into the development of novel green alternatives that may have the ability to replace Pb based compounds in the future for a sustainable environment.

3.2. Introduction

Solid lubricants are commonly employed in tribological interfaces with the purpose to reduce friction and increase the wear resistance of the component. While there are many commercially available solid lubricants (e.g., Graphite, MoS_2, WS_2, PTFE, etc. [1]), MoS_2 – based solid lubricants are most frequently used in extreme environments, such as gas turbine engines [2], due to their favorable tribological behavior (e.g., low friction and low wear). MoS_2 has a layered structure that consists of one atom of Mo which is sandwiched between 2 atoms of S. There exists a strong covalent bond between Mo–S atoms and a weak Van Der Waals attraction between the layers of the atoms [3,4]. The main drawback of using MoS_2 is that its tribological behavior is very sensitive to environmental conditions. While pure MoS_2 performs well in vacuum conditions, it can exhibit higher friction and premature failure when operating in humid/ambient conditions, which is sometimes attributed to the formation of MoO_3 [5,6]. To overcome some of these challenges, MoS_2 is usually doped with metals/composites, such as Au, Ti, Ni, Ag, PbO, Sb_2O_3, WS_2, WSe_2, etc. [1,3,4,7–9] These compounds make the composite coating more reliable and also improves the tribological performance in the ambient conditions. In particular, lead based MoS_2 lubricants have traditionally been used in the aerospace community due to their favorable stability. Pb also has some exceptional features, such as softness, low melting point, high ductility and resistance to corrosion which makes the usage of Pb very critical in the Aerospace Industry [10]. However, due to its toxic nature and its adverse effects on the environment, the usage of Pb has been reduced and many green alternatives have been proposed [10–12].

Wahl et al. [13] showed that MoS_2 doped with a small amount of PbO results in relatively high wear resistance and lower frictional coefficients than pure MoS_2 [14–16]. The sliding induced crystallinity has been observed in Pb based MoS_2 lubricants through Raman Spectroscopy [13,15]. More specifically, at the sliding interface, the initial amorphous MoS_2 coating was converted into crystalline MoS_2 due to the mechanical stresses [13]. However, with crystalline MoS_2, there is a possibility of high wear during the initial stages of sliding which may cause the fracture of crystallites in the microstructure [14,17]. This behavior was not observed for the amorphous Pb-doped MoS_2 films, which could possibly be explained by the fact that the Pb-doped MoS_2 lubricants are less sensitive to delamination [14].

While Pb basedMoS_2 lubricants provide better tribological performance over other solid lubricants, there is a strong desire to replace Pb with ‘green alternatives’ due to health and environmental concerns. One compound that is commonly doped with MoS_2 solid lubricants is Sb_2O_3 [6]. While Sb_2O_3 is not a self-lubricating compound, it has shown to be an effective dopant to MoS_2 in reducing friction and wear. Three main advantages of adding Sb_2O_3 to the composite have been identified in the literature as follows: (i) Sb_2O_3 reduces the intercolumnar porosity and thus, increases density and increases hardness, (ii) it serves as an oxidation barrier and also (iii) it inhibits the crack growth by making the film harder [1,8,18–20].

The main purpose of this study is to compare the tribological behavior of Pb based MoS_2 dry film lubricant (non-green lubricant) to Pb free MoS_2 based dry film lubricant (green lubricant) under a wide range of contact conditions. While both, the green and non-green solid film lubricants are doped with Sb_2O_3, the lubrications strategy for the 'green' alternative was to replace the Pb content with an additional amount of Sb_2O_3. The solid film lubricants were evaluated in terms of their tribological behavior at a wide range of contact stresses, mimicking conditions observed in gas turbine engines. This study has employed some of the characterization techniques, such as SEM, AFM and micro-Raman to provide a better understanding of the interfacial phenomena and the chemical nature of the coatings. The observations from the EDS analysis and the mapping were correlated to the adhesive forces measured using atomic force microscopy. In addition, the tribofilms of the lubricants were investigated in detail by means of Raman spectroscopy in terms of their composition and structure.

3.3. Materials and Methods

In this study, two solid film lubricants are characterized in terms of their tribological behavior. The two solid film lubricants are Everlube 620C (green lubricant) and Lube-Lok 5306 (non-green lubricant). Everlube 620C is composed of MoS_2, Sb_2O_3 (5–10wt.%), and organic compounds as binders. Lube-Lok 5306 has MoS_2, Sb_2O_3 (<10wt.%), lead phosphite (<5wt.%) and organic compounds as binders. More details on the composition of the solid film lubricants can be found elsewhere [21]. The main difference between the 'green' and 'non-green' lubricant is that the lead phosphite present in the 'non-green' version is replaced with an additional amount of Sb_2O_3 in the 'green' lubricant. The MoS_2-based solid film lubricants were deposited onto 304L stainless steel substrates. The solid film lubricants were deposited using the spray bonding process. More details on the process can be found elsewhere [22]. Briefly, prior to the deposition, the stainless-steel substrates were surface polished using the Struers Tegramin polishing and grinding equipment. The surface roughness of the polished sample was measured to be 0.09 microns. Subsequently, grit-blasting was done as a pre-treatment process (i.e., 220 Al_2O_3 grit size was used for grit-blasting). The thickness of the lubricants was in the range of 11-13 microns.

Tribology testing was performed by means of a ball-on-disk linear tribometer (Anton-paar TRB^3 tribometer) using five different loads (i.e., 1 N, 5 N, 8 N, 10 N, 13 N) for 5000 cycles. The sliding speed was set at 3.1 cm/s, which corresponds to a frequency of 1 Hz. The sliding tests were performed for a stroke length of 10 mm. The testing was conducted at room temperature (25–28 °C) and the Relative Humidity was controlled between 15% and 20% by the use of desiccants. The counterface used for the testing was Al_2O_3 with a diameter of 6.35 mm. After the sliding tests, the wear depths were measured using LEXT Confocal Laser Microscopy and also the optical images of the counterfaces were obtained using the Confocal Laser Microscope. The schematic diagram of the tribometer is adapted from one of the author's previously reported works [23].

Coating characterization was performed by means of Hitachi High Technologies America, Inc., USA Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy (EDS) (Pentafet Link, INCA X-sight, Oxford instruments, UK) and Anton–paar Tosca 400 Atomic Force Microscopy (AFM), Switzerland. The SEM was used to obtain the high-resolution images of the wear tracks and the counterfaces and also to study the topography of the images. The EDS analysis was performed on the worn (5 N and 10 N) and unworn surfaces as well as on counterfaces in order to obtain the elemental composition. Subsequently, the AFM was used to obtain the pull-off force (adhesion force) and also to study the resistance to plastic deformation of the coatings. A total of 10 tests (five on worn surface and five on unworn surface) were performed per sample under the contact mode. An FDC (force-displacement curve) is generated due to the deflection in the cantilever tip which helps in determining the maximum adhesion force. A typical force-displacement curve is shown in Figure 3.1 [24,25]. Finally, Micro-Raman spectroscopy was performed on a 10 N worn surface using CNI MGL-U-532 equipped with High Stability DPSS Laser (532 nm), China to understand the crystallinity on the worn surfaces.

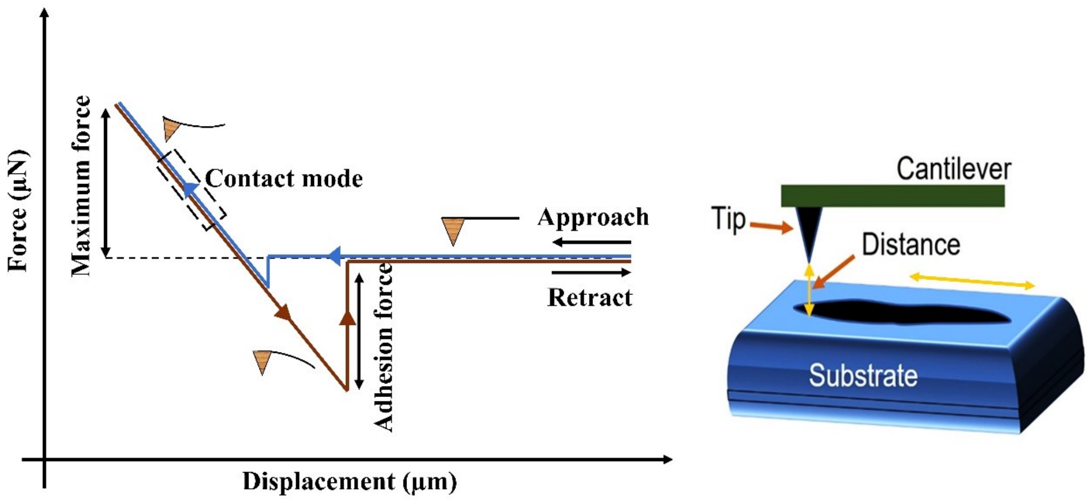


Figure 3.1. Determining adhesion force using Force—Displacement curve [24]

3.4. Results

3.4.1. Friction behavior

Figure 3.2 shows the friction behavior vs. the number of cycles for the green and non-green solid film lubricants. For both lubricants, the coefficient of friction decreased with increasing the normal load. A break-in phases of up to approximately 200 cycles is observed for all conditions. Subsequently, to the break-in phase, the friction coefficient remains relatively steady for the remainder of the test (i.e., steady state regime) with all normal loads except for 13 N on green lubricant. As shown in Figure 3.2(a), with a 13 N load, the green lubricant had worn out resulting in high friction. It should be noted that for the first test with a 13 N load, the lubricant started to wear out at around 3000 cycles, however, during the repeat, the lubricant remained intact and showed a steady state coefficient of friction of 0.09.

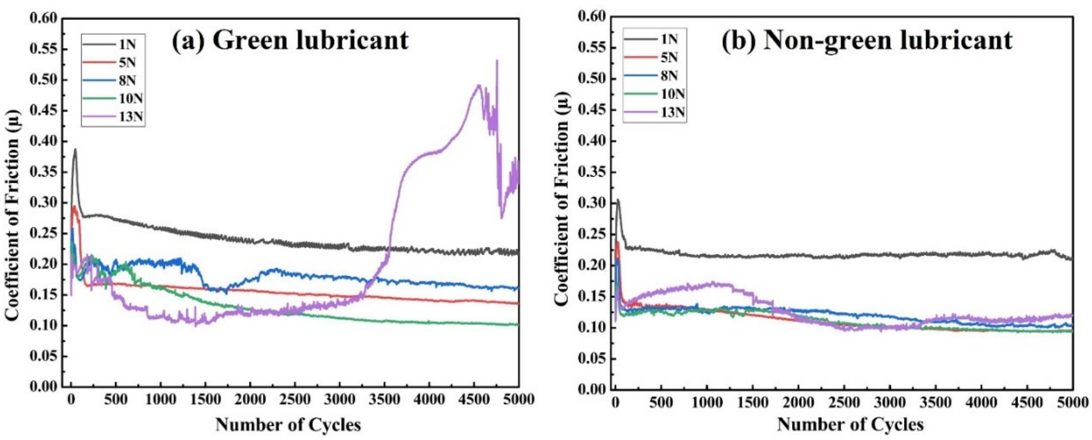


Figure 3.2. Friction coefficient vs. Number of Cycles with various normal loads for (a) Green lubricant and (b) Non-green lubricant.

Figure 3.3 shows the average steady state friction coefficient vs. the Hertzian contact pressures. The corresponding Hertzian contact stresses are calculated for the above-mentioned five different loads which range in between 0.68–1.62 GPa. More details on the calculation of the Hertzian contact stress can be found elsewhere. [26]

Overall, the non-green lubricant (Lube-Lok 5306) showed lower friction values for different contact pressures. The green lubricant showed a large deviation in the friction values with the13 N load, which can be explained by the premature failure of the lubricant at about 3000 cycles, as shown in Figure 3.2(a). This behavior was an indication that the non-green lubricant has a better load carrying capacity compared to the green lubricant. Thus, the inclusion of Pb seems to have an evident impact on the coefficient of friction results.

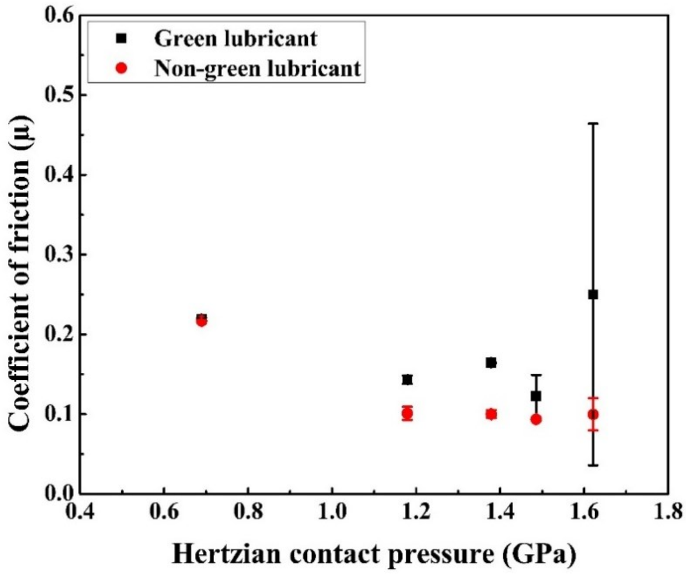


Figure 3.3. Friction coefficient vs. Hertzian contact pressure

Figure 3.4 shows the graph between the friction force and the normal force. A linear fit was performed in correspondence to $F \sim L^m$. The slope from the linear fit corresponds to m, which showed a value of 0.83 for the green lubricant and 0.69 for the non-green lubricant. The m value of 0.69 for the green lubricant is much closer to $F \sim L^{2/3}$ which corresponds to Hertzian elastic contact mode [4,27].

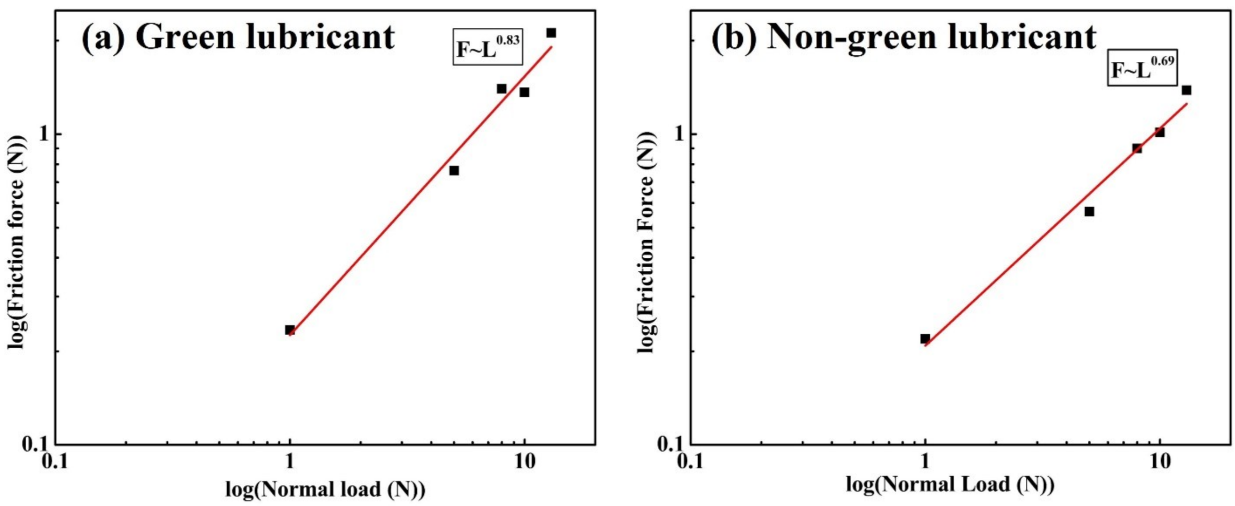


Figure 3.4. Friction force vs. Normal load for (a) Green lubricant and (b) Non-green lubricant

3.4.2. Wear behavior

Figure 3.5 shows the wear profiles of both lubricants for the various normal loads used throughout the testing. The behavior was quite different from the behavior of the coefficient of friction. Overall, the wear for both lubricants increases with increasing normal load. However, the wear depth for all conditions is lower for the non-green lubricant when compared with green lubricant. In particular, when using normal loads above 5 N, the wear of the green lubricant is evidently higher than the non-green lubricant.

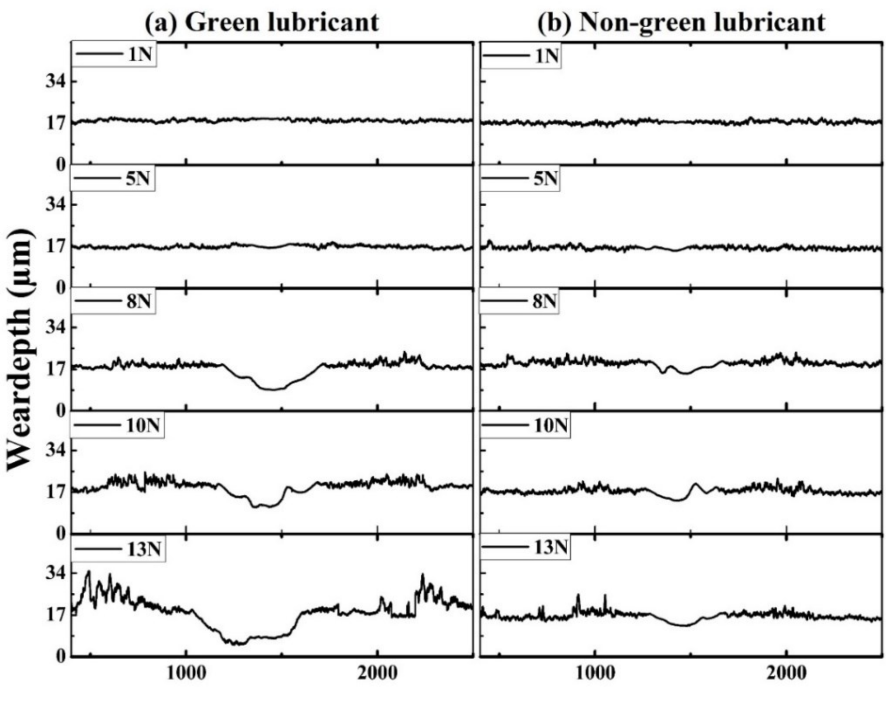


Figure 3.5. Wear depths of (a) Green lubricant and (b) Non-green lubricant

3.4.3. Ex Situ Analysis

Figure 3.6 shows the worn surface morphology of green lubricant and non-green lubricant at both 5 N and 10 N loads. In all conditions, the worn surfaces appear to have formed smooth tribofilms. However, the images of the green lubricant revealed the formation of cracks for 10 N, which were less evident with the non-green lubricant. Figure 3.6 (c, d) shows the wear tracks of green and non-green lubricant at 5 N load, which seems to be less uniform when compared to the tests with the higher normal loads. The tribofilms on the worn surface are shown on the magnified SEM images at both the normal loads.

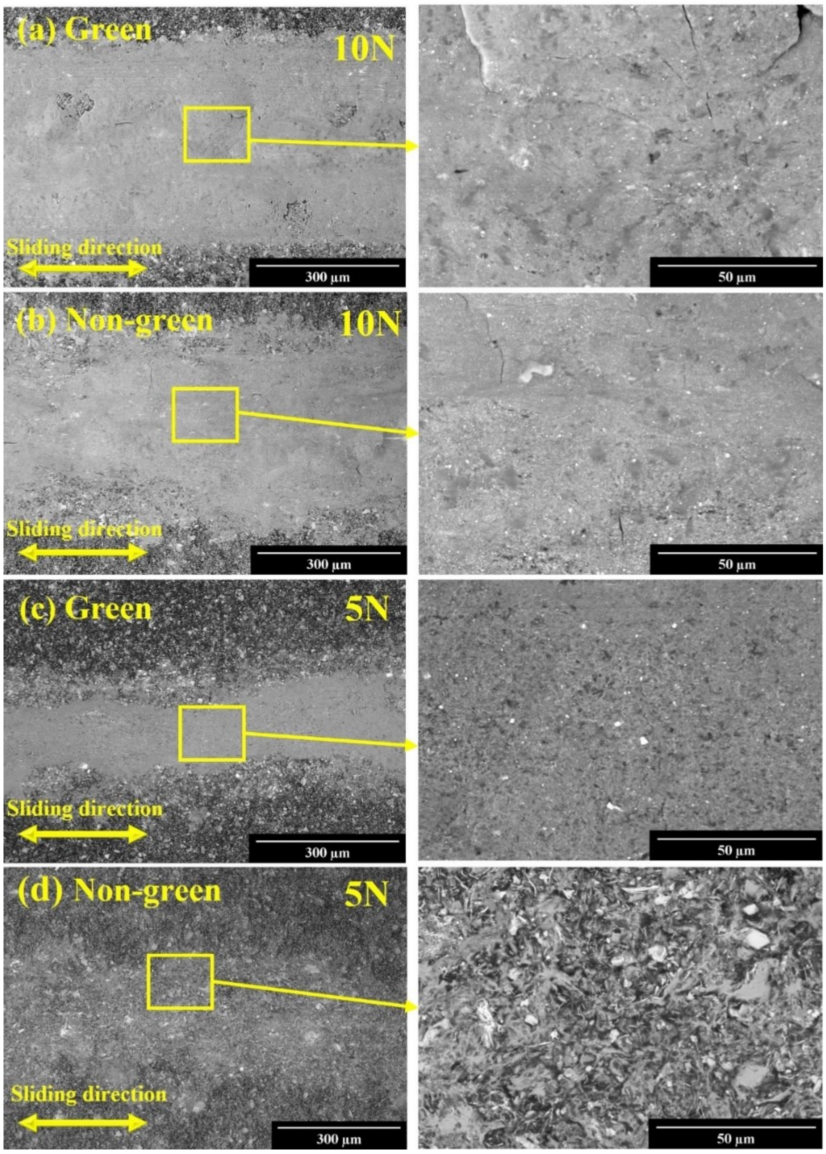


Figure 3.6.Wear scars of (a) Green lubricant at 10N (b) Non-green lubricant at 10N (c) Green lubricant at 5N (d) Non-green lubricant at 5N

Figure 3.7 shows the elemental maps of the wear tracks for both lubricants. The EDX analysis and the elemental maps suggested the presence of Mo, S, Sb, O as the main components in green lubricant. Similarly, the same elements were observed in non-green lubricant with the addition of Pb. The atomic percentages of the elements in green lubricant are Mo (5.89 ± 0.93), S (9.54 ± 1.46), Sb (1.86 ± 0.79), O (13.50 ± 3.55) and Fe (2.03 ± 2.95). The atomic percentages of the elements in non-green lubricant are Mo (7.86 ± 2.66), S (12.59 ± 4.45), Sb (1.25 ± 0.72), O (12.06 ± 6.24), Pb (0.25 ± 0.23) and Fe (0.27 ± 0.05). In addition, the atomic percentages and EDX maps in Figure 3.7(a) showed the traces of Fe content for green lubricant, which indicated that parts of the solid lubricant have been worn out. This correlates well with the observation of the coefficient of friction for the 13 N load test, where the coating has worn out.

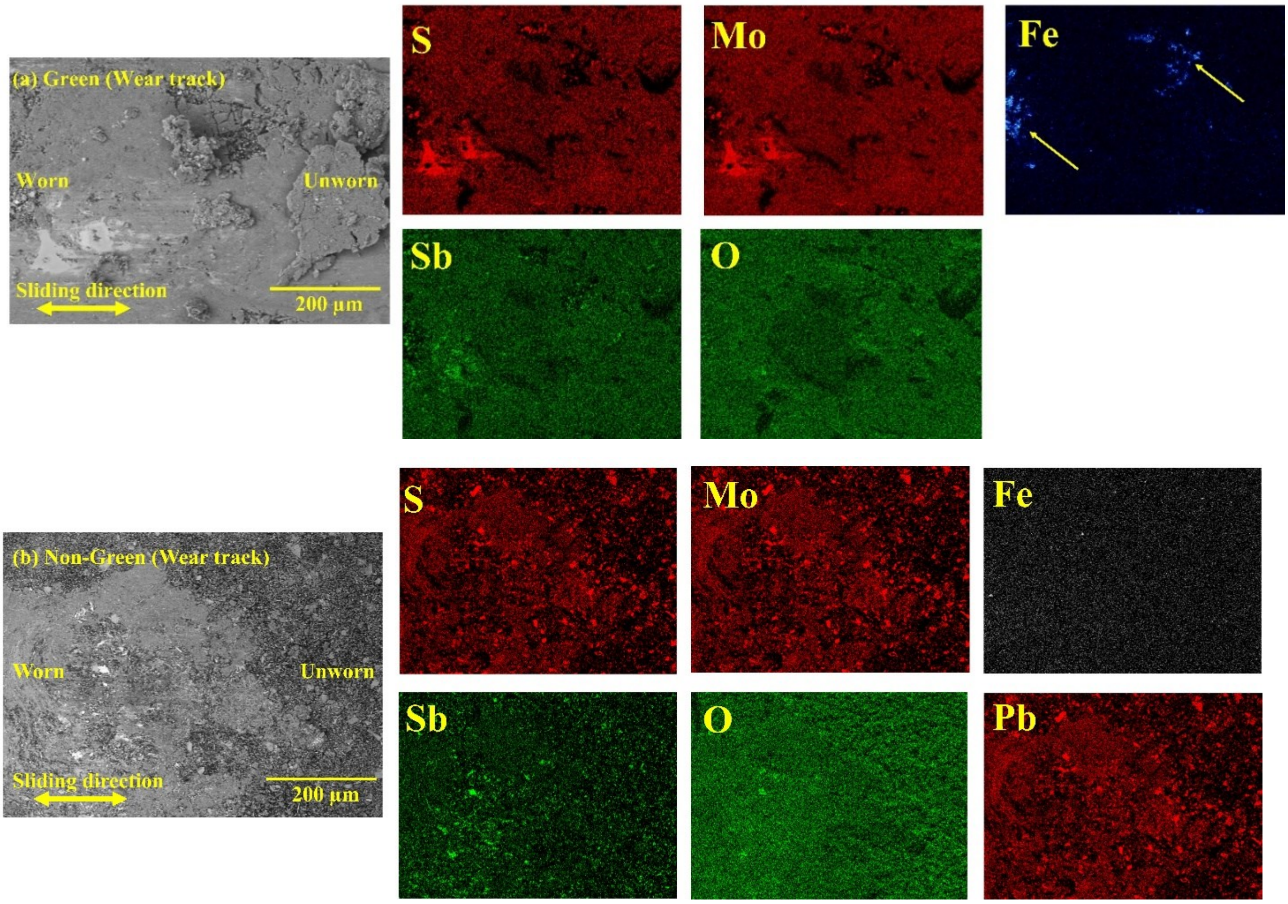


Figure 3.7. (a) EDS mapping of green lubricant worn surface at 10N normal load, (b) EDS mapping of non-green lubricant worn surface at 10N normal load

Figure 3.8 shows the Raman spectroscopy on both the coatings for the worn and unworn surfaces. The peaks at Raman shift approximately 380 cm^{-1} and 400 cm^{-1} are clearly visible from Figure 3.8 which corresponds to crystalline MoS_2 [4,5,9]. For unworn surfaces of both, the green and non-green lubricants, (Figure 3.8(b, d)), the intensity of the peaks corresponding to MoS_2 was similar for both lubricants and relatively low, which could be due to the influence of the additional elements in the lubricant in the as deposited condition. Figure 3.8(a, c) shows the Raman spectra of the corresponding worn surfaces, indicating visible peaks associated with MoS_2. The worn surface of the non-green lubricant shows a higher intensity peak associated with MoS_2 compared to green lubricant, which could indicate that the tribofilm formed with non-green lubricant was MoS_2 rich and more uniform compared to the green lubricant. In addition, this could be due to the basal planes of the MoS_2 oriented parallel to the sliding direction [4].

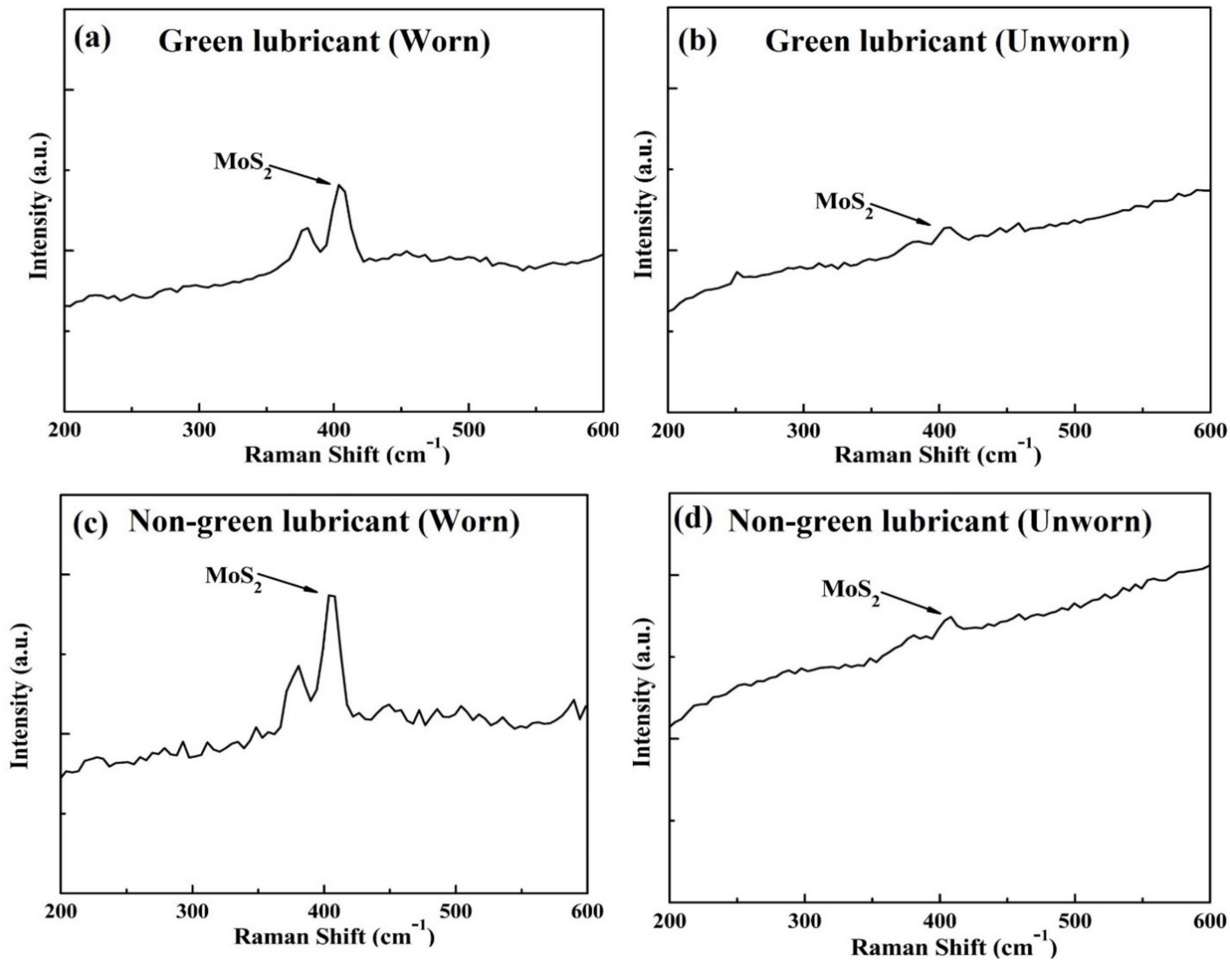


Figure 3.8. Film characterization using Raman spectroscopy for (a) Green lubricant (worn), (b) Green lubricant (unworn), (c) Non-green lubricant (worn) and (d) Non-green lubricant (unworn)

Figure 3.9 represents the pull-off force measurements obtained from the AFM testing. The adhesion (i.e., pull-off) force for both the lubricants was measured by AFM using the Force-Spectroscopy method. The adhesive force is nearly identical for the unworn surfaces of both the lubricants, however, the adhesive force on the worn surface of the green lubricant is evidently higher than the worn surface of the non-green lubricant. In the ambient conditions, the adhesion force typically consists of Van der Waals force, electrostatic force and capillary force [28]. Thus, the observations from the AFM correlate well with the Raman spectra, indicating that there is a higher amount of MoS_2 present on the worn surface of non-green lubricant with the basal planes oriented in the parallel direction to the sliding.

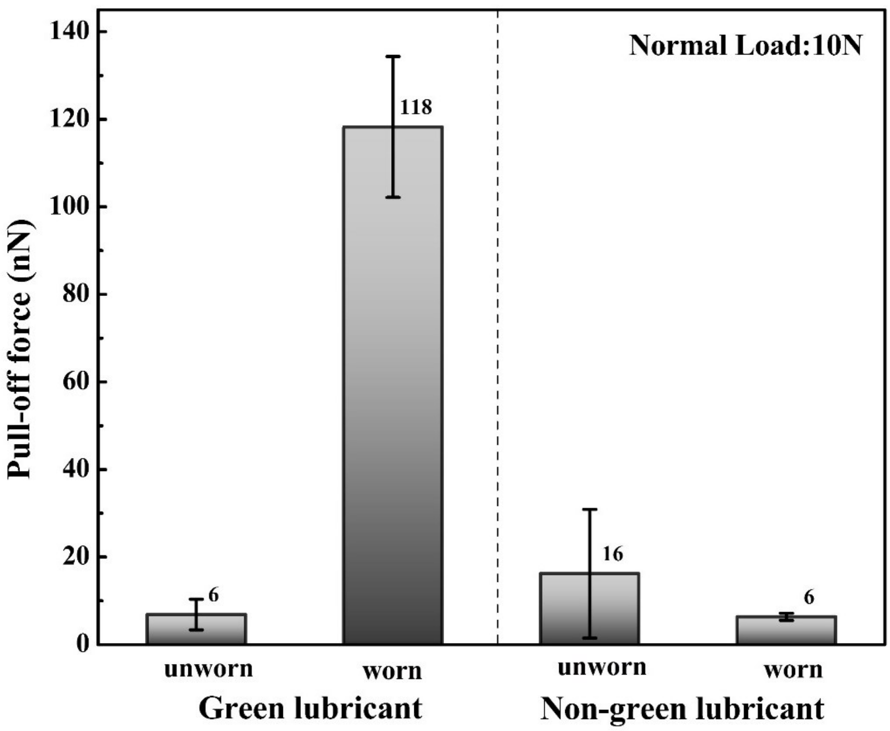


Figure 3.9. Pull-off force measurement using AFM spectroscopy at 10N normal load

Figure 3.10 represents the indentation depth (i.e., inversely proportional to the nano-hardness) of both the lubricants on both the worn and unworn surfaces. The wear depth on the worn surfaces was higher for the green lubricant when compared with non-green lubricant, which illustrates that the tribofilm on the non-green lubricant is harder compared to the one on the green lubricant. Hardness is also increased with increasing density and reduced porosity of the film, which ultimately can help in reducing friction and wear. This is similar to the influence of the hardness of the bulk lubricant on friction and wear [1,6].

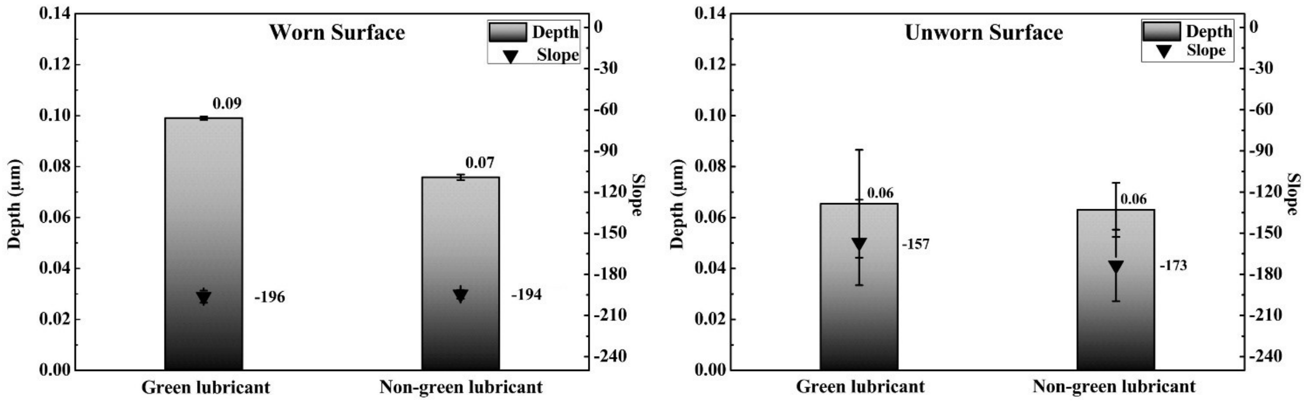


Figure 3.10. Estimation of hardness of lubricants using AFM spectroscopy on (a) Worn surface and (b) Unworn surface

Figure 3.11 represents the SEM images of the counterfaces for green lubricant and non-green lubricant for 10 N load. When compared with green lubricant, the non-green lubricant has a more uniform transfer film, which can result in lower friction and wear. As shown in Figure 3.11, at 10 N load, the amount of debris particles visible is similar for the solid lubricants. However, at 5 N load, a significantly higher amount of loose debris particles can be seen with green lubricant.

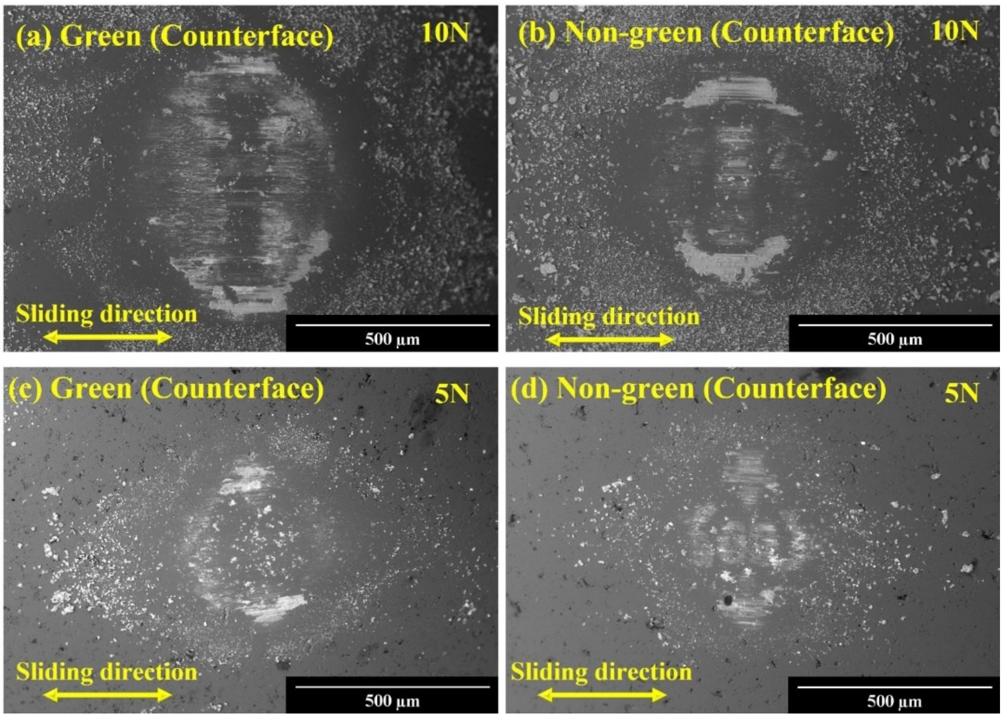


Figure 3.11. SEM image of counterface for (a) Green lubricant at 10N, (b) Non-green lubricant at 10N, (c) Green lubricant at 5N and (d) Non-green lubricant at 5N

Figure 3.12 shows the elemental maps of the counterfaces for both, the green lubricant and non-green lubricant. The EDX analysis shows the presence of Mo, S, Al, Sb and O as the main components in green lubricant and the same elements with the addition of Pb in non-green lubricant. As per EDX analysis, a higher atomic percentage of Sb is observed in green lubricant (3.46 ± 0.75) rather than in non-green lubricant (1.79 ± 0.75), which indicates a higher amount of three-body abrasion with green lubricant.

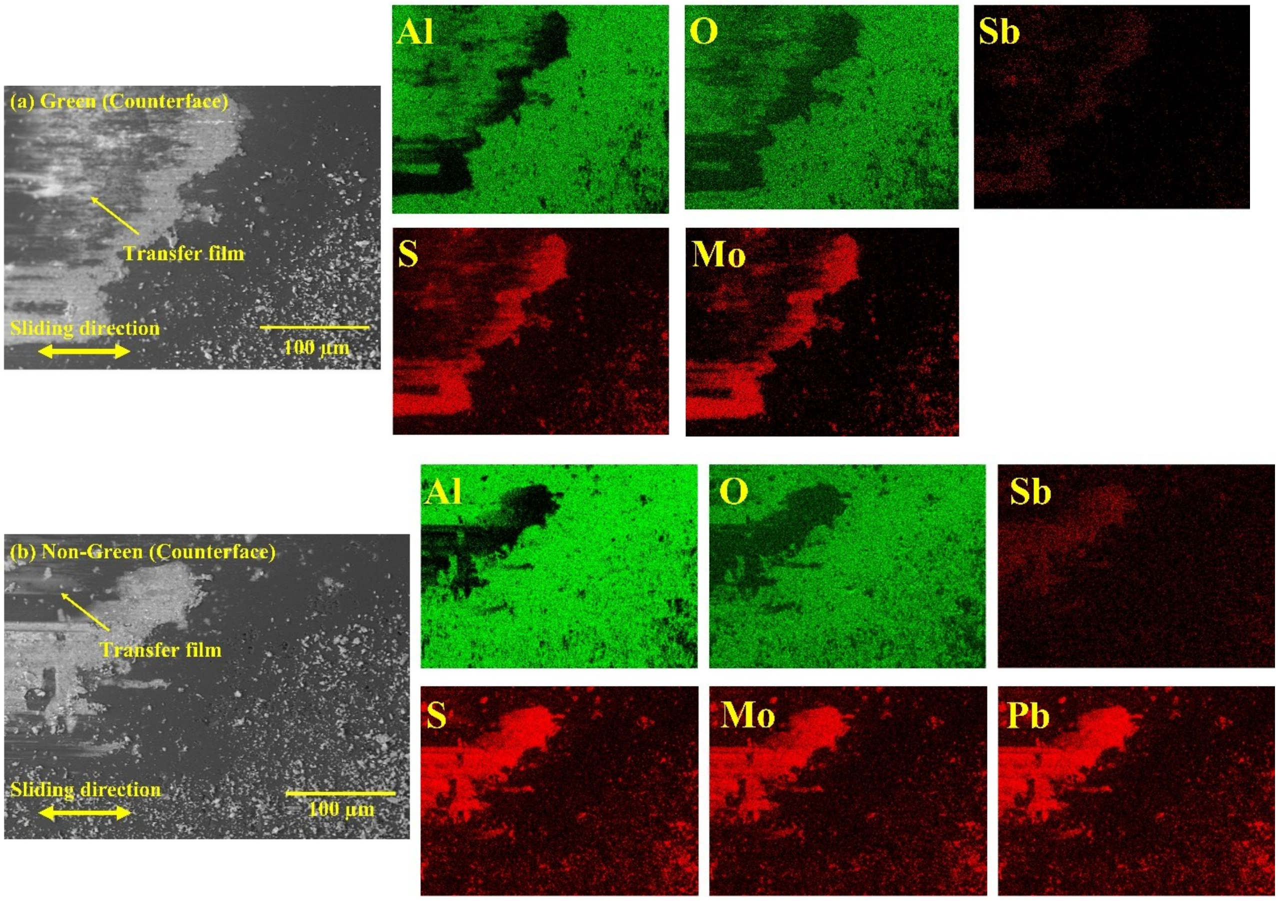


Figure 3.12.(a) EDS mapping of green lubricant counterface at 10N, (b) EDS mapping of non-green lubricant counterface at 10N

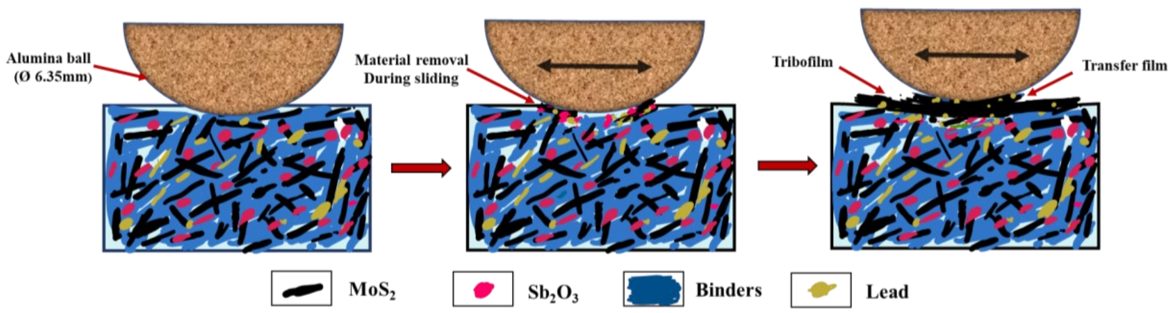
4.5. Discussion

In order to fully capture the tribological behavior of green lubricant and non-green lubricant, it is important to first understand the effect of dopants on the performance of MoS_2. In general, the addition of dopants to MoS_2 imparts specific physical and chemical properties which help in improving the tribological performance of the overall coating. According to literature, the addition of Sb_2O_3 helps the coating in preventing crack growth [8]. In addition, Sb_2O_3 also helps in reducing the intercolumnar porosity and increases the oxidation resistance [8,19,20]. Similarly, the addition of Pb as a dopant also improves the oxidation resistance, however, also facilitates the formation of basally oriented MoS_2 crystallites, as well as increases the hardness and possibly the elastic modulus of the MoS_2 film [13,15,29,30].

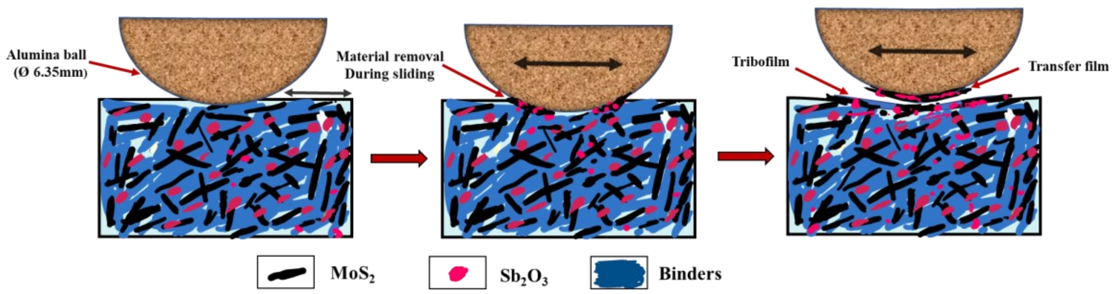
The observations from the tribological testing performed in this study showed that non-green lubricant overall performs better in both, reducing the friction coefficients and the wear depth when compared to the green lubricant. The friction and wear behavior correlated well with the observations from the ex-situ analysis. For instance, the MoS_2 peaks obtained with the Raman spectroscopy (Figure 3.8) were higher in intensity on the worn surface of the non-green lubricant compared to the green lubricant one. This observation indicated that the tribofilm formed on the 'non-green' lubricant contains a higher amount of MoS_2, which is potentially more crystalline in nature [4]. As pointed out above, the addition of Pb to MoS_2 increases the hardness, and therefore, can facilitate the formation of a thin tribofilm and transfer film with basally oriented MoS_2 crystallites. Previous studies have shown that when the basal planes of the MoS_2 are oriented parallel to the substrate, the films showed lower friction coefficient, improved oxidation resistance and increased wear life [1,8,31]. Thus, for the test conditions in this study, the improved wear resistance and reduced friction with the non-green lubricant can be attributed to the presence of a small amount of Pb, which helped with the formation of a more desirable tribofilm. Consequently, this results in a Hertzian elastic sliding mode with the non-green lubricant following $F{\sim}L^{2/3}$ as shown in Figure 3.4. In addition, the ex-situ analysis by means of AFM showed higher adhesive force (pull-off) present on the worn surface for the green lubricant compared to the non-green one (Figure 3.9). This is in line with the observations from the Raman analysis, where the tribofilm generated on the non-green lubricant contains a higher amount of MoS_2 with the basal planes oriented in the parallel direction to the sliding. The lower adhesive force on the surface with the basal planes oriented parallel to the sliding direction can be explained by the fact that the basal planes have lower surface energies compared to the edge planes in the MoS_2 [32]. In addition, the tribofilm generated on the non-green sample may be denser and thus, have a higher hardness, which can result in reduced surface adhesion [33].

Similarly, to the tribofilm, the transfer film generated with the non-green lubricant appears to be more uniform within the contact area. This can possibly be explained by the higher amount of three-body abrasive wear with green lubricant, which is attributed to the higher amount of Sb_2O_3. The Sb_2O_3 can act as abrasive particles within the contact and make it more difficult for transfer film formation.

Figure 3.13(a) shows the wear mechanisms for non-green lubricants and Figure 3.13(b) shows the wear mechanism for green lubricants. For both lubricants, during the initial sliding, debris particles are generated and get attached to the counterface (as shown in Figure 3.11). As per Singer et al. [34], the wear debris can be the compacted wear debris or the loose powdery wear debris. This compacted wear debris during the further sliding helps in the formation of the transfer films. Loose debris particles are often seen in sliding contacts and these debris particles can be either generated during sliding or from reacting with the surrounding environment [35,36]. These particles can influence the friction and wear depending on the coating thickness and the hardness of the coating. The compacted wear particles that are trapped are free to slide and thus sometimes form the transfer films [34]. In the case of the 'non-green' lubricant, upon further sliding, MoS_2 rich tribofilm and transfer film are formed resulting in lower friction and wear. For the green dry film lubricant, the formation of a dense and uniform tribo-/transfer-film is hindered by the higher amount of Sb_2O_3 particles present in the lubricant. Consequently, the insufficient tribo-/transfer-film formation results in higher friction and wear.



(a)



(b)

Figure 3.13. (a) Wear mechanism for non-green lubricant (Less amount of loose debris particles are observed which helped in the formation of uniform and dense transfer film), (b) Wear mechanism for green lubricant (Higher amount of loose Sb2O3 particles are observed which restrict the sufficient amount of tribofilm and transfer film formation)

3.5. Conclusions

In the present study, 'Non-green' and 'Green' MoS_2 based solid film lubricants were deposited using the dip spin process, and the tribological behavior was evaluated under the ambient conditions. The following conclusions have been made:

1. The tribological performance of green and non-green solid lubricants was investigated at various loads (1 N to 13 N) in dry sliding conditions against alumina counterface.
2. The non-green solid film lubricant showed lower coefficients of friction and wear as well as improved load carrying capacity when compared to the green lubricant.
3. The presence of Pb during the sliding motion helps the MoS_2 crystallites to orient themselves in the parallel direction to the substrate
4. The presence of the Pb has increased the hardness and potentially increased the density.
5. The green lubricant resulted in more generation of loose debris particles (i.e., antimony trioxide) which made it difficult to form a thin and uniform transfer film.

Although, the Pb based MoS_2 solid lubricant in this study performed overall better in terms of the tribological behavior (i.e., lower friction and wear), the finding of the interfacial phenomena provided critical insights into the development of novel green alternatives that may have the ability to replace Pb based compounds in the future for sustainable environment.

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Chapter

4. INFLUENCE OF ECO-FRIENDLY CARRIER SOLVENTS ON TRIBOLOGICAL CHARACTERISTICS OF BONDED MoS_2 SOLID FILM LUBRICANTS

In this chapter…

The tribological study between the solvent-borne and water-borne MoS_2 based solid lubricants is provided. The tribological testing and various characterization techniques were employed to understand the influence of carrier solvents on the tribological performance of the solid lubricants.

4.1. Abstract

Solid lubricants have been extensively used in the aerospace industry with the purpose to reduce friction and wear in such demanding environments. One such solid lubricant is MoS_2 which is commonly used in tribological applications due to its low friction behavior. While pure MoS_2 performs well in the vacuum conditions, in humid conditions, MoS_2 exhibits premature failure due to formation of oxides. To overcome these limitations, MoS_2 is usually doped with metals/compounds that improves the tribological performance in humid conditions. Bonded MoS_2 solid lubricants contain "pigment" (i.e., the lubricating solid), binders and solvents that help in dissolving the compounds to form the final cured lubricant. However, with the recent need for environmental sustainability, there is a strong desire to eliminate usage of organic solvents as carrier agents due to the formation of Volatile Organic Compounds (VOCs). The main purpose of this study is to understand the influence of the carrier system on the tribological behavior of bonded MoS_2 solid film lubricants. In this study, two bonded MoS_2 based solid lubricants were evaluated with one lubricant containing a solvent-borne carrier and the other lubricant with a water-borne carrier. The wear test was performed using a ball-on-disc tribometer with various normal loads. Ex-situ analysis was done using Scanning electron microscope (SEM), micro-Raman spectroscopy and Fourier transform Infrared (FTIR) to understand the interfacial processes and chemical composition of the solid lubricants. Overall, the solvent based solid lubricant performed better in terms of the tribological behavior (lower friction and wear) due to the formation of uniform transfer film. The increased coefficient of friction and reduced wear resistance of the water-based lubricant was attributed to the increased cohesiveness between the counterface and the lubricant. Although the solvent-based lubricant has performed better tribologically (i.e., low friction and low wear), the findings of the interfacial phenomenon has provided critical information that the toxic compounds can be replaced with the green alternatives in order to achieve sustainable environment.

4.2. Introduction

MoS_2 based solid lubricant films have been commonly employed within the aerospace industry with the primary purpose to reduce the friction and wear in the contact interfaces[1]. While there are many other commercially available solid lubricants such as Graphite, PTFE, WS2 etc, [2], MoS_2-based lubricants are most commonly used in such applications due to their favorable tribological behavior. Pure MoS_2 generally performs well in vacuum conditions having low coefficient of friction and low wear. However, in humid conditions, pure MoS_2 exhibits higher friction and wear due to the formation of oxide such as MoO_3 that acts as an abrasive compound which may help the lubricant (MoS_2) in premature failure [3,4]. To overcome some of these challenges, MoS_2 is usually doped with metals/compounds such as Au, AG, Ti, PbO, WS_2, Sb_2O_3 etc. [2,5–8] . These compounds when doped with MoS_2 make the composite coating denser and also improves the tribological performance in ambient conditions [5,8,9]. For example, MoS_2 when doped with Au in small quantities has showed lower coefficient of friction and higher wear resistance[10–12]. Similarly, doping MoS_2 with Sb_2O_3 has resulted in several advantages such as i) reducing overall friction and wear when compared with pure MoS_2, ii) acts as an oxidation barrier which may reduce the formation of MoO_3, iii) increases the hardness of the films which may reduce the crack growth formation and iv) increases the density of the overall film thus reducing the intercolumnar porosity[2,13–16].

Generally, bonded MoS_2 based films consists of a lubricating solid called as a pigment and a binding agent which helps to hold the pigment with the metal substrate. The main advantages of bonded solid lubricant films are that they provide good adhesion strength, good abrasion resistance and longer wear life[17]. Since such lubricants are generally applied in the liquid form, solvents come into play which helps in dissolving and then the curing process is started which is done for around 1hr at 400 F [17,18].

Normally, the heat cured resin bonded solvent based solid lubricant coatings have higher percentage of organic solvents which is harmful for the environment. During the process of curing, these solvent based coatings gets volatized to release VOCs (Volatile organic compounds) which are not only harmful for the environment but also to the human race [19]. Previous studies have shown that the human exposure to VOCs have serious health effects due to their toxicity and carcinogenicity. Additionally, the VOCs exposure to environment has caused the potential depletion of ozone layer and also to the greenhouse emissions[19,20]. To overcome these negative effects, water based coatings should be employed which are eco-friendly and also are non-toxic and economical. Although, the solvent based coatings are corrosion resistant and are preferred over water based coatings in extreme environments, it is important to limit the usage of solvent based lubricants due to their negative impacts on the ecosystem[18]. Thus, there is a strong desire to employ water based MoS_2 bonded films in the aerospace industry, however, their tribological performance has not been widely studied. In addition, the influence of the organic solvent on the interfacial processes with such lubricants has received little attention.

The main purpose of this study is to critically evaluate water borne MoS_2 based solid lubricants and compare the tribological performance to solvent borne MoS_2 based solid lubricant. The binding agent used in these two solid lubricant films are epoxy resin. The only difference between these two solid lubricants are the carrier agents where one lubricant has a solvent borne carrier and the other has the water borne carrier. Since both the solid lubricants are similar in terms of their composition, the impulse is to be more environmentally sustainable by implementing the green alternatives such as the water borne carriers. The two solid lubricant films were investigated in terms of their tribological behavior at different contact stresses and at ambient conditions. The study has also employed some of the characterization techniques such as SEM, Micro-Raman and FTIR spectroscopy to understand the interfacial processes and the chemical nature of the solid lubricants.

Table 4.1. The material composition for Ecoalube 643 and Everlube 9002

	Ecoalube 643	**Everlube 9002**
Pigment	MoS_2	MoS_2
Dopant	Sb_2O_3	Sb_2O_3
Binder	Epoxy resin	Epoxy resin
Carrier	Solvent borne	Water borne

4.3. Materials and Methods

In this study, two solid film lubricants (Ecoalube 643 and Everlube 9002) were characterized in terms of their tribological behavior. Ecoalube 643 lubricant is a high molecular weight epoxy based MoS_2 solid lubricant that was composed mainly of MoS_2, Sb_2O_3 (10 wt.% -15 wt.%) with solvent borne carrier. On the other hand, Everlube 9002 consists of the same composition but utilized water borne carrier. More details on the composition of the solid film lubricants can be found elsewhere [21]. The MoS_2-based solid film lubricants were deposited onto 304L stainless steel substrates by spray brush process. The details of solid film deposition is described elsewhere [22]. Prior to the deposition, the stainless-steel substrates were surface polished and maintained the surface roughness of ~0.08 µm. Subsequently, 220 Al_2O_3 grit was used for grit blasting as a pre-treatment process prior to the deposition. The thickness of the solid film lubricants was in the range of 11-13 µm.

The friction testing was performed by means of a ball-on-disk reciprocating tribometer (Anton - paar TRB^3 tribometer) using five different loads (i.e., 1N, 5N, 8N, 10N, 13N) for 5000 cycles. The friction test parameters are described in Table 4.2. The testing was conducted at room temperature (25°C - 28°C) and the Relative Humidity (RH) was maintained between 15% and 20% by using desiccants. The schematic and description of the tribology testing is described in [23].

Table 4.2. The tribological testing parameters

Tribological Testing Parameters	Values
Applied Normal Load (N)	1N, 5N, 8N, 10N, 13N
Reciprocating velocity (cm/s)	3.14 cm/s
Frequency (Hz)	1 Hz
Stroke length (mm)	10 mm
Total sliding distance (m)	100 m
Counterface	Al_2O_3 (Ø 6.35 mm)

After the sliding tests, the solid lubricants were characterized by Hitachi High Technologies America, Inc., USA Scanning Electron Microscope (SEM). Moreover, the elemental compositional analysis of the films, wear tracks and countersurface was determined by SEM/Energy Dispersive Spectroscopy (EDS) analysis (Pentafet Link, INCA X-sight, Oxford instruments, UK). Later, micro-Raman spectroscopy (CNI MGL-U-532, China) was performed on the unworn and 10 N worn surfaces using 532 nm wavelength laser to detect the phases of the films. Finally, Fourier Transform Infrared Spectroscopy (FTIR) (Thermo Scientific Nicolet iS20 with Smart iTX ATR Module, USA) tests were performed on the unworn surfaces of both the solid lubricants to detect the presence of water molecules.

4.4. Results

4.4.1. Friction behavior

The friction behavior of the solvent and water based lubricants is shown in figure 4.1. It can be seen that the coefficient of friction decreased with increasing normal load for both cases. For solvent based lubricant, firstly, friction increased in the beginning of few cycles, fluctuated and later started decreasing. Finally, it reached plateau at 3500 cycles. The highest coefficient of friction for solvent based lubricant was observed for 1 N (0.39), whereas the lowest coefficient of friction was at 13 N load (0.06). The trend of friction coefficient for water based lubricant was similar for all loads except for 1N and follow similar to solvent based lubricant. However, at 5000 cycles, the COF at 13N load for both the solid lubricants was almost equivalent (0.06).

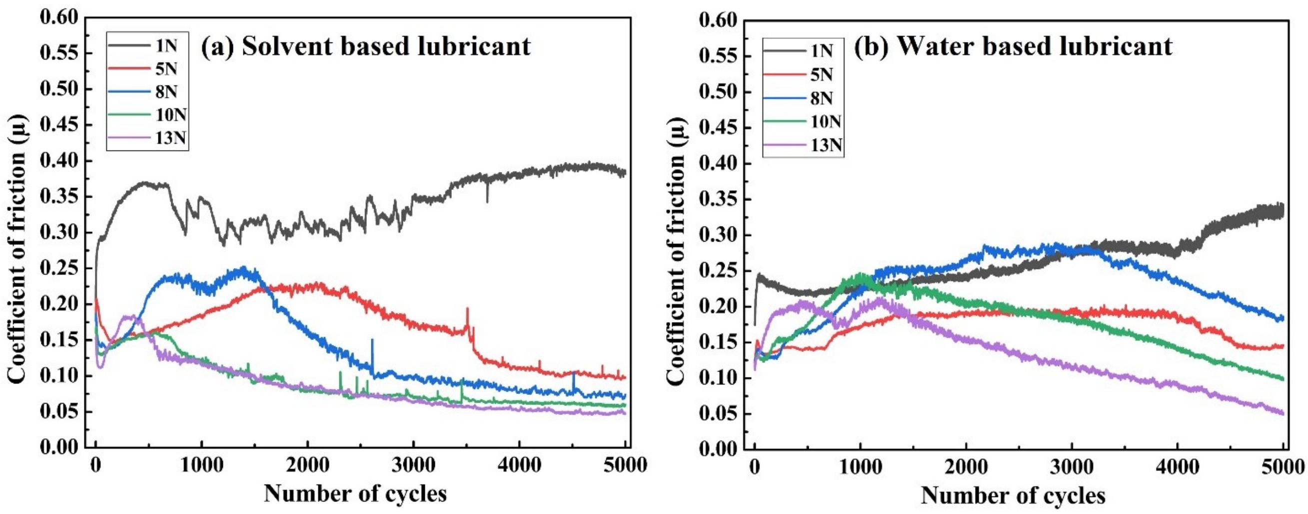


Figure 4.1. Friction coefficient vs. Number of cycles with various normal loads for (a) Solvent-based lubricant and (b) Water-based lubricant

In figure 4.2, the inverse hertzian contact pressure was plotted against coefficient of friction. This linear fit was plotted for the steady state frictional values of 4000-5000 cycles. Overall, the solvent based lubricant showed lower frictional values compared to water based lubricant. It is well known that the friction coefficient is dependent on the interfacial shear strength and contact pressure [6,7] which can be expressed in following way

$$\mu = \frac{S_0}{P} + \alpha,$$

where, S_0 is the interfacial shear strength (velocity accommodation parameter), P is the contact pressure. and α represents limiting coefficient of friction. Based on the fit in figure 4.2, the interfacial shear strength was higher for Water based lubricant as compared to Solvent based lubricant.

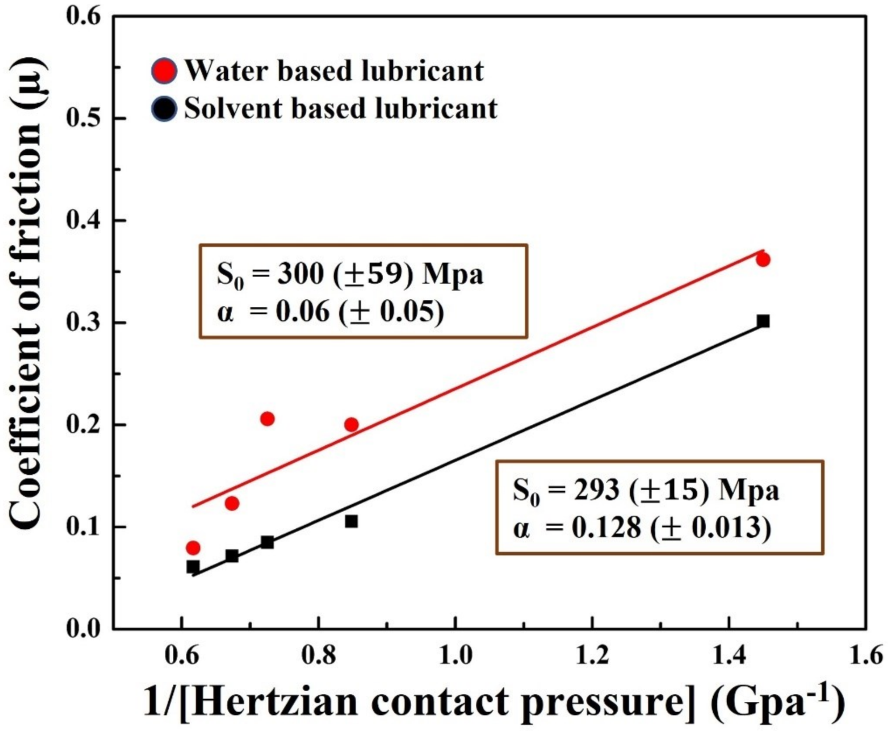


Figure 4.2.Friction coefficient vs Inverse of hertzian contact pressure

4.4.2. Wear behavior

Figure 4.3 represents the wear depth profiles for both the lubricants at different normal loads varying from 1 N to 13 N. Overall, the wear depth increased with the increase in normal load for both the lubricants. The figure 4.3 highlighted that the wear depth of water based lubricant was slightly lower than the solvent based at 1N and 5N. However, with increased normal loads the wear depth of water based lubricant was higher that indicated low load bearing capabilities than solvent based lubricant.

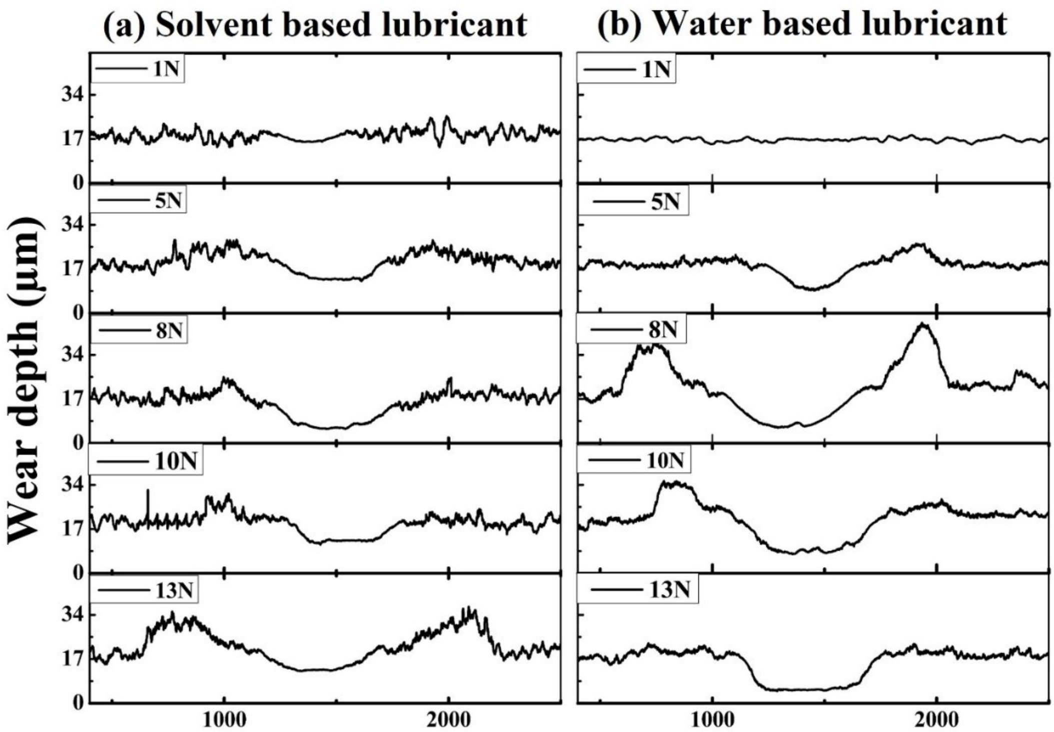


Figure 4.3.Wear depths of (a) Solvent-based lubricant and (b) Water-based lubricant

4.4.3. Ex situ analysis

Figure 4.4 shows the SEM images of solvent and water based lubricant at 5N and 10N load. At 10N normal load, cracks were visible on both solvent-based lubricant as well as water-based lubricant. However, on water-based lubricant, cracks were visible even on 5N normal load. Overall, at 5N normal load, the wear track of the solvent-based lubricant looks smoother when compared with water-based lubricant.

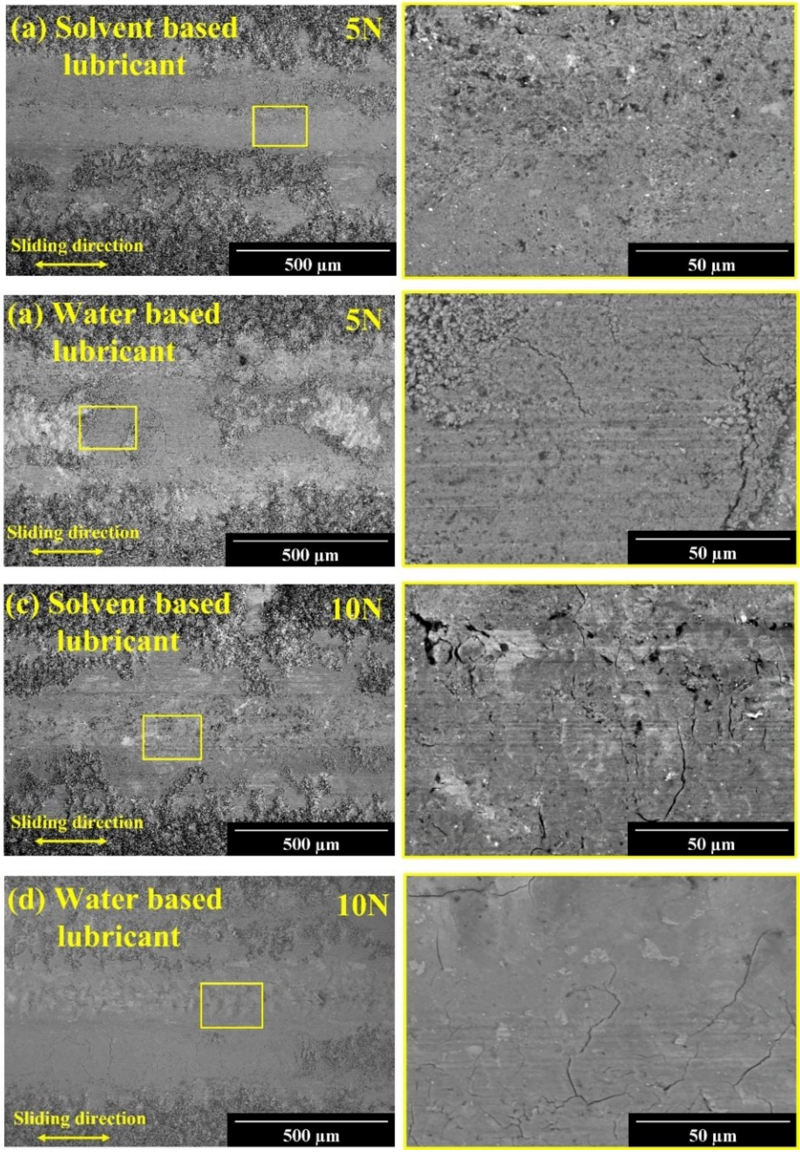


Figure 4.4. Wear scars of (a) Solvent-based lubricant at 5N, (b) Water-based lubricant at 5N, (c) Solvent-based lubricant at 10N and (d) Water-based lubricant at 10N

Figure 4.5 shows the elemental composition maps of the wear tracks for the solid lubricants. As per the EDS maps, Mo, S, C, O and Sb were found in both the solid lubricants. However, higher traces of Fe were observed on the surface of Water based lubricant, which is likely originating from the substrate and correlates well with the higher wear depth.

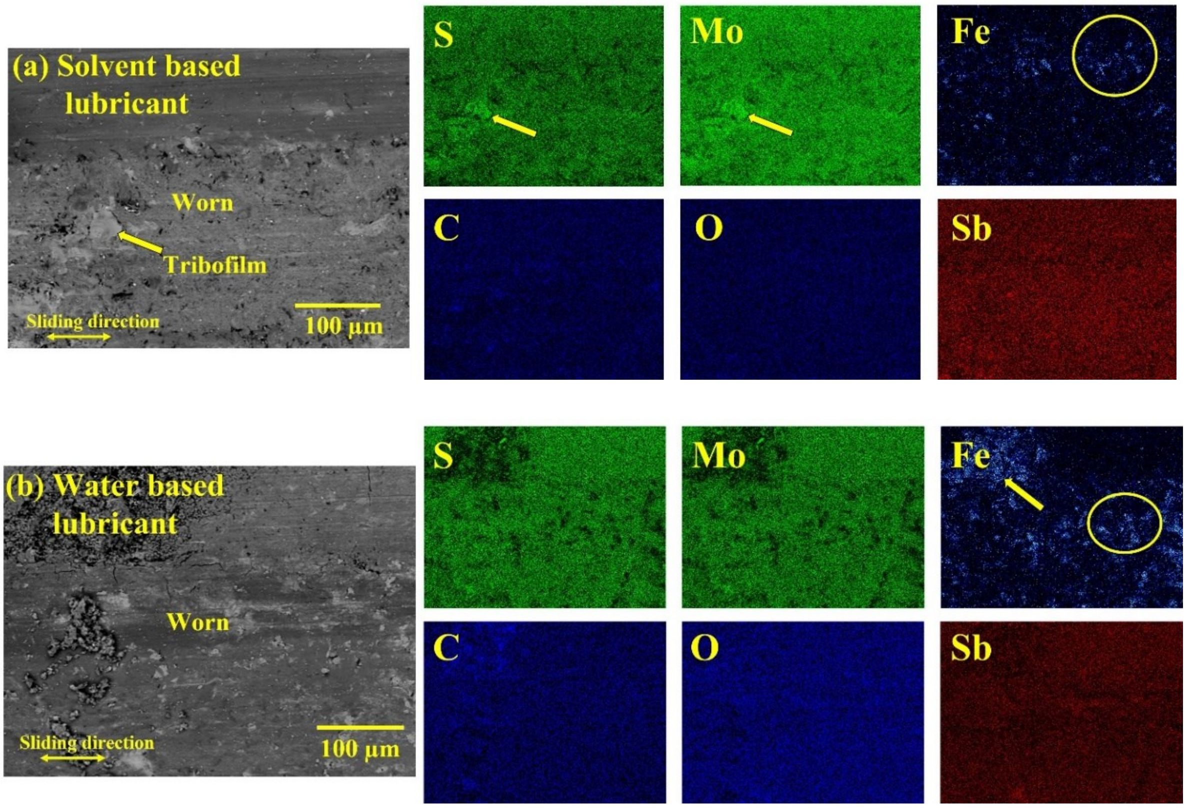


Figure 4.5. (a) EDS mapping of solvent-based lubricant worn surface at 10N normal load and (b) EDS mapping of water-based lubricant worn surface at 10N normal load

The micro-Raman spectroscopy on the unworn and worn surfaces of solvent and water based lubricants was performed and depicted in Figure 4.6. The peaks detected at 420 and 260 raman shift on unworn surfaces for both lubricants corresponded to MoS_2 and Sb_2O_3 respectively [6,13,24]. The MoS_2 peak intensities were relatively low when compared to the ones on the worn surface. In addition, a higher intensity peak was observed with solvent based lubricant when compared with water based lubricant, which could indicate that the tribofilm formed on the surface of the solvent-based lubricant is MoS_2 rich and crystalline[6]. Interestingly, no peaks consistent with Sb_2O_3 are observed on the worn surfaces of both the lubricants, indicating that the tribofilms formed are mostly composed of MoS_2.

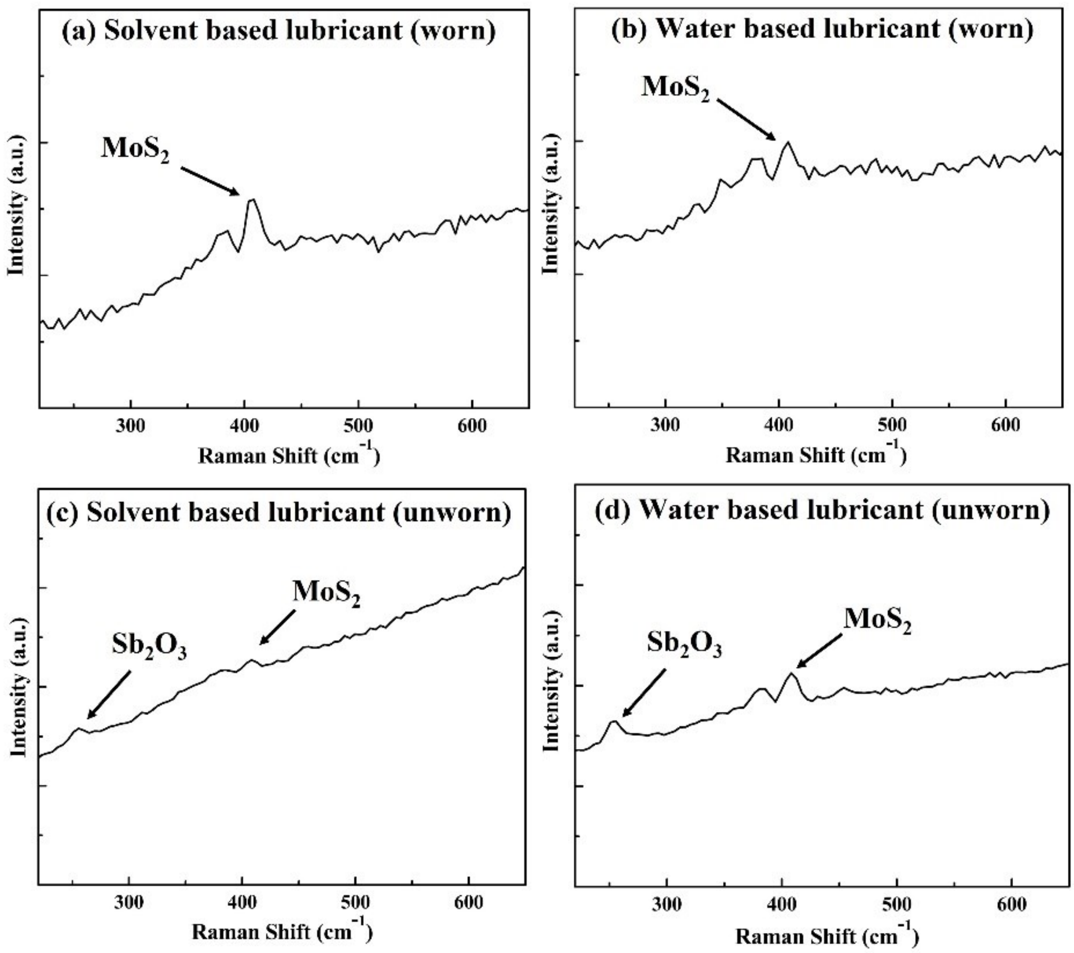


Figure 4.6.Film characterization using Raman spectroscopy for (a) Solvent-based lubricant (worn), (b) Water-based lubricant (worn), (c) Solvent-based lubricant (unworn) and (d) Water-based lubricant (unworn)

Figure 4.7 represents the SEM images of the counterfaces for both the lubricants. It is observed that a transfer film was formed on both the counterfaces. However, on the counterface of water based lubricant, the transfer film looks much broader and also the material transfer was more in patches. This is observed from figure 4.7 (b), where the entry zone of the transfer film looks more denser and thicker.

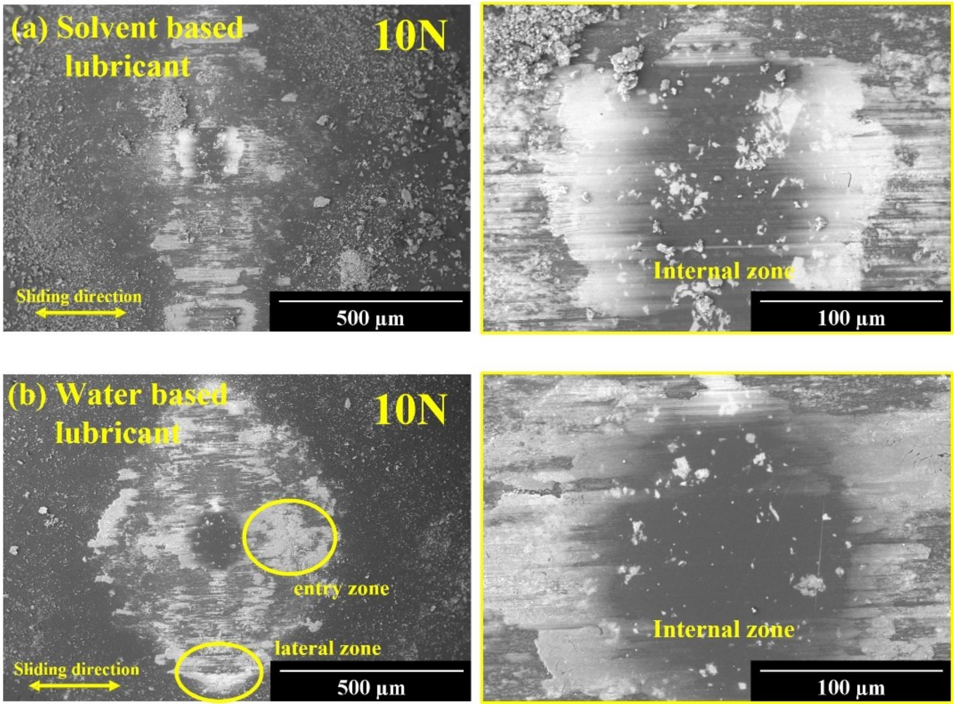
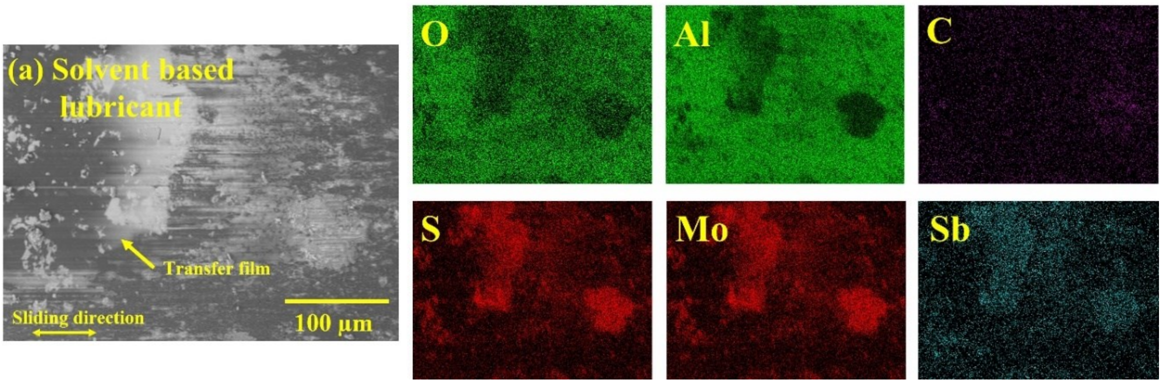


Figure 4.7. SEM image of counterface for (a) Solvent-based lubricant and (b) Water-based lubricant

Figure 4.8 represents the SEM elemental maps of both the solid lubricants. The EDS mapping shows the presence of Mo, S, O, Al, Sb and C as main elements. As per the EDS maps, the atomic percentage of Mo, S and Sb was found higher for water-based lubricant when compared with solvent-based lubricant.



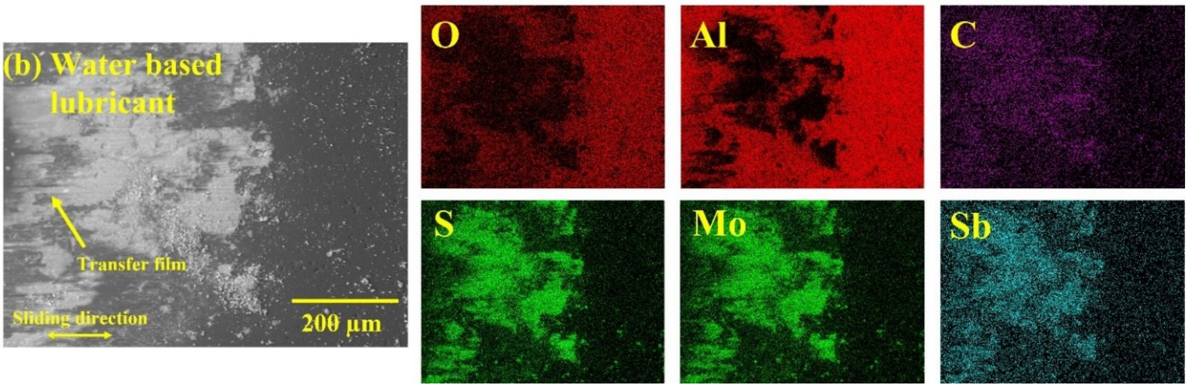


Figure 4.8.(a) EDS mapping of solvent-based lubricant counterface at 10N normal load and (b) EDS mapping of water-based lubricant at 10N normal load

Figure 4.9 represents the FTIR test that was conducted on both the solid lubricants. The FTIR spectroscopy is used to classify different types of materials such as organic, inorganic and polymeric [25]. In this study, the FTIR spectroscopy was performed mainly to identify the presence of water molecules in the water-based lubricant that may have trapped after the curing process. From the figure 4.9, a functional group of O-H is confirmed with the minor peak shifts which was observed mainly for the water-based lubricant [26].

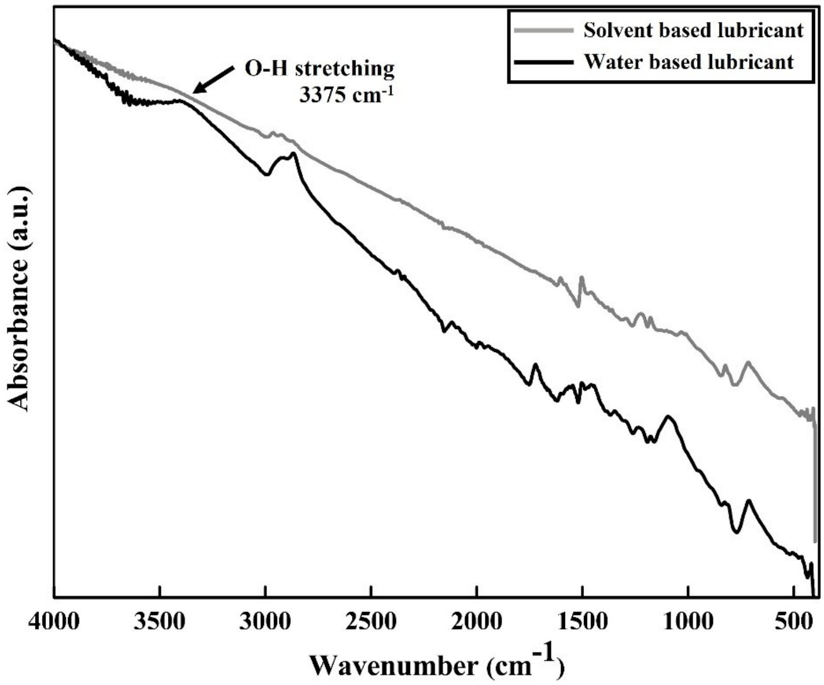


Figure 4.9. FTIR spectroscopy of solvent based lubricant and water-based lubricant

4.5. Discussion

The tribological testing in the study indicated that the solvent borne MoS_2 based solid lubricant performed better in terms of reducing the friction and wear. The higher friction coefficient with the water based lubricant corelates well with a higher interfacial shear stress, as shown in figure 4.2. The difference in the interfacial shear stress values between the two lubricants can be explained with the observations from the SEM image of the counterface (figure 4.7), which show that the transfer film formed on the counterface of the water based lubricant is thicker when compared with the solvent based lubricant.

As previously proposed by Descartes and Berthier [27] the contact region on the counterface can be categorized into three zones as a function of the presence of the third-body: 1) the entry zone, which can be a source for the natural third-body. The presence of this zone is mainly regulated by contact's geometry, the stiffness of the mechanism and the amount of the recirculation of third bodies 2) the internal zone, where the third-bodies are fed from the entry zone as well as can also be the source for natural third-bodies and 3) the lateral zones, which are usually situated on the either side of the internal zone. This zone is formed similar to the entry zone, however, the third-bodies are slithered laterally on the counterface while adhering to it simultaneously. In this study, the entry zone in the case of the water-based lubricant appears to be thicker and denser when compared to the one of the solvent-based lubricant. This can be explained by the higher cohesive force within the lubricant as well as the adhesion acting between the lubricant and the counterface. In addition, the EDS analysis performed on the internal zone shows higher concentration of Mo and S on the solvent based lubricant, which is an indication for the formation of thin transfer film. However, on the water based lubricant, the EDS analysis on the internal zone shows the higher percentages of Sb and Al which indicates the lack of MoS_2 rich transfer film formation. These results correlate well with the wear depths of the solid lubricant films. On the water based lubricant, a higher and much broader wear depth is observed when compared with the solvent-based lubricant. This could be due to the presence of water molecules in the lubricant that was trapped after the curing process. This result can be shown from the FTIR spectroscopy (figure 4.9), which shows the presence of O-H functional groups especially on the water based lubricant.

Similarly, to the observations of the transfer films, the peak intensity of MoS_2 from the Raman Spectroscopy (figure 4.6), on the worn surface is higher on the solvent based solid film lubricant, which illustrates that the tribofilm formed is more crystalline in nature. The intensities for Sb_2O_3 as well as MoS_2 is observed at 260 and 420 raman shifts respectively which is not observed on the worn surface of both the solid film lubricants. According to Zabinski et.al.[13], before the sliding motion, the orientation of materials is in random order. However, during sliding, the initial random orientation is converted into orderly fashion due to the tribo-stress. A thin layer of MoS_2 is formed on the surface with an immediate layer of Sb_2O_3 right beneath the layer of MoS_2. It is known that the good lubricating properties are achieved when thin layers of MoS_2 are present on the harder material such as Sb_2O_3. Hence, the peak intensity of Sb_2O_3 was not observed on the worn surface.

The lubrication mechanism shown in the figure 4.10 depicts the influence of third bodies on the tribological behavior of solid lubricants especially on MoS_2. A third bodies can be defined as the detachment of particles/materials from two first bodies during the sliding motion or the introduction of particles from the external source. These third bodies usually have different compositions. The process by which the third bodies are created and flow during operation is described from the tribological circuit which is shown in the figure 4.10. This circuit shows the different components that are responsible for the formation of tribofilms or third bodies; external contaminants ($\boldsymbol{Q_s^e}$) or from the internal source ($\boldsymbol{Q_s^i}$), flow within the contact of two first bodies ($\boldsymbol{Q_i}$), flow that is escaped from the contact due to the difference in the sliding velocities of the first two bodies ($\boldsymbol{Q_e}$), the wear flow ($\boldsymbol{Q_w}$) and the recirculating flow external to the contact ($\boldsymbol{Q_r}$). The ($\boldsymbol{Q_s^e}$) and ($\boldsymbol{Q_s^i}$) are the main source for the formation of particles (third bodies). The wear flow ($\boldsymbol{Q_w}$) is composed of third body particles that are ejected from the system and they usually form the loose debris particles. The recirculating flow ($\boldsymbol{Q_r}$) is composed of third body particles that repeatedly comes in contact and contributes to the velocity accommodation method. These are usually the compacted wear debris particles.

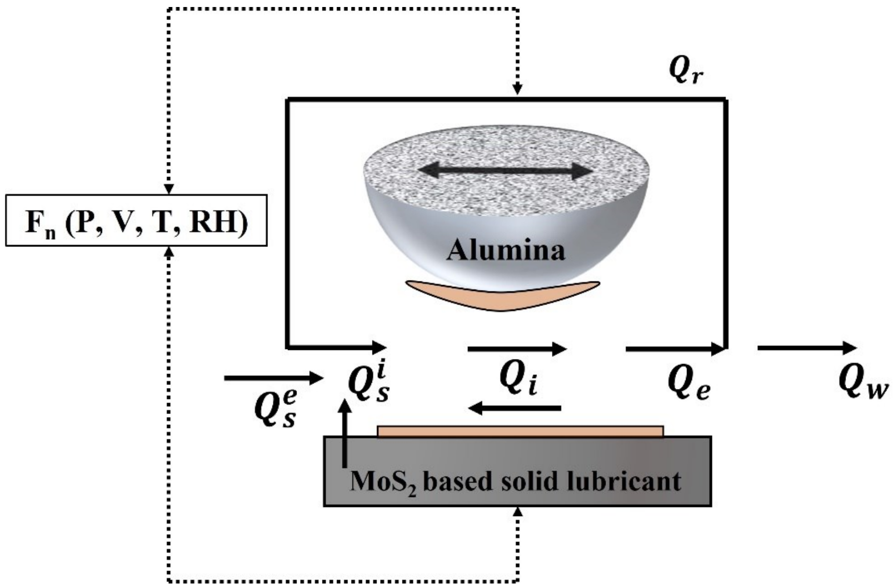


Figure 4.10. Tribological circuit showing the flow process during sliding [27]

Figure 4.11 represents the tribological circuit for both solvent-based lubricant as well as water-based lubricant during a) the initial cycles and b) steady state. Throughout the initial cycles, for the water-based lubricant, the influence of the internal source ($\boldsymbol{Q_s^i}$) is higher when compared with the solvent-based lubricant. Apart from the internal source, the influence of the escape flow ($\boldsymbol{Q_e}$), wear flow ($\boldsymbol{Q_w}$) and the recirculating flow ($\boldsymbol{Q_r}$) remain similar for both the solid lubricants. However, during the steady state phase, as represented from Figure 4.11(b), the influence of the internal flow ($\boldsymbol{Q_i}$) along with escape flow ($\boldsymbol{Q_e}$) and the wear flow ($\boldsymbol{Q_w}$) remain higher for water-based lubricant. These findings corelate well with the ex situ analysis for the different contact regions. As shown in figure 4.7 (b) with the SEM image of the counterface of water based lubricant, the entry zone of the transfer film appears thicker and denser which was mainly formed due to internal source ($\boldsymbol{Q_s^i}$) and the internal flow ($\boldsymbol{Q_i}$) along with the recirculating flow ($\boldsymbol{Q_r}$). Consequently, the higher amount of transfer resulted in an additional shear component within the transferred materials. It has been reported that the moisture condensation during the sliding motion increased in additional VAM which is interfilm shearing and thus increased the coefficient of friction [28]. Accordingly, due to the presence of water molecules, instead of forming a molecularly thin transfer film, a large cluster of MoS_2 particles formed the transfer film on the water-based lubricant. This formation of the patchy transfer film resulted in higher friction and wear [29,30].

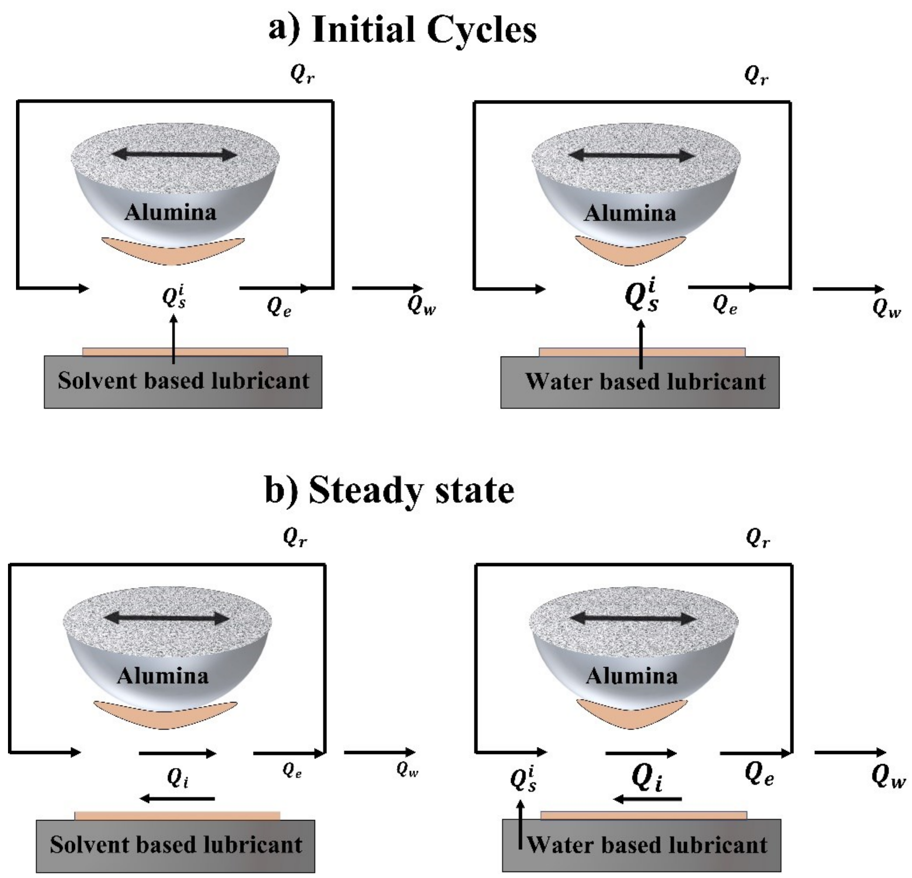


Figure 4.11. Tribological circuit showing the flow processes for acting on solvent-based lubricant and water-based lubricant during the (a) Initial cycles and (b) Steady state

5.5. Conclusions

In the present study, the tribological behavior of environmentally friendly carriers in MoS_2/Sb_2O_3 based solid film lubricants were critically evaluated and compared to lubricants with solvent based systems. In addition, the influence of the carrier system on the interfacial processes was investigated and correlated to the tribological behavior. The tribological performance of the solid film lubricants was investigated at various contact conditions (i.e., normal loads varied between 1 N and 13 N) using a ball-on-flat configuration. The environmentally friendly (i.e., water-based) solid film lubricant showed overall higher coefficients of friction and wear when compared to the non-green (e.g., solvent-based) lubricant with the higher normal loads. The higher friction and wear with the water-based lubricant was attributed to an increased amount of transfer materials onto the counterface, resulting in shear of the transferred material. The higher amount of transfer with the water-based system was explained with the FTIR analysis revealing the presence of water molecules after curing. The transfer film with the solvent base lubricant, on the other hand, was thin and more uniform compared to the water-based system. Similarly, the tribofilm formed on the solvent based lubricant was composed mainly of MoS_2, as revealed with Raman spectroscopy.

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Chapter

5. CONCLUSIONS AND FUTURE WORK

In this chapter…

The overall major conclusions are provided along with the proposal for future work

6.1. Conclusions

MoS_2 based solid film lubricants have been applied in the aerospace industry for more than 50 years, and with the recent inclination to be more environmentally sustainable, this thesis illustrates the tribological behavior of green lubricants and non-green lubricants as well as captures the interfacial phenomenon at various normal loads. The specific conclusions for each study have been summarized in their respective chapters. In this chapter, the major findings of the thesis are outlined:

1. A methodology has been identified for critically assessing green solid film lubricants in terms of their tribological behavior in gas turbine engines.
2. The tribological performance of the green lubricant (without Pb based compound) and non-green lubricant (with Pb based compound) were investigated using a methodology developed in this thesis. The non-green lubricant performed better tribologically (i.e., low friction and low wear). The improved tribological performance of non-green lubricant was attributed due to the formation of uniform transfer film and tribofilm.
3. The tribological performance of the solvent-based lubricant and the water-based lubricant were investigated at various contact pressures. The improved tribological behavior (i.e., low coefficient of friction and high wear resistance) was observed with solvent-based lubricant. From the FTIR spectroscopy, the presence of water molecules were identified in the water-based lubricant which resulted in higher friction and higher wear.
4. The addition of the smaller amounts of the dopant such as Sb_2O_3 to the MoS_2 based solid film lubricant has made the overall composite denser and also increased the oxidation resistance.

6.2. Future Work

1. Next generation green composites can be developed by altering the dopants such as addition of Bi based compounds (e.g., Bi_2S_3) instead of Pb based compounds and Sb_2O_3. Bi_2S_3 as such can achieve low coefficient of friction due to the layered structure similar to MoS_2.

2. Multilayer coatings can be developed with MoS_2/Au or MoS_2/WS_2 with pure MoS_2 as a top layer specifically employed for space mechanisms that can achieve ultra-low coefficients of friction and higher wear resistance even at lower normal loads.
3. Additional characterization of these lubricants can be performed using actual engine components to closer mimic the conditions observed in the actual application.