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Study of Tribological Properties of Laser Micro-Texturing Titanium Surfaces under Lubrication with Protic Ionic Liquids

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Study of Tribological Properties of Laser Micro-Texturing Titanium Surfaces under Lubrication with Protic Ionic Liquids

by

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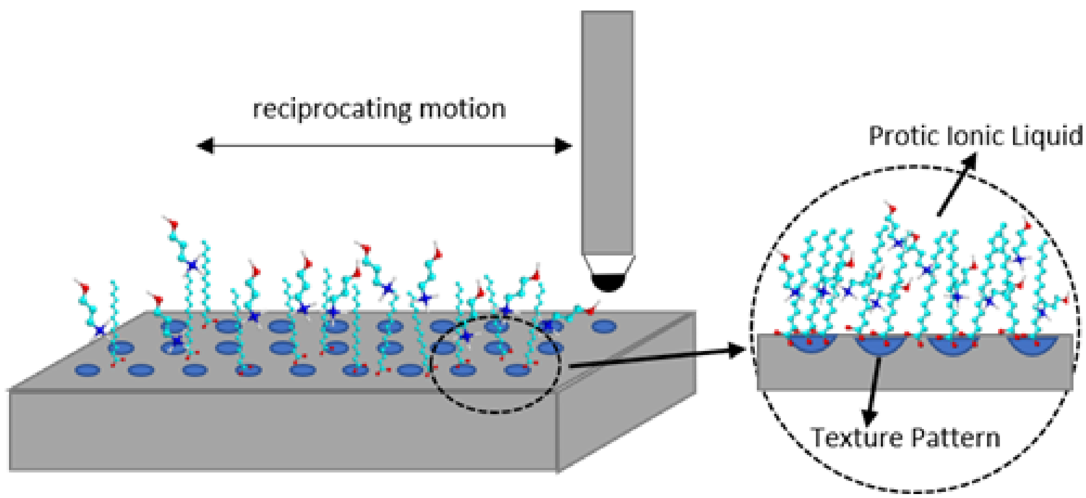
ABSTRACT

Adding micro textures by laser texturing technology to one or both sliding surfaces of relative motion has been recently studied as an environmentally friendly and efficient way to improve tribological behaviors of metals, including the reduction of friction and wear. Meanwhile, protic ionic liquids are gradually gaining increasing attention as neat lubricants and lubricant additives because of their simple synthetic procedures where the halogen elements can be easily avoided from their molecular components. The eco-friendly protic ionic liquids can be strongly adsorbed on the substrate surfaces to form ordered lubricant films which prevent the rubbing pair from direct contact. Also, protic ionic liquids may have tribo-chemical reactions with the contact materials to generate the tribo-layer on the top of the surface which may be responsible for good tribological performance.

This study focuses on the influence of laser micro textures on the tribological performance of titanium alloy—Ti6Al4V lubricated by polyalphaolefin (PAO) 40 and its mixture of 2-hydroxyethylammonium 2-ethylhexanoate (Eet). Multiple texture types are created by varying the energy density of pulse and the distance between dimples. The parameter adaptations modify the outer layers of the Titanium alloy with specific topographies and properties, and the microstructural modifications and oxidation processes lead the textured surfaces with different surface roughness and wettability. A custom-designed reciprocating ball-on-flat tribometer was used to assess the tribological performance of the textured surfaces at room temperature. The wettability of these tribological systems is characterized by dropping lubricants on textured and untextured surfaces to measure the contact angle.

The friction coefficient and wear volume of textured surfaces are decreased compared to the untextured surface under different lubricant conditions. Compared to the traditional lubricant – PAO40, when employing protic ionic liquid mixture, the more significant reduction of friction and wear volume can be observed, especially for the textured surface with variations of energy densities. It is believed that both laser surface texturing and the use of PILs have a positive effect to improve the tribological properties of titanium alloys under a variety of extreme conditions. Meanwhile, the combination of laser texturing technology and protic ionic liquid has been proved as a more efficient way to reduce the frictional behavior of titanium alloys, which exhibits the great potential of using protic ionic liquid for the titanium applications to extend their tribology applications in aerospace and other fields.



The schematic diagram of lubrication process on the laser textured surfaces

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

1.0 PROBLEM INTRODUCTION

Tribology is defined as an engineering subject that studies the contacting surfaces in many kinds of relative motions and involves the application of the mechanisms of three parts including friction, lubrication, and wear. Because of the rugged surfaces in contact systems, important amount of energy dissipates from friction losses, which results in important economic losses [1]. Therefore, how to reduce friction and wear of surfaces in contact become indispensable for most materials, especially for titanium alloys.

Titanium alloys (Ti-alloys) have been widely used in numerous manufacturing fields such as aerospace, biological and marine engineering, because of their outstanding mechanical and chemical properties such as high strength-to-weight ratio, excellent corrosion endurance and biocompatibility [2]. Among those applications, Ti-alloys are primarily used to manufacture aeronautical components such as turbine blades and loaded parts. However, Ti-alloys were often found to undergo plastic shearing when slid against other metallic materials, along with high and unstable friction coefficient and large wear volume [3,4]. Recently, research has proven that surface engineering methods are the most efficient way to improve the tribological behavior of the surface of titanium alloys, such as wear and corrosion resistance [5].

Nowadays, with the development of surface engineering, many methods including ion implantation, thermal oxidation, anodizing and deposition coating have been researched for the reduction of wear and friction of titanium alloys. Ion implantation and thermal oxidation processs consume plenty of time, large amounts of energy and are not applicable for titanium alloys. Anodizing of titanium only generates an extreme thin coating, mainly applied for decorative and bonding, and has limitations of being applied for anti-wear purposes. Deposition coatings, whose properties include high strength and high hardness, are too difficult to be directly arranged on the surfaces of soft metals such as titanium and Ti6Al4V alloys. With the aim of enhancing the tribological performance of titanium alloys, it is essential to find a simpler and more adaptable surface method for wear protection [6, 7].

Recently, laser surface texturing (LST) has gradually become a competitive surface treatment method to produce manageable micro-scale textures which can significantly improve the tribological behavior of material surface. Massive studies have proved that friction and wear can be considerably reduced on the surfaces that are applied laser surface texturing technology [8]. Martinez et al. proved that micro-grooves created by LST with scanning speed of the beam and the energy density of pulse can significantly improve the tribological behavior of titanium alloy and achieve the 70% reduction of friction and wear compared to untextured surface [9].

Based on the properties mentioned before, LST is a simple and effective way to enhance the tribological properties of titanium alloys. However, in-depth and systematic research on the topic is very few, especially on tribological properties and wear mechanisms using different lubricants.

Ionic liquids (ILs) are a type of salts with low melting points that can even keep in the liquid state at room temperature. They have been the main focus of tribology research about how to reduce the friction and wear of different material pairs efficiently and environmentally friendly. ILs can be easily absorbed on metal surfaces and react with them to form tribolayers to reduce friction and wear. ILs have shown immense potential as lubricants [10,11] or lubricant additives [12]. Ionic liquid can form ordered layers in liquid state and generate tribo-layers on metal surface, which can protect metal surfaces against sliding process and reduce the friction coefficient and wear volume. The boundary lubrication film which was formed by tribochemical reactions of magnetic ionic liquid and steel surface has been investigated to enhance the tribological performance of steel including friction-reducing and wear reduction [13]. Nowadays, the most widely used ILs are aprotic ionic liquids (AILs) with halide counter-ions [14]. However, if exposed to moisture, AILs with toxic elements could destroy the surfaces of the tribological system. Moreover, because of the complexity of the industrial synthesis process, the price of AILs is too high-priced to produce plentifully [15,16]. Compared to AILs, protic ionic liquids (PILs) are easier to synthesize and more efficient to protect the interacting surfaces.

Given that, Sameer et.al studied the friction and wear reduction of Titanium alloys lubricated by a PIL as lubricant additive to a biodegradable oil (BO). The results showed that the PIL formed a carbon-richened tribolayer on the titanium surface which improved the tribological behavior of titanium-alloys compared to the surface lubricated with neat BO [17].

Meanwhile, the relationship between surface roughness and the generation of tribolayer plays an important role in tribological process. According to the results of Gutierrez et.al, ordered fluids such as ILs, are easier to generate a tribo-layer on the normal ground surfaces compared to the super-finishing surfaces [18]. In light of this, the hypothesis of this thesis would be that increasing the roughness of surfaces might expedite and promote the formation of ILs tribo-layers. Because LST can increase the roughness of surfaces, in this work PILs will be used as additives to lubricate Ti-alloys surfaces processed by LST. It is believed that both LST and the use of PILs would help improve the tribological properties of titanium alloys under a variety of extreme conditions and to develop their novel applications with excellent tribological properties in aerospace and other fields. This study aims at revealing the mechanisms of how surface texturing and the use of PILs as additives affect the sliding wear behavior of the Ti6Al4V at room temperature.

2.0 THE RESEARCH QUESTIONS

As mentioned before, ILs have been proven to be efficient lubricants and additives, mainly due to the formation of ordered layers between rubbing surfaces (as shown in Figure 1), that reduces friction and wear. It is also known that texturing the surfaces in contact will also improve their tribological performance. In this work, I hypothesize that the addition of texture to the metal surfaces would expedite and promote the formation of ILs tribo-layers and increase the ability of lubricant retention, resulting in a synergistic effect of both lubricating technics. In this thesis, the following research questions will be answered:

1: Does tribological performance of textured surfaces depend on the laser patterning parameters including energy density and distance between dimples? If so, how much will the performance depend on these parameters (Quantitative analysis with friction coefficient and wear volume)?

2: Can the use of ILs as additives to a lubricant improve the tribological behavior of textured surfaces facilitating the formation of a tribolayer?

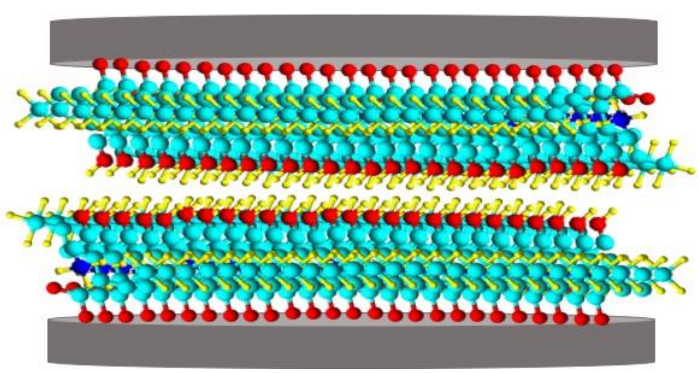


Figure 1. The ordered layers of ILs between rubbing surfaces

3.0 LITERATURE REVIEW

3.1 Tribology

Tribology is defined as an engineering subject that studies the contacting surfaces in many kinds of relative motions and involves the application of the mechanisms of three parts including friction, lubrication, and wear. [19]. It plays an important role in energy consumption where 23% of energy is disputed from tribological contacts per year. In order to reduce economic losses caused by tribological contacts, more and more research focus on the impact of friction and wear [20, 1].

Friction is the force generated to resist the relative motion between solid-solid and solid-soft surfaces or fluid layers which are sliding against each other. Many considerations including adhesion, interlocking of asperities, and surface deformation might cause friction. There are 2 types of friction [21], which is static friction and kinetic friction. In our study, we choose friction coefficient to assess friction impact, which is a dimensionless quantity defined as the ratio of friction existing two bodies and the force pressing the surfaces together.

Wear is the loss of material from a solid surface removed by the motion of another material, which leads to the creation of material particles or debris in the tribological system [22]. There are many kinds of wear happened during wear process including sliding wear, rolling wear, fretting wear, erosive wear, rolling-sliding wear, and cavitation wear. Specific wear type depends on the relative motion between bodies in contact.

Nowadays, many research works [23– 25] have been done to reduce friction coefficient and wear losses. The use of novel lubricants, new materials and effective surface technologies have been proved as efficient ways to improve the tribological performance of tribological systems.

Ionic liquids (ILs) are a type of salts with low melting points that can even keep in the liquid state at room temperature. They have been the main focus of tribology research about how to reduce the friction and wear of different material pairs efficiently and environmentally friendly. As can be accumulated easily on the surfaces and generate protective tribo-layers, ILs have shown immense potential as lubricants or lubricant additives [26, 27].

Surface texturing is also paid great attention to reduce friction and wear by modifying surface conditions. There are many technologies of surface texturing such as laser method, MAM and Vibromechanical texturing [9]. In our study, we choose laser method as our surface texturing technology because of its efficiency and eco-friendliness.

3.2 Titanium and titanium alloys

3.2.1 Overview

Titanium and its alloys (Ti-alloys) are applied widely in many manufacturing fields, especially aerospace, because of their outstanding properties including specific strength-to-weight ratio, high rupture strength, and unique anti-corrosion property. In addition, the research on titanium and Ti-alloys in other engineering fields such as surgical implantation, nuclear waste storage, electrochemistry and so on, are also attracting more and more attentions [12,14 – 16]. The chemical elements of titanium alloys are classified into 3 kinds, which are neutral, α-stabilizers or β-stabilizers, based on the effect on stabilizing α or β phases of the Ti-alloys. The elements have been summarized in Table 1 which also includes the atomic arrangement (interstitial or substitutional) of these elements in the substrate [17]. Accordingly, Ti-alloys can also be further grouped as α-alloys (high temperature creep strength and oxidation resistance), β-alloys (high strength up to intermediate temperature level), and α+β alloys (medium to high strength levels and good hot forming qualities) [18]. Among all the titanium alloys, Ti6Al4V has become one of the most widely used Ti-alloys due to its low density, outstanding anti-corrosion property and great biocompatibility, where its application includes gas turbines, implants and prostheses, and marine products [18].

Table 1. Categorization of selected alloy elements utilized in titanium alloys [34]

	α-stabilizer				**β-stabilizers**						**Neutral**		
					β-eutectoid			β-isomorphous					
	Al	O	N	C	Mo	V	Fe	Cr	Mn	H	Ni	Sn	Zr
Substitutional*	✓				✓	✓						✓	✓
Interstitial*		✓	✓	✓			✓	✓	✓	✓	✓		

* Substitutional alloy: the atoms from each element can occupy the same sites as their counterpart. Interstitial alloys: the atoms do not occupy the same sites.

3.2.2 Properties and application (Ti6Al4V)

Recently, many researchers are concentrating on the possibility of applying Ti-13Nb-13Zr and Ti-6Al-4V to different manufacturing conditions. In Cviiovic's studies [28], the wear performance and corrosion resistance of Ti-13Nb-13Zr alloy and Ti-6Al-4V extra low interstitial (ELI) alloy have been compared. Analyzing their corrosion behavior as well as the tribological performance, Ti-6Al-4V ELI alloy was concluded to have a much better wear resistance compared to Ti-13Nb-13Zr alloy. Ti-6Al-4V ELI alloy was reckoned as the perfect fit to satisfy the engineering demands of low corrosion behavior and high wear resistance compared to other Ti-alloys.

Generally, annealing and solution treatment and aging (STA) are the two main heat treatment methods employed for Ti6Al4V alloy to modify its physical and chemical properties [17]. After being treated by these two different methods, the mechanical properties of the Ti6Al4V alloy have been provided in Table 2 [29]30].

In some engineering conditions, the Ti-6Al-4V can also be an alternative for high-carbon steel being used as the connecting rods, movable turbocharger vanes, and intake valves because of its excellent mechanical performance. However, in some studies, researchers have pointed out the poor sliding friction and wear performance of the Ti-6Al-4V. It has high fatigability due to wear and unstable friction under specific conditions. To overcome these problems, surface engineering techniques are gradually explored for Ti6Al4V under different tribological conditions [31]

Table 2. Important properties of Ti-6Al-4V alloy in its two main metallurgical conditions [46,47]

Material	Tensile Strength [MPa]	Yield Strength [Mpa]	Young's modulus [GPa]	Hardness [HV]	Thermol Conductivity [W/mK]	B-Transus [℃]
Ti-6Al-4V (annealing)	895	825	110	340	7.3	995
Ti-6Al-4V (STA)	1035	965	---	360	7.5	995

3.3 Surface texturing technology

3.3.1 Overview

Surface texturing is one of the engineering processes applied to modify the properties of materials and satisfy different industrial demands, especially to solve the tribological issues. Until now, different manufacturing techniques and methods have been invented to realize the modification of materials with various surface texturing [32]. The most common used methods include laser treatment, vibromechanical texturing, micro - casting, Focused Ion Beam (FIB) machining and so on. It is noted that every method has its own advantages and disadvantages. So the appropriate surface texturing method is often selected based on the specific conditions and industrial requirements [33]. In this work, laser surface texturing (LST) will be used.

3.3.2 Laser Surface Texturing (LST)

3.3.2.1 Overview

To improve tribological behavior of materials, especially Titanium and Ti-alloys, under different tribological contacts, massive research work has been done. Laser surface texturing (LST) has been studied as an effective and ecofriendly way to decrease friction coefficient and enhance wear resistance of industrial components [34, 29].

A number of studies concentrated on the process design of LST methods [30,35,36]. Based on the principles of industrial design for surface texturing creation, the LST methods can be clarified as three groups: (1) laser-induced ablation used to remove material directly, (2) laser interference used to melt materials, and (3) laser shock used to shape and redesign the material surfaces, which results in the increase of surface plastic deformation phenomena [37]. Laser ablation is a method that operates a laser beam for treating and removing materials of solid surfaces [38– 40]. As being treated with this method, the particular texture patterns such as dimples and grooves are created by losing localized materials [41]. Laser-induced ablation has been commonly applied on a range of engineering applications. For instance, Fang et al. [42] conducted LST which employed a commercial pulsed Q-switched Nd: YAG laser to conduct a wavelength of 355 nm laser to an Al2O3/Mo laminated composite surfaces. Two texture patterns: micro-dimples and grooves, were created successfully on the composite surfaces. Laser interference, which is also defined as Direct Laser Interference Pattering (DLIP), has been considered as another efficient procedure for LST. During this process, the interference of coherent laser beams are utilized to generate a periodic shape of textures [43,44]. Compared to laser-induced ablation, materials modified by laser interference technique can be regionally removed at the peak of maximum interference with adequate laser energy [45,46]. Even though there are many advantages of using direct laser ablation and laser interference technique to modify material surfaces, it cannot be ignored that the heating effect during laser process may create by-products which affect initial properties of materials including material degradation, phase alteration and thermal-elicited tensile residual stress [47]. For example, Syed et.al [48] demonstrated that direct laser ablation changed the ferrite phase of a low carbon steel from pearlite phase to a harder phase such as martensite or bainite. Targeting to undesired problems caused by direct laser ablation and laser interference techniques, laser shock processing (LSP) has been gradually researched as a novel process treatment method. LSP is defined as an manufacturing process of advanced laser-based surface, where compressive residual stress together with the toughening effect are presented by laser-induced shockwave on the specific material surfaces [49 – 51]. Some research works have illuminated that the anti-wear property of materials can be significantly improved by LSP, in which hardening effect and compressive residual stress are attributed to the anti-wear mechanism together[52]. To compare 3 different LST techniques, they have been reviewed in Table 3 in the main conditions. In our study, we use direct laser ablation to generate dimples on Ti-alloy surfaces.

Table 3. Comparison of LST techniques

Criteria	Laser ablation	Laser interference	Laser shock processing
Flexibility	Very high	Very high	High
Efficiency	High	Extremely High	High
Texture feature resolution limit	1 μm for titanium[53]	0.1 μm for silicon substrate[54]	10 μm for aluminum alloy[55]
Surface hardening effect mechanism	Heat caused the phase transformations (only for some metals)	Heat induced phase transformation (only for some specific metals)	Surface plastic deformation for all metallic materials
Applicable materials	Metals, polymer, ceramics, and composite materials	Metals, polymer, ceramics, and composite materials	Only metals

With the progress of the research work on LST methods and manufacturing process, LST has gradually been considered suitable for numerous applications because of its exclusive advantages including rapid sensibility, accurate control, extreme efficiency, eco-friendly property and high reliability of complexed manufacturing process of different surface textures [54,56,57]. In the tribological research field, many surfaces of engineering contacts in the relative motion have been treated by the micro-textures to improve tribological behavior, such as mechanical seals, thrust bearing, piston rings, and magnetic storage devices [58]. Recently, LST can also be employed on surfaces of ceramics [59,60] and polymers [61] to enhance tribological behavior, especially for wear resistance.

3.3.2.2 Tribological performance of materials treated by LST.

3.3.2.2.1 Overview

Targeting to investigate the hypothesis between ionic liquids and laser surface parameters in this study, it is essential to further consider this knowledge to explain the mechanisms responsible for improving tribological behavior of materials. In this part, the influence of laser textures on the tribological behaviors of engineering components is summarized. Friction coefficient and wear resistance are discussed as two key factors of tribological performance of materials treated by LST under dry and lubricant conditions.

3.3.2.2.2 Influence of LST surface texturing on the friction coefficient under dry condition and lubricant condition

The controllability of friction coefficient in engineering components is essential in evaluating the whole tribological behavior of the contacting system [62]. The friction coefficient is commonly studied as the combined results of adhesion and plowing components [63,64]. The adhesion component is generally accepted to be affected by the practical area in contact and lubricant condition, but the plowing component is reckoned to rely on the plastic deformation generated at the specific roughness condition [65]. It is feasible to influence the friction coefficient by applying LST technology for adapting the surfaces macrotextures including the geometry and orientated range of textures [66].

Vast research works have focused on the investigation of LST effect on the friction coefficient of tribological system without lubricant. A comprehensive summary of the recent research has been provided in Table 2. It can be concluded that the reduction of actual contacting areas is responsible for the decrease of friction coefficient compared to the untextured surfaces. For example, Rosenkranz et al. [67] reported that the reduction of friction coefficient in the stainless-steel contacts is up to 50% when using LST to design the surfaces compared to untextured surfaces. Gualtieri et al. research group [68] hypothesized that the reason why nitride steel after processed by LST gained 30% reduction of friction coefficient is the surface hardening effect except for the reduction of contact area. The authors also claimed that the surface hardening effect was caused by the reduction of grain size during laser heating process. According to the investigation of Borghi et al. [69], circular dimples with parameters of 100 μm diameter, 50 μm depth, and 40% surface density were regularly arranged on surfaces of 30NiCrMo12 nitride steel to achieve the 15% reduction of friction coefficient. Table 4 has clearly shown that the proper application of LST technology can significantly reduce friction coefficient and improve the overall tribological performance of different materials.

Table 4. The summary of recent research about the impact of LST techniques on the friction coefficient of different materials during tribological tests under dry condition

Material	LST method	Texture design	Effect on friction coefficient
Ni-based composite	Laser ablation	Circular dimples	Reduced by 50%[70]
Nitride steel	Laser ablation	Circular dimples	Reduced by 37.5%[68]
Stainless steel	Laser interference	Linear grooves	Reduced by 50%[67]
Cast iron	Laser ablation	Circular dimples	Reduced by 57.9%[71]
Al2O3/TiC composite	Laser ablation	Linear grooves	Reduced by 16.7%[72]
Ti-6Al-4V	Laser ablation	Circular dimples	Reduced by 40%[73]
304 stainless steels	Laser ablation	Circular dimples	Increased by 272.3%[74]
AISI 1045 steels	LSP	Square dimples	Reduced by 34.2%[75]
100 Cr steel	LSP	Circular dimples	Reduced by 18.2%[76]
Al 6061 alloy	LSP	Circular dimples	Reduced by 18.3%[77]

Recently, the tribological performance of surfaces modified by LST under different lubricant conditions gradually attracts a lot of attention and interest [43]. For example, Wan et al. [51] drew the conclusion that the friction coefficient was reduced up to 71% on T8 steel surfaces processed by LST with micropores lubricated by water compared to textured surfaces. The authors explained the improvement was mainly due to the decrease of plowing component and increase of lubricant retention ability. Kovalchenko et al. [46] detected the lubrication regime was transferred from boundary regime with high friction to mixed regime with low friction during the tribological tests of textured surfaces. Ze et al. [40]. added micro-grooves on the cemented carbide substrate to achieve significant reduction of friction coefficient, where the system was lubricated by solid lubricants. In the Salguero et al.' s study, the energy density of pulse and scanning speed of the laser have been chosen as laser parameters to create different texture patterns. These micro-textures have significantly improved the lubricant retention on the textured surfaces, which reduced friction up to 62% and decreased wear volume more than 200% [78]. In Table 5, the effect of LST processing for different materials on the friction coefficient under lubricant condition has been reviewed in detail.

Table 5. The summary of recent research about the influence of LST techniques on the friction coefficient of different materials during tribology tests under lubricant conditions

Material	LST method	Texture design	Lubricant used	Effect on Friction coefficient
Stainless steel	Under water laser ablation	Circular dimples	Mobil 1045 lubricant	Increased by 400%[52]
Grey cast iron	Laser ablation	Rectangular dimples	Polyalphaolefin oil	Reduced by 60%[79]
T8 steel	Laser ablation	Circular dimple	Smeared oil	Reduced by 80.1%[40]
100Cr6 steel	Laser ablation	Circular dimples	Polyalphaolefin oil	Reduced by 60%[80]
Cemented carbide	Laser ablation	Linear grooves	Liquid drops (not specified)	Reduced by 46.1%[81]
Copper	LSP	Circular dimples	Mobile Vacuoline 1405	Reduced by 50%[82]
Ti6Al4V alloy	LSP	Circular grooves	Polyalphaolefin oil	Reduced by 24.7%[9]

Although the results in Table 4 and Table 5 may be just reasonable under specific conditions and environments, they have shown the potential of LST to be used to control and adapt the friction coefficient of tribo-pairs under no matter dry condition or lubricant conditions. Some studies revealed the tribological performance of the textured surfaces did not depend on the kind of lubricant, which was illuminated by Tripathi's group [83]. The group compared the different friction coefficient values of grey cast iron contacts treated by LST with different dimple densities and the samples were lubricated by different lubricants with high and low viscosity. The results revealed the friction coefficient strongly depends on dimple densities but there is no obvious difference when using different lubricants.

3.3.2.2.3 Improved wear resistance by LST under dry condition and lubricant condition

Wear resistance is another essential aspect to evaluate the overall tribological behavior of engineering components in relative motions. The durability and quality of materials can be analyzed from their wear resistance capability. There are tremendous studies about the relationship between wear resistance and LST technology, where the tribo-pairs are placed under different conditions including dry and lubricant conditions.

The same as what I mentioned before, the reasons why LST has the ability to improve wear resistance of materials are mainly summarized as surface hardening effect and reduction of real contacting area [34,35]. For example, Hussein et al. [36] have proven that a 700% reduction of wear rate can be gained for aluminum alloys when they are processed by LST compared to the ones that are untreated. The authors assumed the combination of increase of surface hardness and surface texturing improved the wear resistance of aluminum alloys. Wu et al. [73] conducted the sliding tribological tests for titanium alloys textured with dimples under dry condition. After analyzing 3D geometry profiles and 2D cross-section profiles, the depth and width of wear tracks on laser texturing surfaces were found considerably smaller than untreated surfaces.

Meanwhile, many researchers have noticed some engineering materials after processed by LST having a better tribological performance, especially wear resistance, at a server environment such as high temperature and dry condition. For example, Sun et al. [84] illuminated that LST reduced a large amount of the wear loss of TC11 alloy tribo-pairs at 500 °C. In their research work, the authors hypothesized that abrasive wear caused by wear particles was avoided because the micro-textures created by LST collected wear debris. Importantly, initial titanium oxide layers generated by laser heating and oxide layers of the wear tracks generated by TC11 alloy reacted with oxygen in air at high temperatures provided higher hardness and additional load-bearing capacity.

Compared to untextured surfaces, larger amounts of oxide layers could be observed on the textured surfaces, which was mainly concluded as an important factor to improve the wear resistance of TC11 alloy.

In most of the engineering conditions, materials demand proper lubricants to extend the engineering components life. The micro dimples and grooves created by LST can efficiently improve the ability of lubricant retention [37] and lubricant reserved between micro-textures can be considered as micro-bearing to bear loads and thus extend fatigue time of materials. In some studies, micro-dents can collect wear particles during the sliding tribological tests to reduce the material loss caused by the wear debris [30]. Additionally, Kümmel et al. [41] proved the chemical activity of melt bulges created by LST on Ti6Al4V surfaces were significantly decreased, which eliminated the potential adhesive wear effect.

Thus, LST has been studied as an efficient way to enhance the anti-wear property of many kinds of materials. Recently some researchers claimed that LST can extend surface lifetime of engineering components. [44]. For example, Li et al. [70] examined the tribological properties of the nickel-based composite whose surface is treated with laser micro-texturing, under lubricating with the solid MoS2 powders. During the testing process, the authors observed that the MoS2 powders and wear debris could be gathered by micro-dimples formed by direct laser ablation technique. According to the results, the lifetime of composite was substantially improved by LST, and the threshold of valid lubricating temperature of MoS2 was risen from 300°C on untextured surfaces to 500°C on textured surfaces. The mechanism related to the increase of anti-wear properties under lubricant condition has been analyzed by Hao et al. [81]. In their research, they used LST to create oleophobic micro-textures on the surfaces of cemented carbide and they found the wear resistance was significantly improved. They explained that this improvement was mainly due to the increase of lubricant retention ability of textured surfaces, especially for the friction pair interface. Besides, the lubricants could be easily accumulated by oleophobic micro-texturing surfaces towards the friction pair interface, which could explain the variation of lubricant condition for the friction pair interface further.

3.4 Ionic liquids in lubrication

3.4.1 Overview

Ionic liquids (ILs) are a type of salts with low melting points that can even keep in the liquid state at room temperature. They have been the main focus of tribology research about how to reduce the friction and wear of different material pairs efficiently and environmentally friendly. As can be accumulated easily on the surfaces and generate protective tribo-layers, ILs have shown immense potential as lubricants or lubricant additives. Meanwhile, ILs possess excellent physicochemical properties such as low flammability, negligible vapor pressure, and high thermal stability [85,86], show immense potential as lubricants [87] or lubricant additives [88]. From the literature articles, ILs can be strongly physically adsorbed or chemisorbed on metal surfaces to form stable ordered layers in liquid state (as can be seen in Figure 2) to prevent the workpieces from contact to reduce friction. In addition, ILs may react with the elements of the substrate to generate a tribolayer on top of the metal surface to protect it from wear[89].

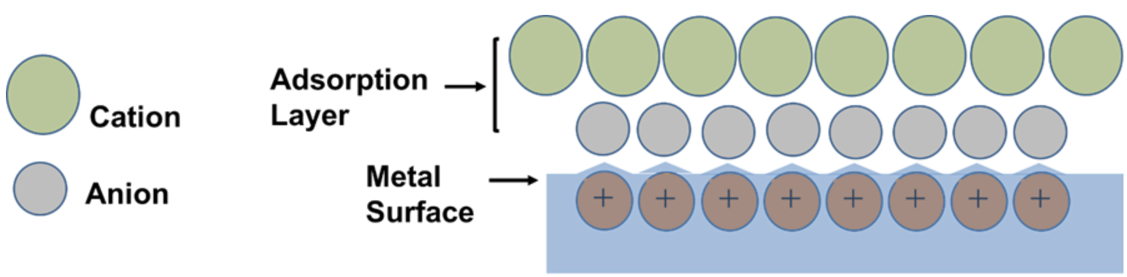


Figure 2. The ordered lubricant layer generated by ionic liquid

Nowadays, the most widely used ILs are aprotic ionic liquids (AILs) [87] (Figure 3), which has been proved to have great influence on tribological performance of materials when used to be lubricants and lubricant additives. Unfortunately, when exposed to moisture, AILs containing halogen elements (such as F, Cl) could be harmful to the surfaces of contact pairs because of the formation of toxic acids. Additionally, because of the complexity in the industrial synthesis process, the price of AILs is too expensive to be affordable [89,90]. Compared to AILs, protic ionic liquids (PILs) are easier to be synthesized as can be seen in Figure 4, where these basic processes exhibit one of merits of PILs.

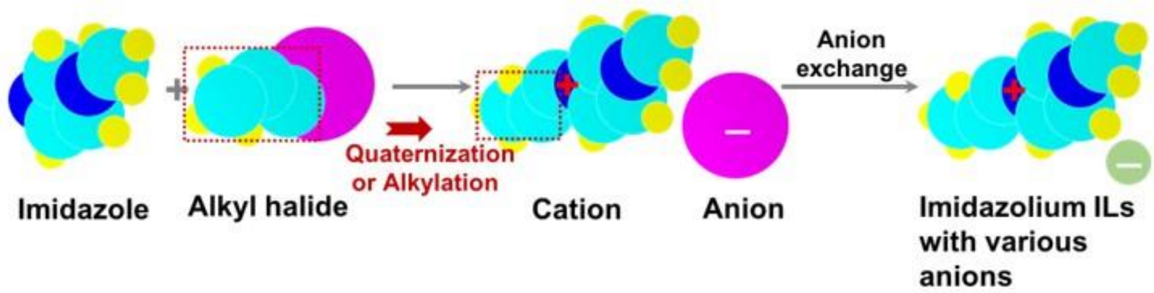


Figure 3. The synthesis process of AILs

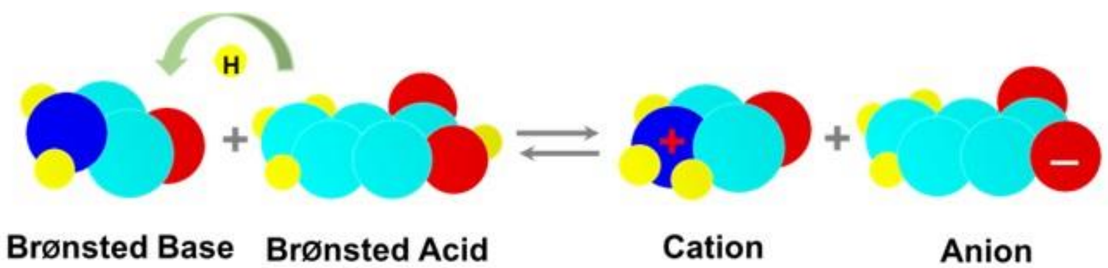


Figure 4. The synthesis process of PILs

3.4.2 Aprotic ionic liquids as lubricants and additives to base lubricants

The early studies of AILs in lubrication are mainly focused on the imidazolium - based ILs because of their feasibility [92], and almost all of them display a better friction-resistant and wear resistant performance than the traditional lubricants under steel-steel and steel-aluminum contacts [93], [94]. In massive literature, pyrrolidinium, ammonium, and phosphonium - based ILs have shown a bigger reduction of friction and lower wear rate as compared to the equivalent imidazolium - based IL in some tribological systems [95, 96].

The research work about ILs have confirmed their effective friction reduction and anti-wear performance. However, given the cost of AILs and their potential damage, especially corrosion which may cause the failure of engineering materials, the usage of ILs as neat lubricants is restricted. Additionally, a large amount of lubricants are in need to improve the tribological performance and extend lifetime of the working components under some specific working conditions, the cost of substituting traditional lubricants (mineral oils or synthetic oils) with AILs is not affordable for most of the customers [97]. To address the application problems of AILs in the manufacturing areas, an alternative solution is to add AILs as additives to the other lubricants. Actually, the use of AILs as lubricant additives have been studied and proved to effectively manipulate friction and wear performance in many sliding tribological systems [98]. Table 6 has summarized the tribological performance of different contacts when AILs were used as lubricant additive.

Table 6. Tribological effect of AILs used as lubricant additives

Base lubricant	Condition	Contact	Tribological performance	Tribofilm
Water	2 wt.% AIL add to water [99]	Ceramic-ceramic	Lower friction and wear rate	An electric double layer
Nonpolar oil	a serious of imidazolium ILs as additives in 1 wt.% to paraffinic-naphthenic mineral oil [100]	steel-Al contacts	Lower friction coefficient and wear rate	effective lubricating layers
Polar oil	0.5%-5% imidazolium-based ILs containing phenol groups added to PEG [101]	steel-steel systems	Anti-wear properties were improved by 100 times	Generation of boundary lubrication film

Moreover, researchers found that the formation of IL tribolayers depends on many factors, such as the components and structures of ILs, the contacting materials of the workpieces, and surface roughness of the rubbing pair. Gutierrez et al. [10] investigated the effect of roughness of surfaces on the tribological performance when lubricated by base oils, commercial oils with additives, and [THTDP][NTf2] blends. The authors observed that tribo-layers were easier to be generated on the surfaces with a certain level of asperities compared to the super-finish surfaces. They also hypothesized that sulfur element from the additives combined with [THTDP] [NTf2] would promote the generation of tribo-layers to reduce friction and wear on the normal ground surfaces.

3.4.3 Protic ionic liquids as lubricants and additives to base lubricants

As mentioned before, it is easy to synthesize PILs through proton transfer from a Brønsted acid to a Brønsted base. The crucial advantage of PILs is their low cost and potential to be used as eco-friendly lubricants compared to AILs. Although most of the ILs under studied are aprotic, the research about PILs in lubrication is gaining more and more attention, especially halogen-free PILs that can be used as efficient lubricants and lubricant additives [105,106].

In Kondo's study [104], the PIL synthesized by reacting perfluoropolyether (PFPE) and carboxylate-based salt was tested to meaningfully reduce friction coefficient and material loss as being used as a neat lubricant compared to the traditional PFPEs. The authors concluded that the unique molecular component of the PIL caused the improvement of wear resistance and anti-friction properties, in which the ordered layers were formed by PIL polar end to cover the surfaces evenly. From the research work of Bermudez et al. [105], bis (2- hydroxyethylammonium) succinate was added to the pure water to form PIL blend. The results showed that this PIL blend generated a shielding film to obtain lower fiction coefficient in the sapphire-stainless tribological system.

Additionally, the authors also found that the PILs comprising of the same cation but different carboxylate-based anions exhibited better tribological performance when they were tested under the copper sliding condition [106]. Furthermore, Espinosa's research group [106] synthesized several PILs comprising ammonium as the cation and different carboxylate anions, and tested them as neat lubricants under copper-copper contacts. The highest friction and wear reductions were obtained when the PIL, that has the highest extent of hydrogen bonding between the hydroxyl substitutes of ammonium, was used.

Recently, Guo et al. [87,111,112] synthesized three hexanoate-based PILs with different ammonium cations, which have been studied as neat lubricants and lubricant additives under steel/steel contact. The three PILs have reduced the wear volume and friction coefficient. It has been proved that the ordered lubrication layers generated by the strong physisorption of the PILs on the steel/steel surfaces improve the lubrication performance. In addition, the authors observed that carbon- and oxygen-enriched layers are generated on worn steel surfaces to reduce friction and wear. The authors hypothesized that the high temperature around the contact area and the contact pressure promoted the reactions between the PILs' function groups and the steel active elements to form the tribolayers.

3.5 Conclusions

From the literature review, we know that LST has been developed as a mature technique to improve overall tribological performance of materials. The initial properties of materials have been changed by creating micro texturing patterns, such as surface roughness, contact angle and so on. Additionally, some researchers have found the higher surface roughness has the positive effect on the formation of absorbed layers on the substrate surfaces. For instance, Brizmer et al [109] investigated the relationship between the formation of absorbed layer and surface roughness. They utilized ZDDP as additive mixed with PAO base oil on the surfaces with different roughness under rolling/sliding contacts and examine the absorbed layers built up by ZDDP physically and theoretically. Analyzing the experiments results, the authors claimed the roughness was a key factor to influence the formation of ZDDP absorbed layers, where ZDDP absorbed layer was easier to generate on the surfaces with higher roughness.

As mentioned before, PILs as novel lubricants and lubricant additives have been demonstrated to be used in different tribological systems to reduce friction and material loss. The ordered absorbed layers of PILs and the generated protective PIL- tribolayers have been proven the main mechanism to explain the excellent tribological performance.

Therefore, the method in my study is to combine LST technique and PILs under Ceramic-Ti6Al4V contacts. I will investigate the overall tribological performance of textured Ti-6Al4V and the effect of roughness varying by different laser parameters on the formation of the adsorbed PIL layers and the consequently PIL-tribolayers.

4.0 OBJECTIVES & HYPOTHESIS OF THIS RESEARCH WORK

There are three objectives in my study:

1. To investigate physical properties of Ti6Al4V samples including roughness and wettability.
2. To examine the tribological performance of the textured surfaces lubricated with base oils and base oils having PIL as an additive.
3. To analyze the wear mechanism of Ti6Al4V with different textured surfaces and lubricants.

There are three hypotheses in my project:

1. Applying the LST on the surfaces of Titanium alloy would improve their tribological performance.
2. Increasing the roughness of surfaces might expedite and promote the formation of ILs tribo-layers.
3. Utilizing PIL on the laser micro textures would achieve even better tribological behavior according to the No.2 hypothesis.

5.0 MATERIALS AND EXPERIMENTAL PREPARATION

5.1 Preparation of laser textured surfaces

The titanium alloy used as substrate in my work is Ti6Al4V (Grade 5), and its chemical composition has been summarized in Table 7. The Ti6Al4V specimen with a thickness of 5.0 mm has a preliminary roughness of Ra < 0.05 μm. As can be seen in Figure 5, 8 mm × 8 mm samples with different laser-textured appearance were created on top of the Ti6Al4V by employing a 20 W Ytterbium fiber infrared laser (Rofin EasyMark F20). The laser was performed in the open-air atmosphere by changing the pulse energy densities (Ed) and the dimples were laid linearly with varying distance. The samples and their laser surface treatment parameters have been listed in Table 8 and 9. It is noted that the linear dimples would allow to retain high volume of lubricant under the working conditions in my study, which may contribute to low friction and wear.

Table 7. The chemical composition of Ti6Al4V

Element	N	C	O	Fe	Al	V	Ti	Others
Content (%w/w)	0.05	0.10	0.20	0.30	5.50-6.75	3.50-4.50	Balance	0.40

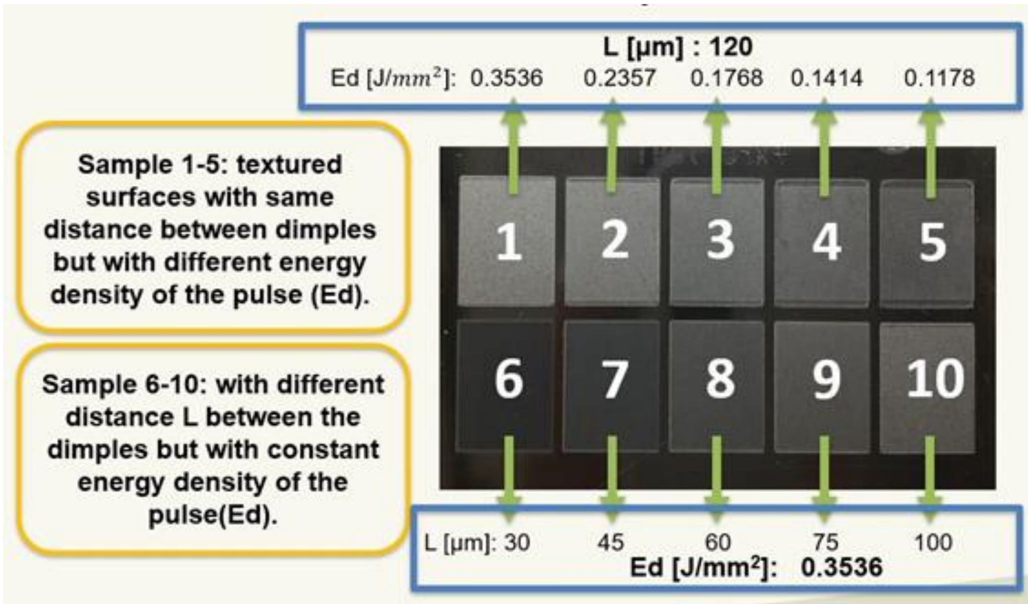


Figure 5. The optical images of different laser-textured surfaces

Table 8. The surface laser texture parameters of sample 1-5

Sample	P [W]	F [kHz]	Et [mJ]	Fluence Ed [J/mm²]	Vs [mm/s]	L [μm]	Area activated %	Peak Power [W]
1	20	20	1.0000	0.3536	2400	120	20	10000
2	20	30	0.6666	0.2357	3600	120	20	6666.6
3	20	40	0.5000	0.1768	4800	120	20	5000
4	20	50	0.4000	0.1414	6000	120	20	4000
5	20	60	0.3333	0.1178	7200	120	20	3333.3

Table 9. The surface laser texture parameters of sample 6-10

Sample	P [W]	F [kHz]	Et [mJ]	Fluence Ed [J/mm^2]	Vs [mm/s]	L [μm]	Area activated %	Peak Power [W]	Overlap %
6	20	20	1	0.3536	600	30	100	10000	39.7
7	20	20	1	0.3536	900	45	100	10000	14.9
8	20	20	1	0.3536	1200	60	79	10000	0
9	20	20	1	0.3536	1500	75	51	10000	0
10	20	20	1	0.3536	2000	100	29	10000	0

5.2 Textured surface characterization

The laser-textured surfaces on Ti6Al4V have been characterized by measuring the surface finish, inspecting surface by optical microscopy, and examining of wetting behavior of lubricant on each of them through contact angle measurement.

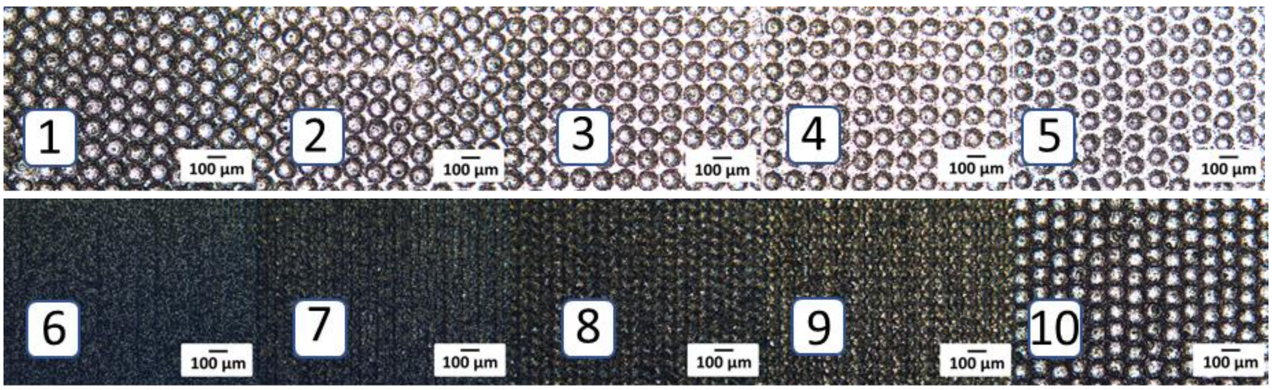


Figure 6. Optical images of samples

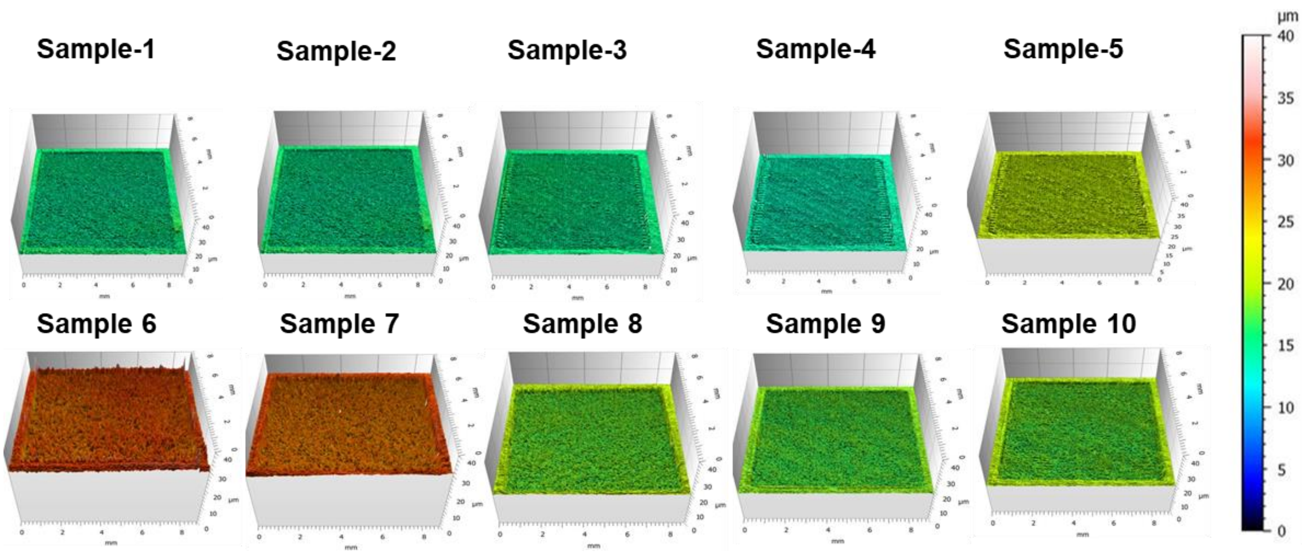


Figure 7. 3D profiles of samples surface roughness

Optical images of micro textures are shown in Figure 6, where the effect of different laser parameters on the geometrical features of surfaces can be observed. Surface finish can be assessed by average roughness (Ra) and maximum height on single measurement length (Rz). 3D profiles and micro textures schemes of the textured surfaces and untextured surface can be seen in Figure 7, which provide direct insight into roughness variation among different laser pattern parameters of surfaces. The surface finish measurements were conducted by using a Nanovea ST400 non-contact profilometer (Figure 8). To minimize the standard error, at least ten measurements are performed over the laser textured areas. In Figure 9, 2D profiles of textured surfaces have been summarized, where the depth of dimples can be calculated. In Table 10, the sample 6 with the smallest distance between textures has the biggest dimple depth which is up to 8 microns (Table 10).

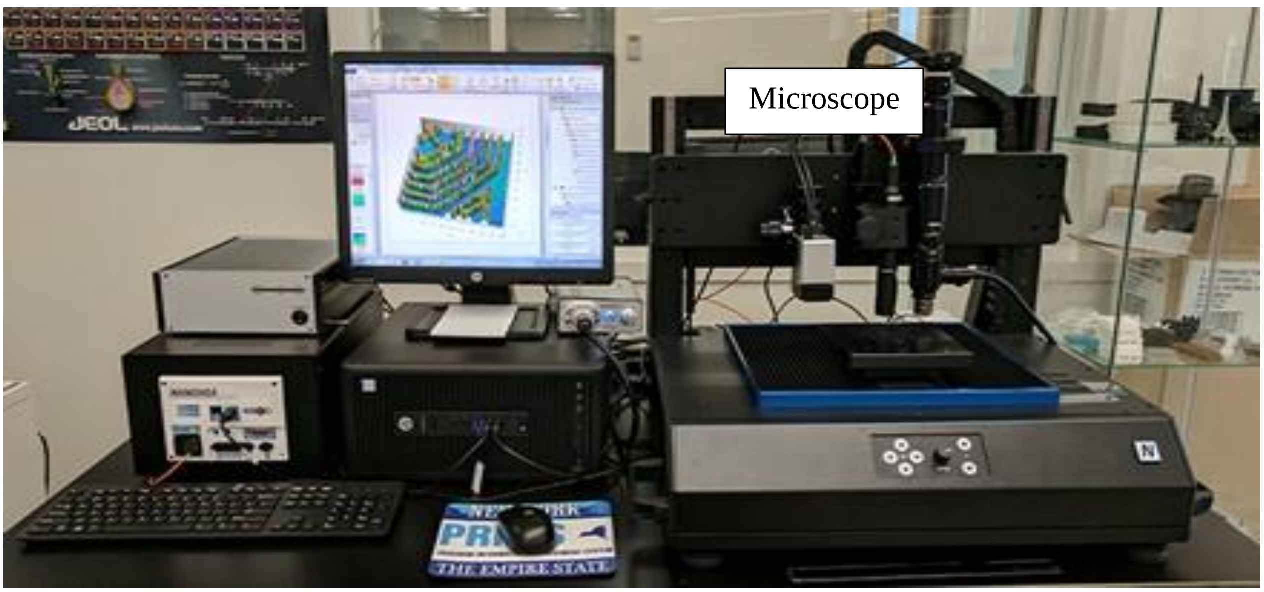
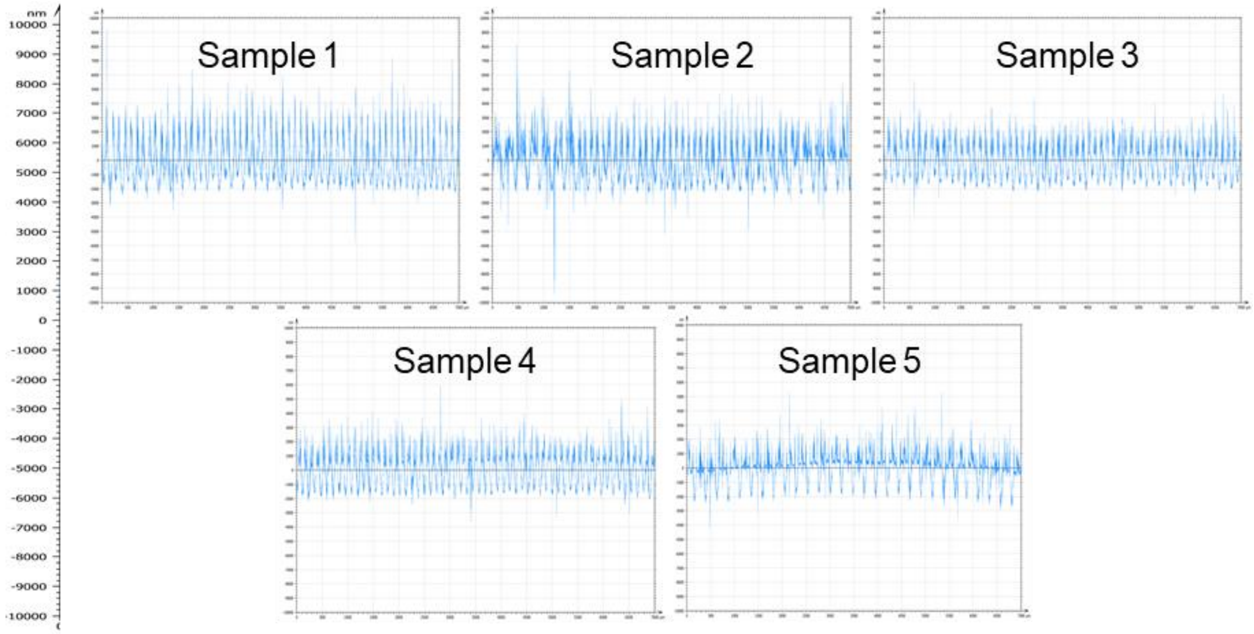


Figure 8. Nanovea ST400 non-contact profilometer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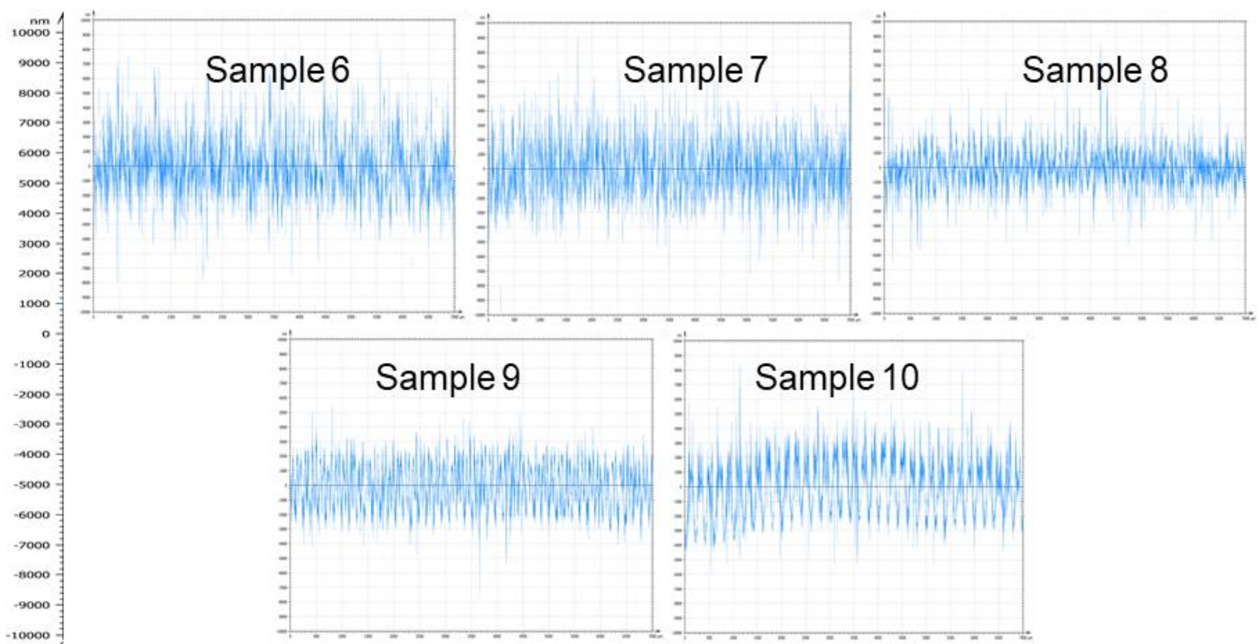
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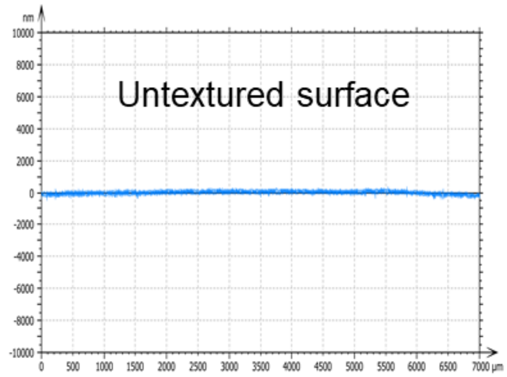


Figure 9. Surface 2D profiles of samples and untextured surface

Table 10. Dimple depth of samples

Laser Parameters		Sample Number	Dimple Depth (micron)
Energy Density [J/mm^2]	0.3536	1	6
	0.2357	2	5
	0.1768	3	4
	0.1414	4	5
	0.1178	5	4
Distance [µm]	30	6	8
	45	7	7
	60	8	4
	75	9	5
	100	10	6

The lubricant retention capacity might be affected by laser micro-textures. Targeting to this purpose, the wettability of this tribological system in terms of contact angle measurement have been investigated by using Rame-Hart 250 Goniometer (see in Figure 10) and DROPimage Advanced software as image processing software. The readings are recorded instantaneously over time for each trial when the contact angle is stable. The reading after the fifth minute is collected and averaged over three measurements for each lubricant.

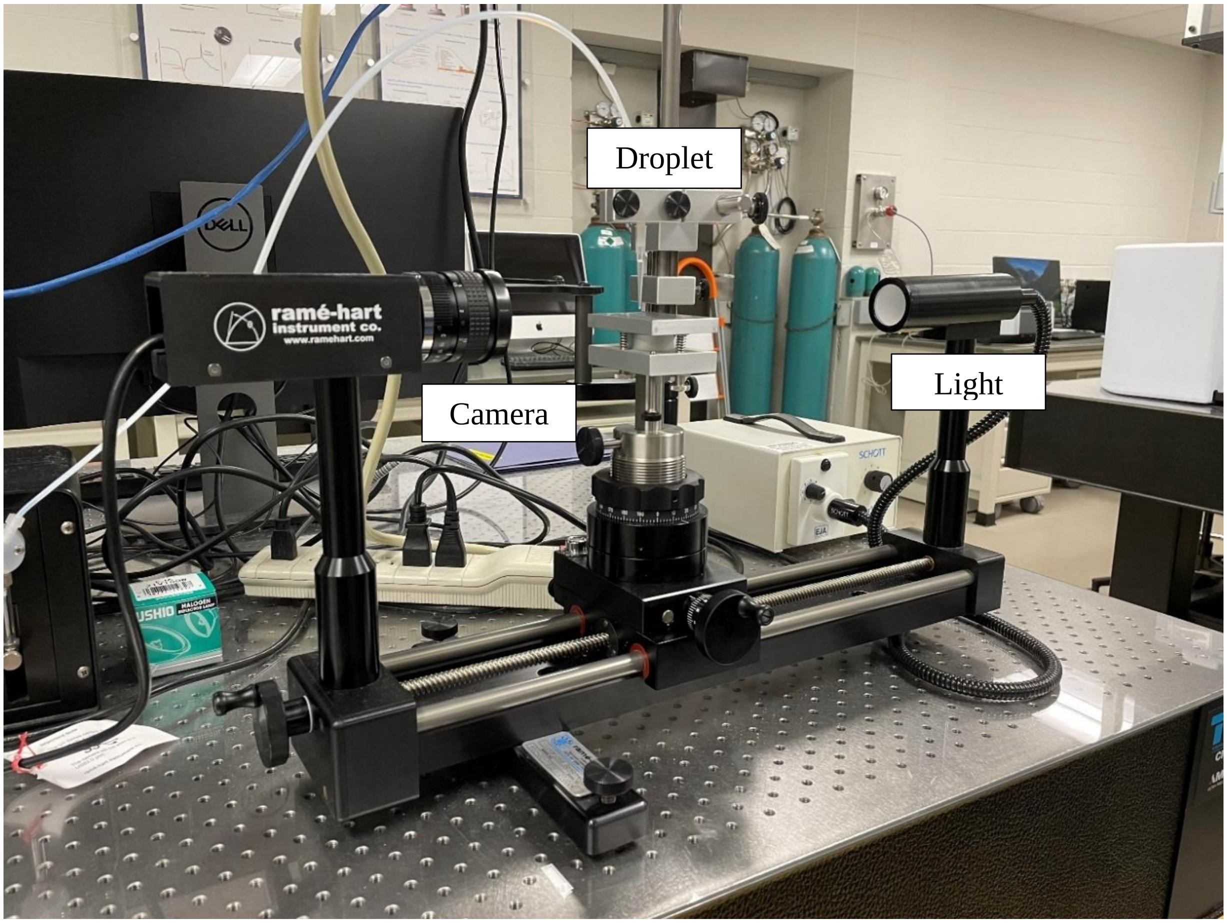
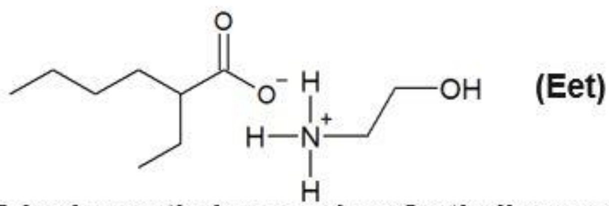


Figure 10. Rame-Hart 250 goniometer

5.3 Lubricants and their physicochemical properties

In this study, the nonpolar oil, Polyalphaolefin 40 (PAO40) is used as the neat lubricant. In addition, PIL 2-hydroxyethylammonium 2-ethylhexanoate (Eet) will be used as an additive with a concentration of 1 wt.% to the base oil to form the homogeneous mixtures by ultrasonicating for 1 hour. The molecular structure of Eet is shown below in Figure 11.



2-hydroxyethylammonium 2-ethylhexanoate

Figure 11. The name and the molecular structure of PIL used in this work

The dynamic viscosity and thermal stability are important properties for designing the lubricants with high performance. In this work, the physicochemical characteristics of PAO40 and the PIL mixture are provided in the Table 11.

Table 11. Viscosity and thermal behavior of PAO 40 and PIL mixture

Lubricant	Density (g/mm^3)	Kinematic Viscosity @ 100 ^{o}C (cSt)	Dynamic Viscosity (cP)			Onset Temperature (^{o}C)
			25 ^{o}C	40 ^{o}C	100 ^{o}C	
PAO40	0.842	4	810.34	449.14	38.63	295
1%Eet+PAO40	--	--	914.4	451.0	36.70	284.19

Thermogravimetric analysis (TGA) of PIL-mixtures will be conducted by using a TA Instrument Q500 (see in Figure 12). Each lubricant sample is placed in a platinum pan, and the temperature is increased from 20 °C to 600 °C at a heating rate of 10 °C/min under air atmosphere.

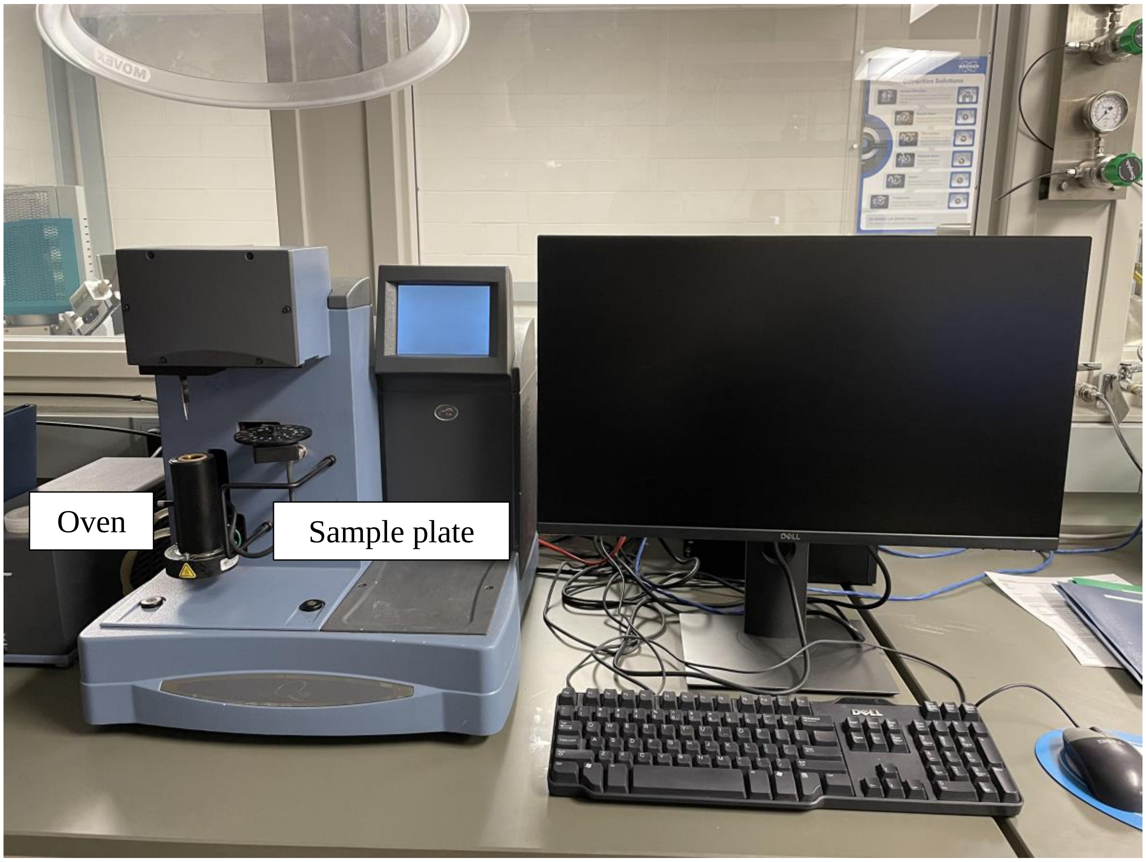


Figure 12. TA Instrument Q500

The dynamic viscosity of each PIL mixture will be examined within a temperature range of 25–100 °C using a Brookfield DV2T-LV Viscometer where the temperature is controlled with a Thermosel System.

5.4 Tribological tests

The frictional tests will be carried out in a ball-on-flat reciprocating tribometer (see Figure 13), with the textured surfaces and untextured surface sliding against the tungsten carbide ball in a diameter of 1.5 mm. All tribological tests are completed with a normal load of 3 N, a sliding distance of 14.4 m and a sliding speed of 0.012 m/s. During these tests, the average Hertz contact pressure and the maximum contact pressure are 1.54GPa and 2,3 GPa respectively.

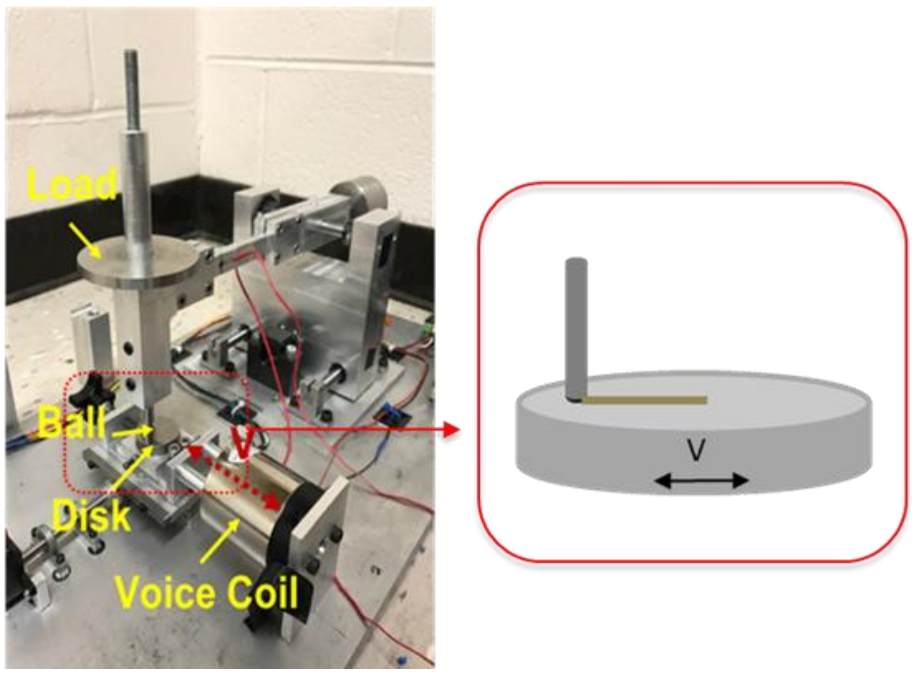


Figure 13. The ball-on-flat reciprocating tribometer

To minimize the experimental error, at least two frictional tests will be repeated under the same conditions on each sample. Before starting each test, 1mL lubricant will be added on the Ti6Al4V samples and no additional lubricant will be added during the sliding process. Once completing each trial, the specimen will be placed in an ultrasonic cleaner with Isopropyl Alcohol (99.5%) until the sample is cleaned completely, and then will be dried in air. Friction coefficients will be recorded over time and calculated as average of each running. Images of the worn tracks will be captured by optical microscopy - Olympus BH-2 Optical Microscope. Image processing methods are employed to calculate the area of adhered material to the ceramic ball.

Because of the irregularities of surfaces caused by micro textures, the method, which is to use the 3D profilometer to calculate the wear loss, recommended by ASTM G133 is not appropriate. The bigger standard error will be caused [117]. Because of particularity of laser textured surface, an evaluation based on the Eq. (1) [118] proposed by Jun Qu et.al, has been adopted to assess the volume loss (Vf) after tribological tests.

$$V_f = L_s\left[R_f^2 \arcsin\left(\frac{W}{2R_f}\right) - \frac{W}{2}\left(R_f - h_f\right)\right] + \frac{\pi}{3}h_f^2(3R_f - h_f)$$

$$h_f = R_f - \sqrt{R_f^2 - \frac{W^2}{4}} \quad (1)$$

Where:

V_f = Wear volume,

L_s = Stroke length,

R_f = Radius of the ball,

W = Width of the wear scar, and

h_f = Wear depth.

5.5 Worn surface characterization

In order to observe the wear morphology of the wear tracks on different textured surfaces, the Nanovea ST 400 profilometer will be also used to study the 3D images of the wear tracks. What is more, a Tescan Mira3 Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectrometer (EDS) (see the Figure 14) will be used to analyze the wear mechanism and surface interaction between lubricant and the contacting Ti6Al4V surfaces.

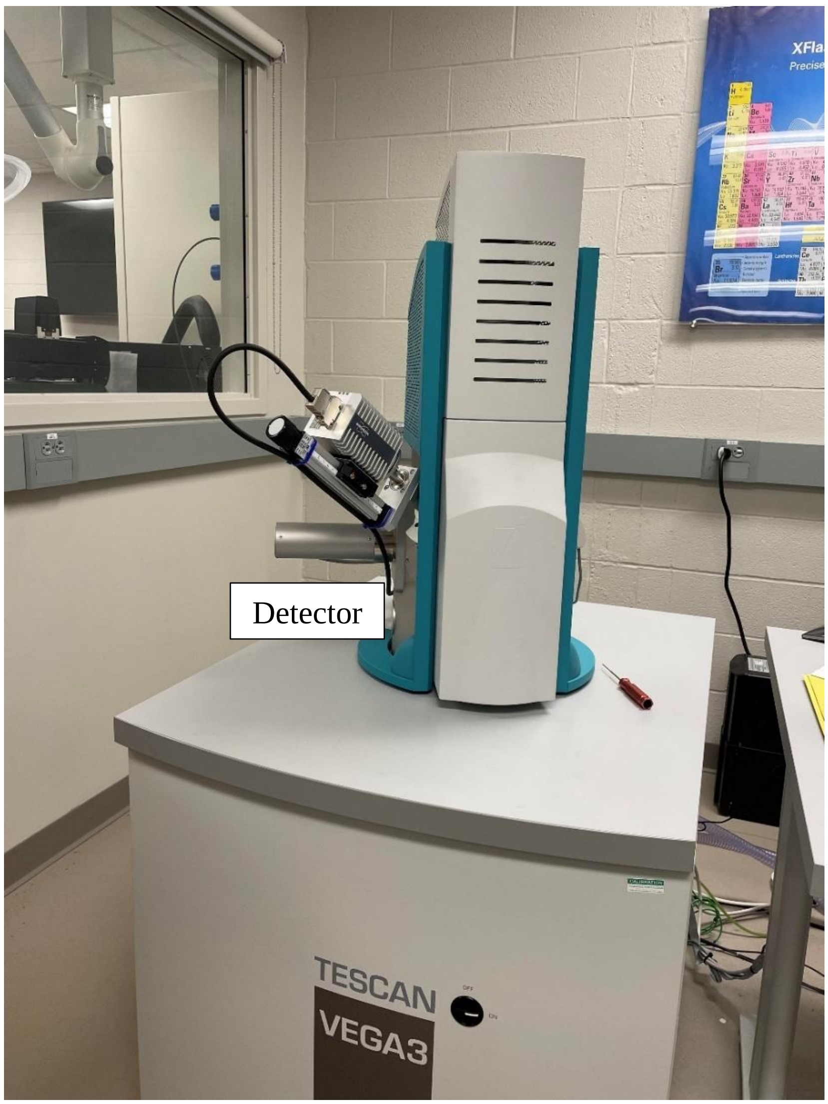


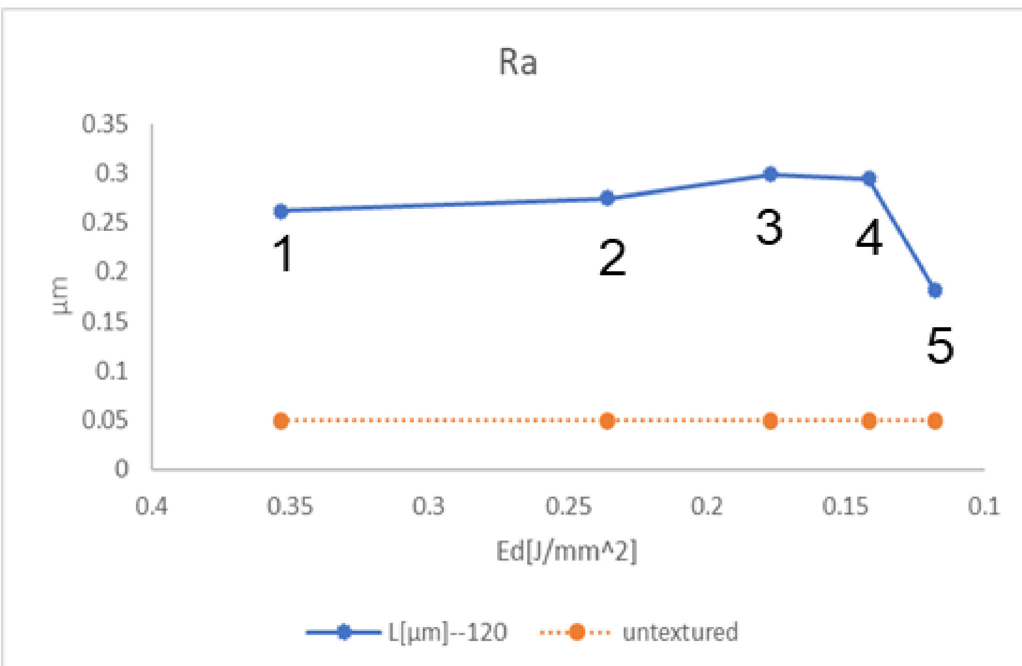
Figure 14. Tescan Mira3 scanning electron microscope coupled with the energy dispersive X-ray spectrometer

6.0 RESULTS AND DISCUSSION

6.1 Roughness characterization of textured surfaces

The characterization of geometrical features for laser micro textures proves many parameters of surface roughness, especially Ra and Rz, are influenced by laser parameters including energy density of pulse and distance between dimples created by LST.

Analyzing the results in Figure 15 and Figure 16, Ra and Rz of textured surfaces have been improved compared to untextured surfaces. From Sample 1 to Sample 4 with the energy densities from 0.35 to 0.15 J/mm^2, a light increase of Ra and Rz can be observed. However, when observing the results of samples with different distances between the dimples in Figure 15 and Figure 16, Ra and Rz were gradually reduced with the increment of distances.



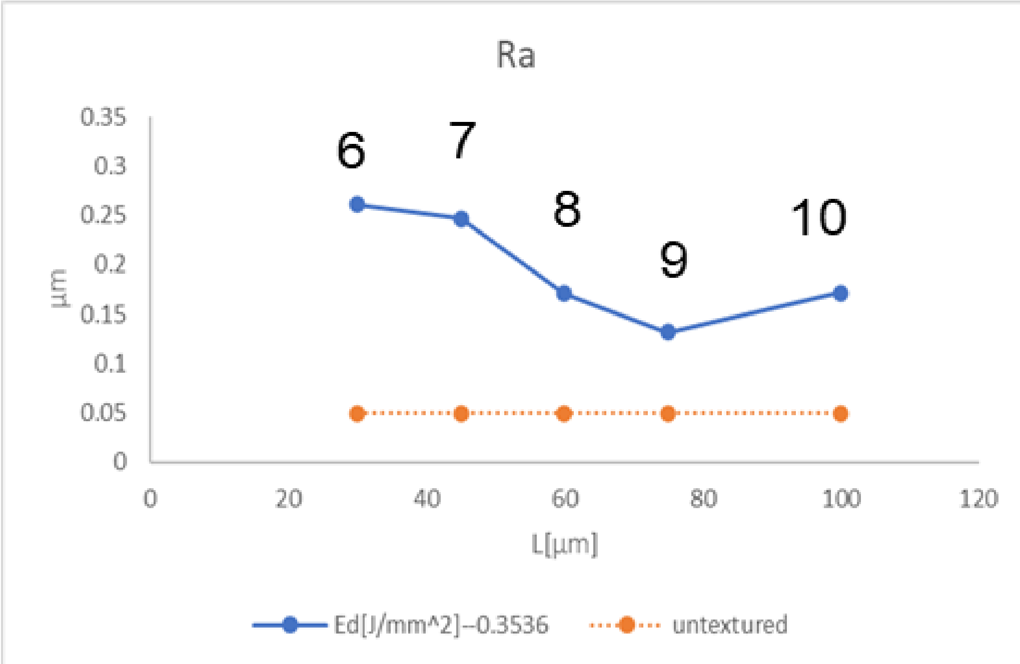
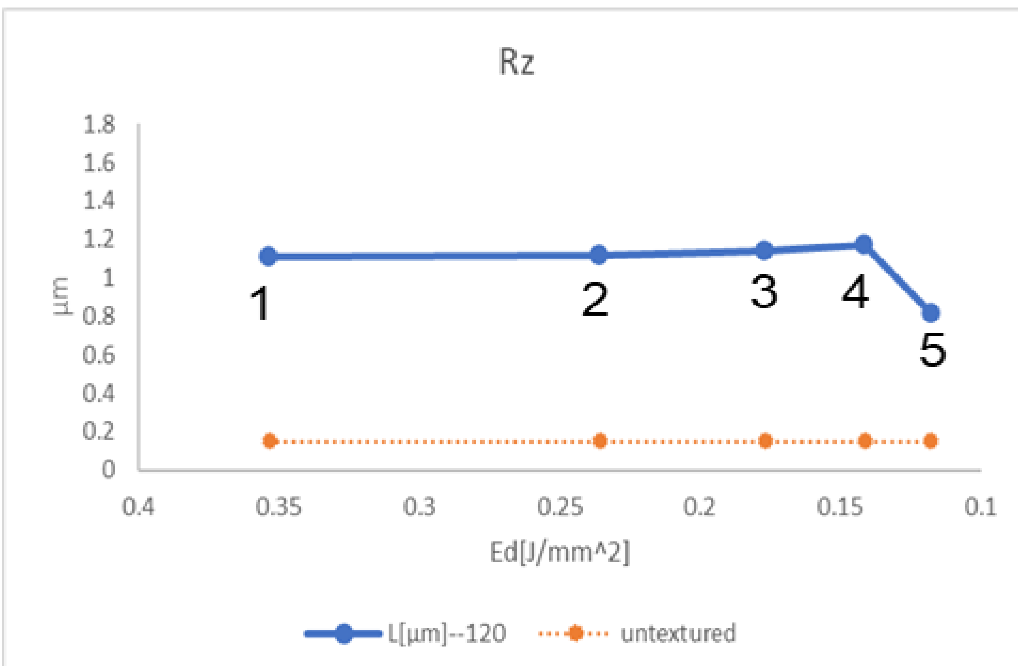


Figure 15. Ra roughness value of samples



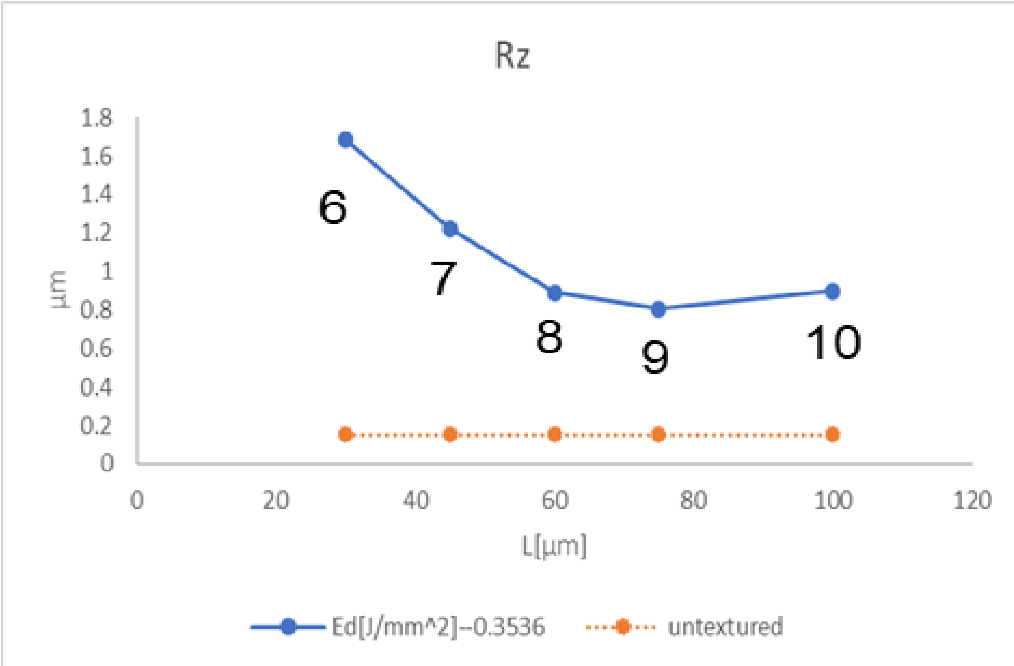


Figure 16. Rz roughness value of samples

6.2 Influence of laser micro textures on contact angle measurement

The contact angles of PAO40 applied on untextured and textured surfaces were measured to exhibit the different lubricant absorption properties. Analyzing the results, all textured surfaces with different laser parameters have smaller contact angles compared to untextured surfaces, which reveals the lubricant retention ability has been improved by laser micro textures on the samples with different parameters. The enhancement of lubricant retention ability is often related to the improvement of tribological behavior of Titanium alloy. Analyzing the results of Figure 15, Figure 16 and Figure 17, the direct dependence can be noticed between different behaviors of roughness parameters and variations of contact angle, which corresponds with the Cassie-Baxter and Wenzel models [114,115]. The increase of contact angle indicates that the lubricant can be efficiently stored in the lasered textures. Therefore, in some sliding processes, it would be helpful for surface-lubricant interaction to improve wear resistance of materials compared to untextured surfaces. According to Fan et al.'s research, the variations of contact angle can also be correlated to the lubricant-film thickness, which explains the variations in the friction coefficient of surfaces treated by LST [112].

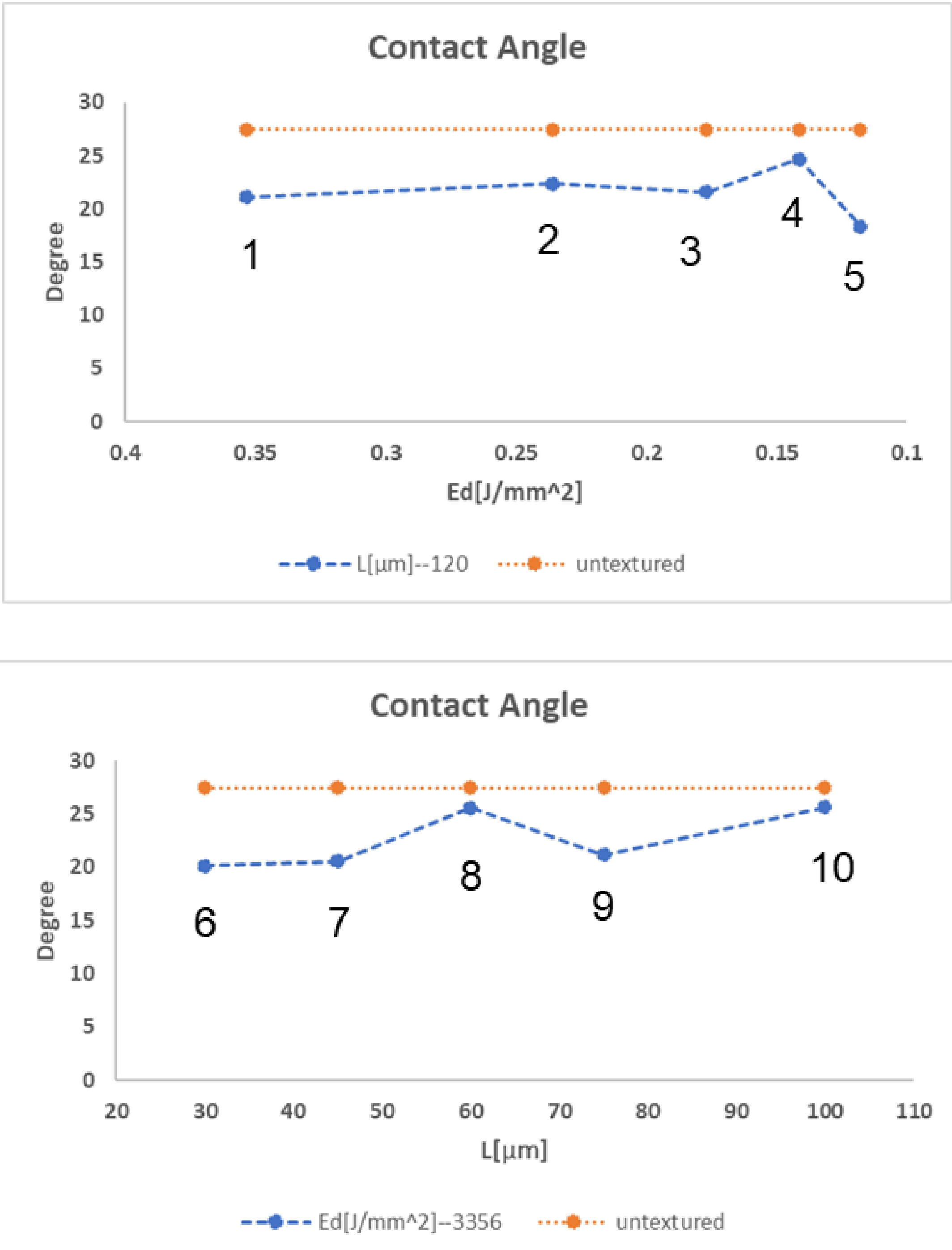
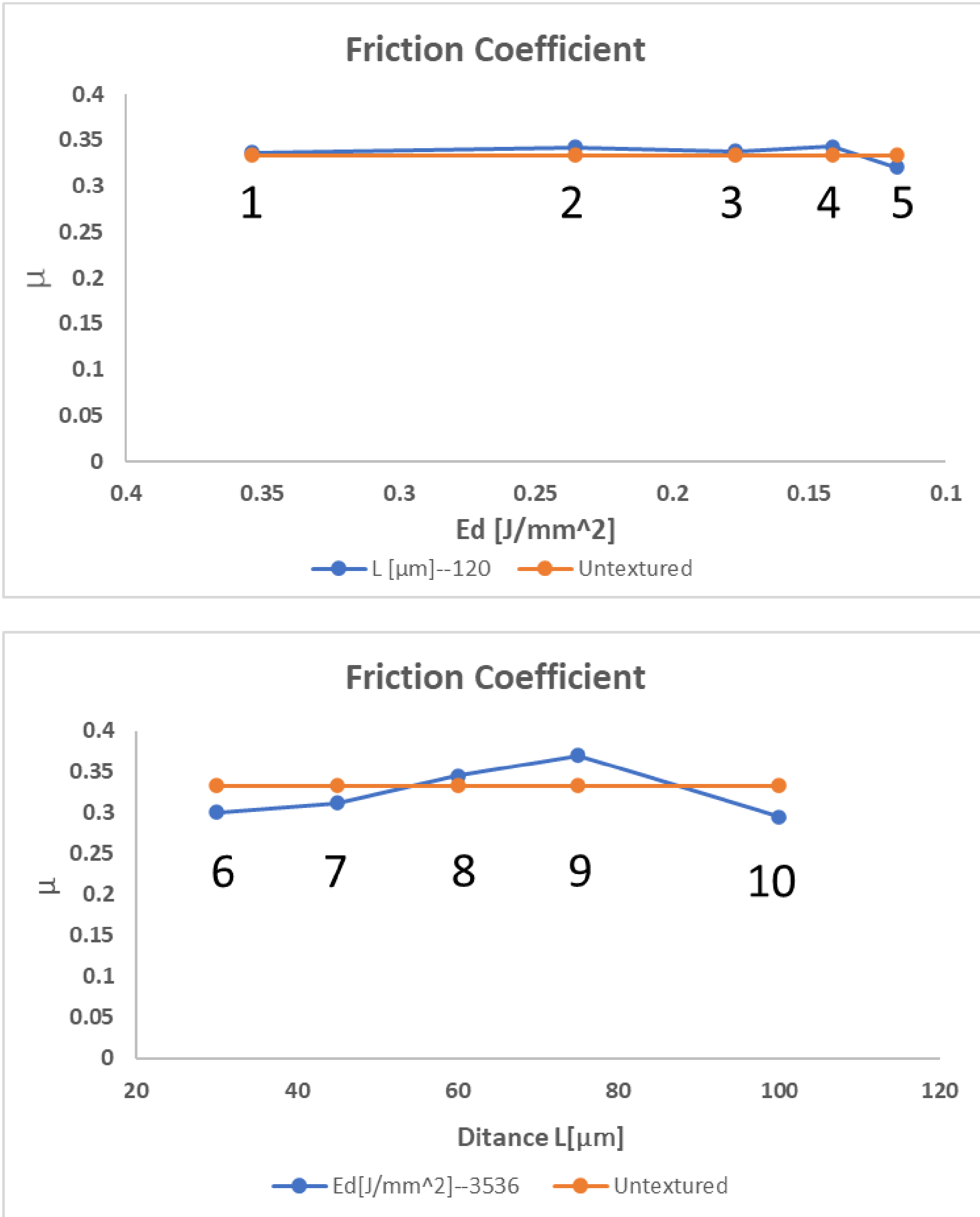


Figure 17. Contact angle (lubricant) behavior for textured sample 1 to sample 10 and untextured surfaces

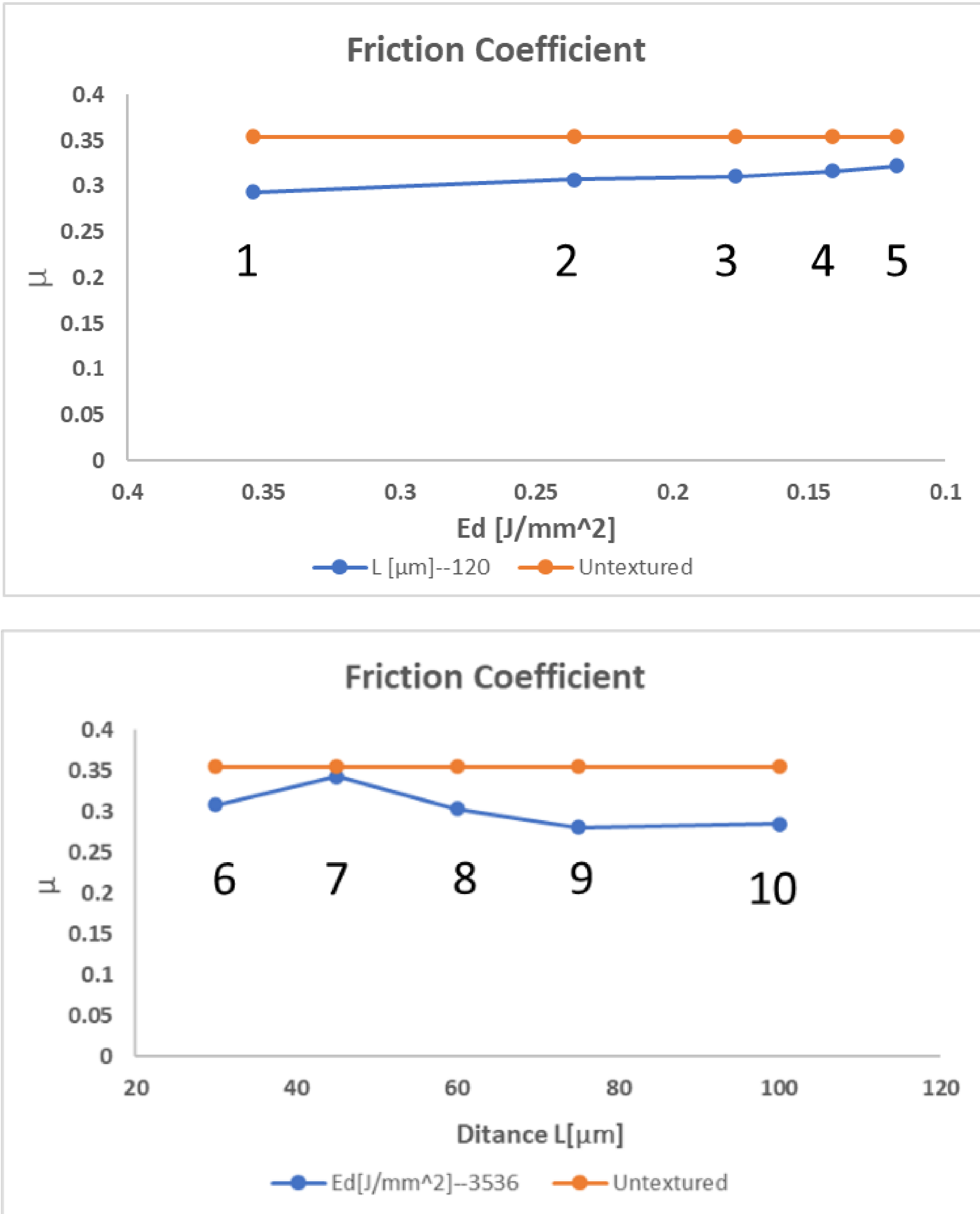
6.3 Tribological behavior of textured surfaces under different lubricant conditions

Laser texturing technology has been proved to play an important role of improving the tribological performance during relative motion of mechanical components. Modifications of micro-geometrical features and surface properties created by laser texturing technology are considered to cause the appearance of a series of tribological phenomena and subsequently the variation of the involved behavior, especially friction coefficient and wear volume. Through adding micro textures crated by the laser parameters including energy density of pulse (Ed) and distance between dimples (L) to Ti6Al4V surface, the influence on tribological performance were studied.

When analyzing the friction results of samples lubricated by PAO40 ((a) in Figure 18), friction coefficient generally increased with L for sample 6 to sample 10, which present opposite stages as Ra and Rz roughness evaluation. When evaluating the effect of different Ed on friction coefficient, only slight reduction is achieved by sample 5, which might be due to the minor changes of roughness of Ti-alloy surfaces textured by different Ed. Generally, the friction coefficient of textured samples barely has difference compared to the textured surface when lubricated by PAO40.



(a) Lubricant condition: PAO40

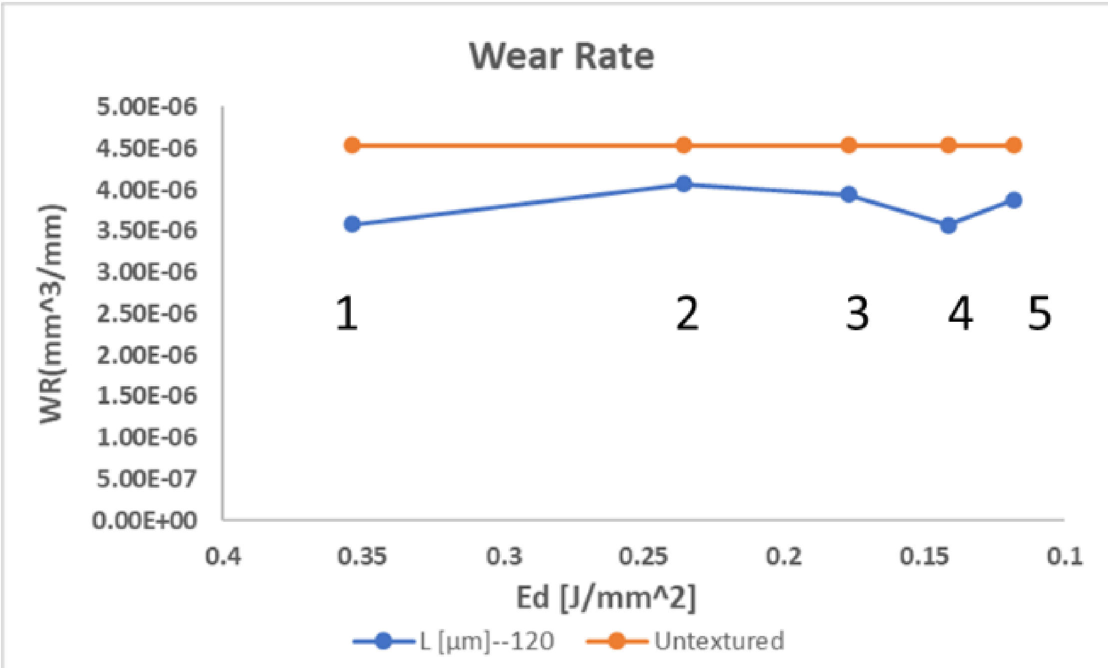


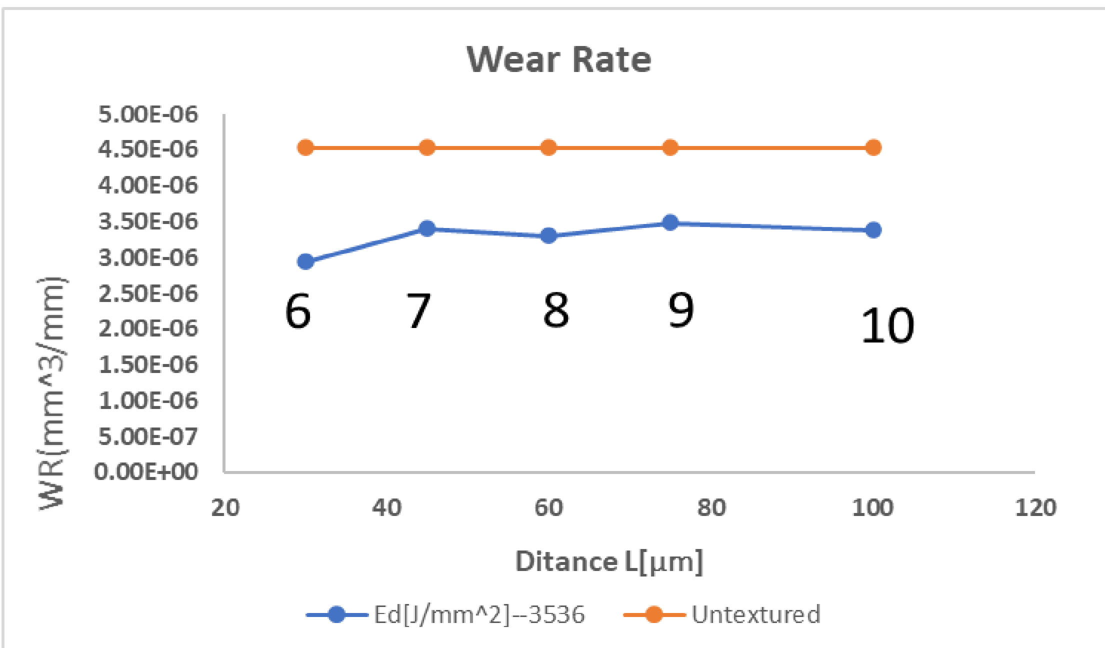
(b) Lubricant condition: the PIL mixture

Figure 18. Friction coefficient behavior for lubricated textured and untextured surfaces under different lubricant conditions

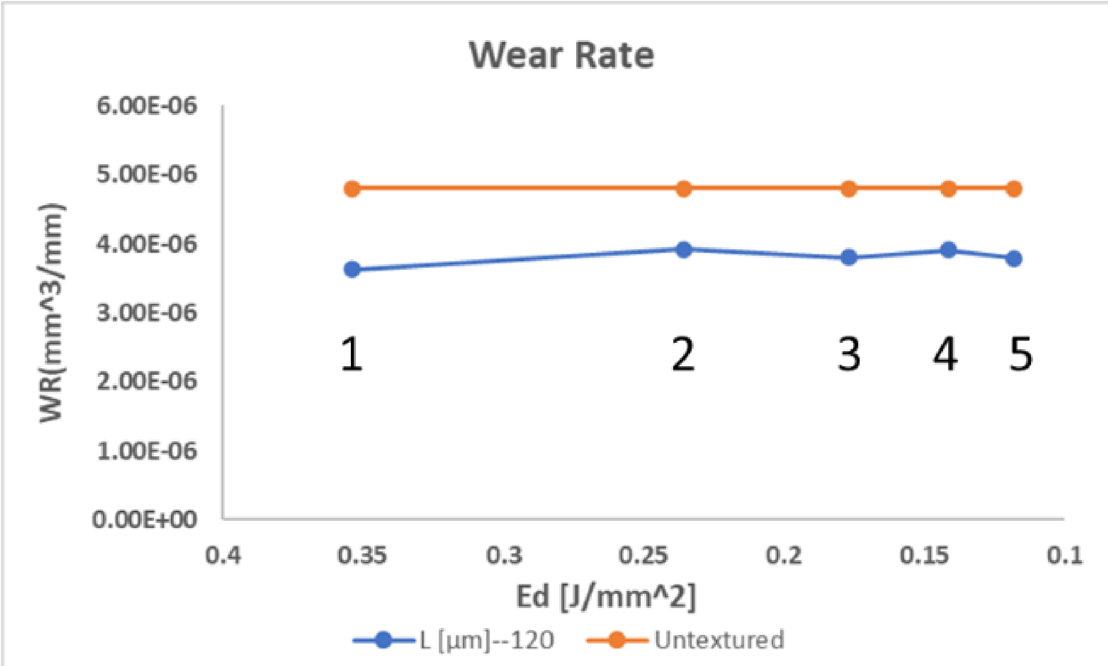
However, compared to employing the PAO40 as the lubricant, the friction coefficients of textured samples have the significant reduction compared to textured surfaces when applying the PIL mixture as the lubricant, where the biggest reduction of sample 10 is up to 20%. The friction coefficient of sample 1 to sample 5 are generally increased with the decrement of energy density ((b) in Figure 18).

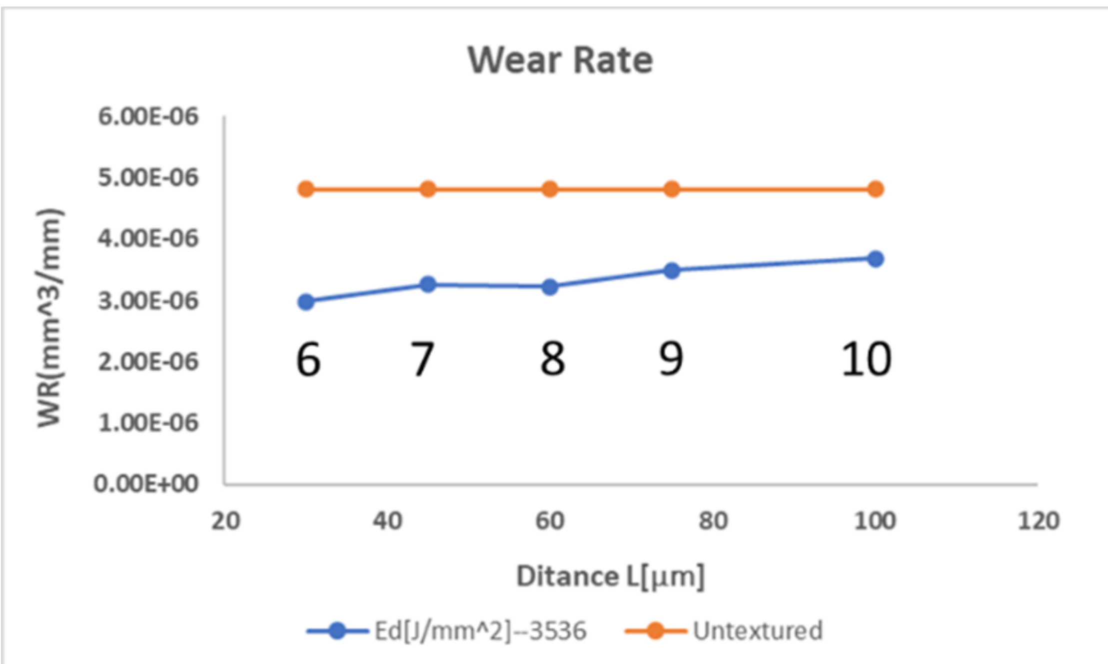
The geometrical features and dimensions of wear scars are affected by different laser texturing parameters but not as strong as expected. Because of the irregularities of surfaces with laser micro textures created by LST, the method recommended by ASTM G133 to calculate the wear volume is not suitable. Due to this reason, the equations presented by Qu et al. [113] are adopted to calculate the wear volume by the width and depth of wear tracks generated by a ball-on-flat reciprocating tribometer. The width and depth are measured by Optical microscopy. Compared to the untextured surfaces, all textured surfaces have the reduction of wear rate no matter lubricated by PAO40 or the PIL mixture. When the lubricant is only the base oil, among the samples with different energy density, the reduction is up to 21%, which is achieved by sample 1 with the biggest energy density. When observing the results of samples with different distances between dimples, the biggest reduction is gained by sample 6 with the smallest distance, which is up to 35%. When applying the PIL mixture as lubricant, the results are quite similar, where the sample 1 and sample 6 have the most significant reduction. According to the Figure 19, the wear rate is increased with the increment of distance between dimples.





(a) Lubricated by PAO40

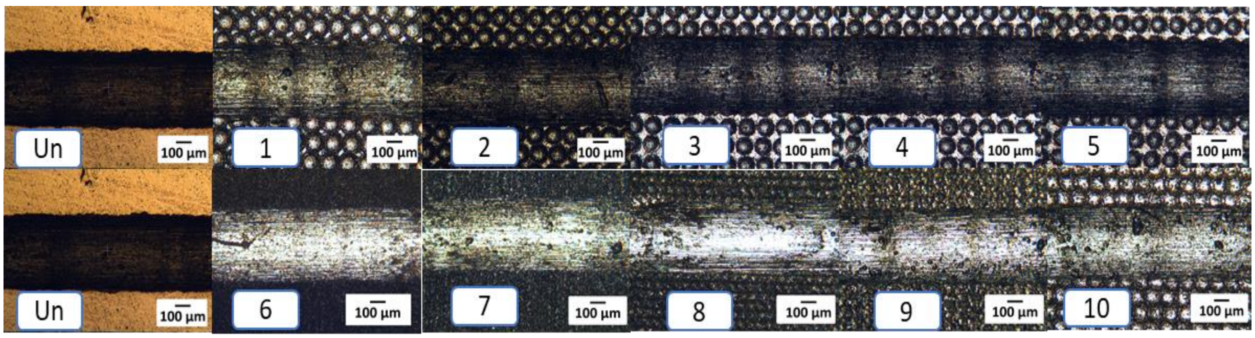




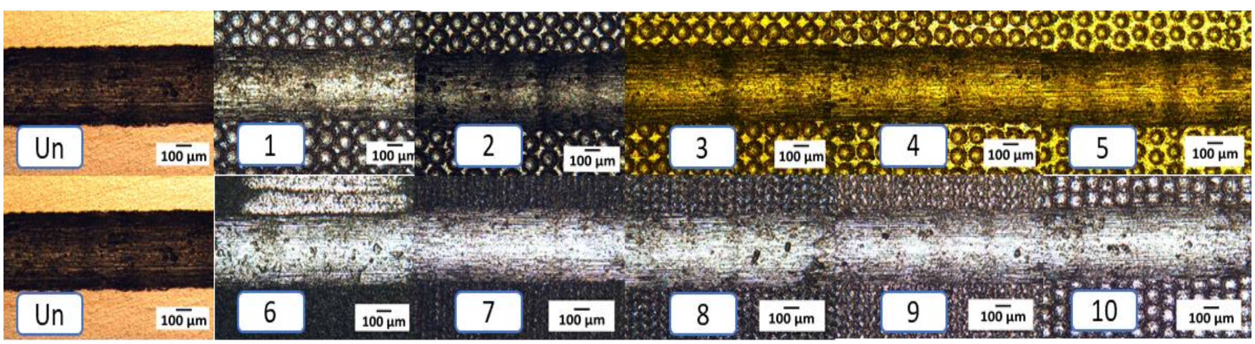
(b) Lubricated by the PIL mixture

Figure 19. Wear rate of sliding track on different textured surfaces under different lubricant conditions

To observe the topographical features of wear tracks, the optical microscopy is responsible for capturing the pictures. The optical images in Figure 20 have exhibited the characters of wear scars zoomed 100 times, where the dimension of wear tracks on textured surfaces are observed to be slightly smaller than the wear scar of untextured surface no matter lubricated by PAO40 or the PIL mixture.



(a) Lubricated by PAO40

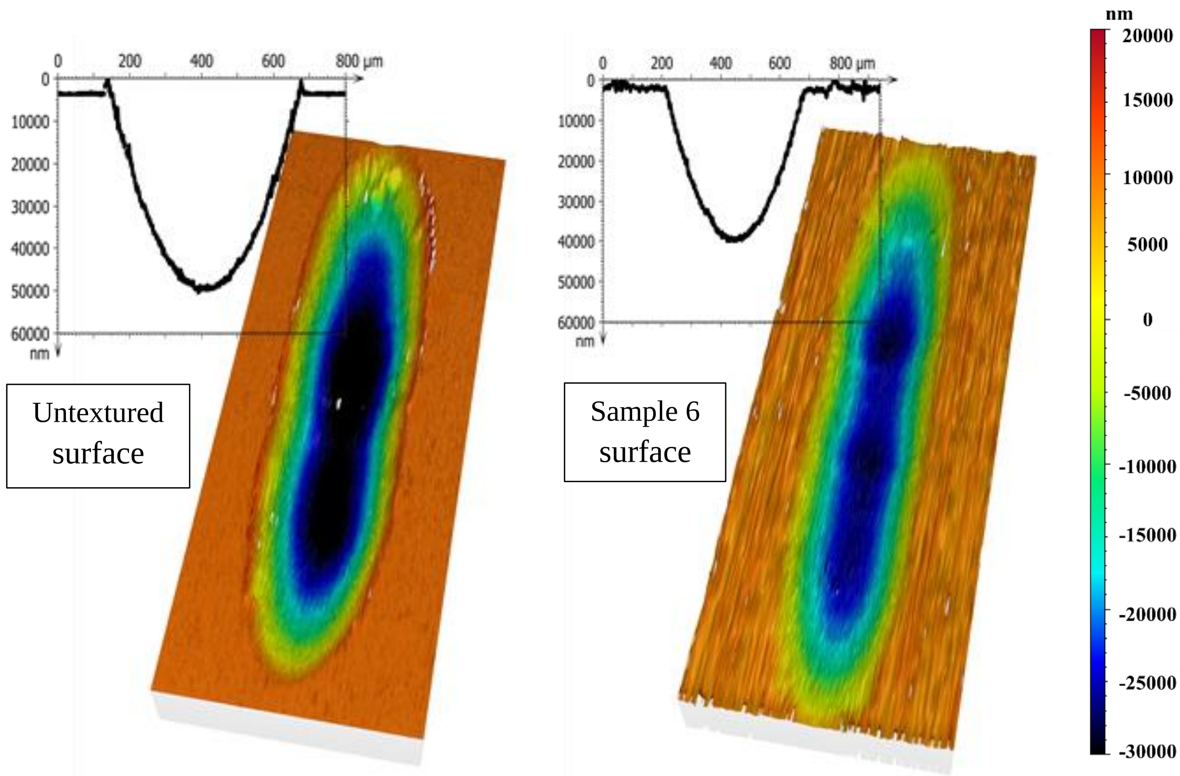


(b) Lubricated by the PIL mixture

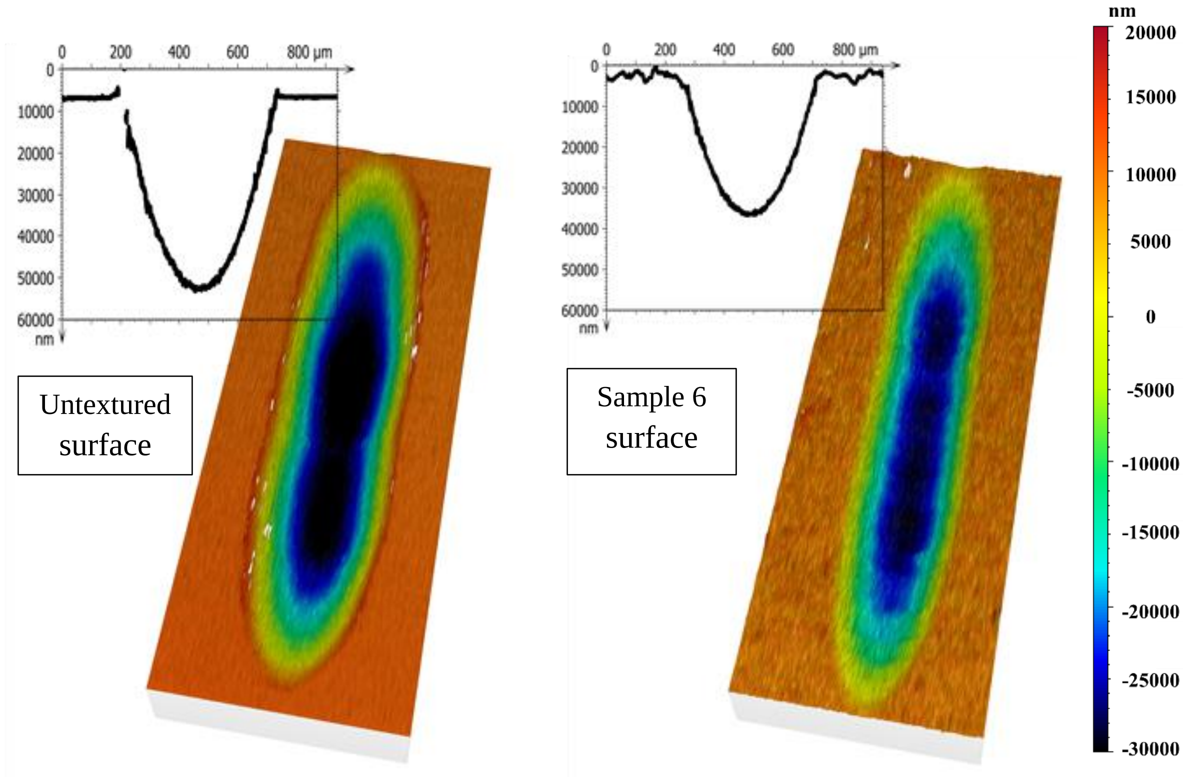
Figure 20. Optical images of sliding track on different textured surfaces under different lubricant conditions

To assess the geometrical characters of the wear scars, the 3D profilometer are utilized to examine the wear tracks of untextured surface and textured surfaces. The sample 6 achieved the best tribological performance no matter lubricated by PAO40 or the PIL mixture among 10 samples.

When observing the 2D profiles and 3D images of wear tracks (in Figure 21), the wear track of sample 6 is the shallowest no matter lubricated by PAO 40 or the PIL mixture.



(a) Lubricated by PAO40



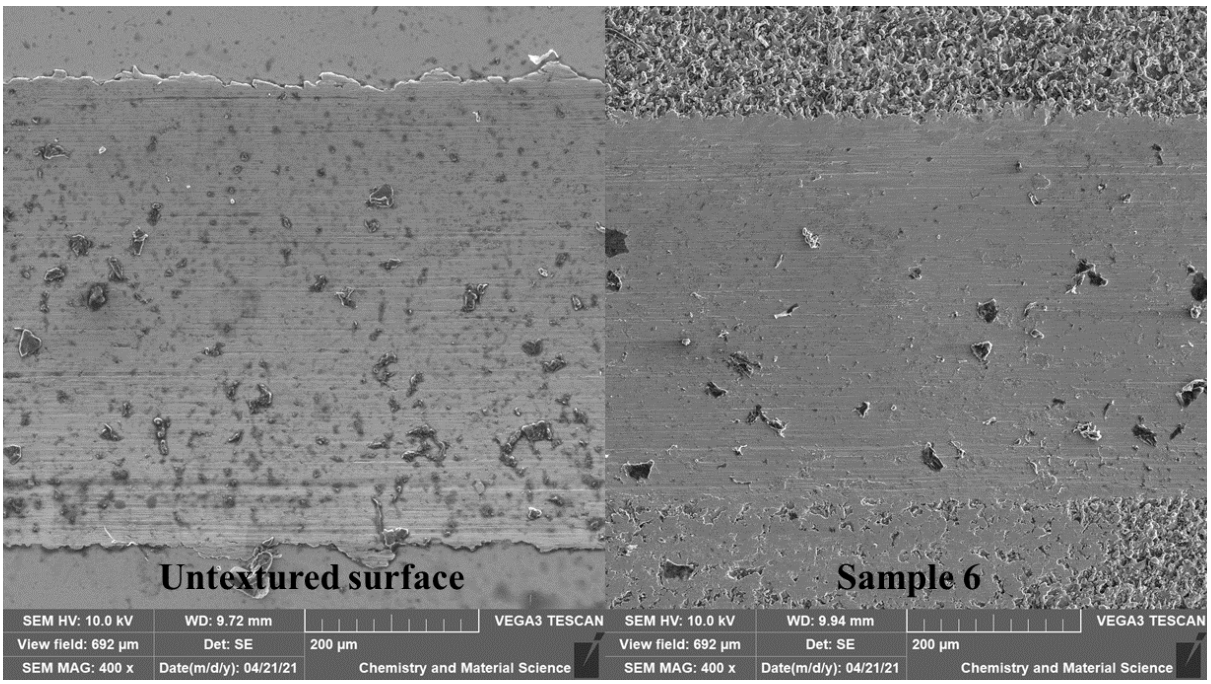
(b) Lubricated by the PIL mixture

Figure 21. 3D images and 2D profiles of untextured surface and sample 6 under different lubricant conditions

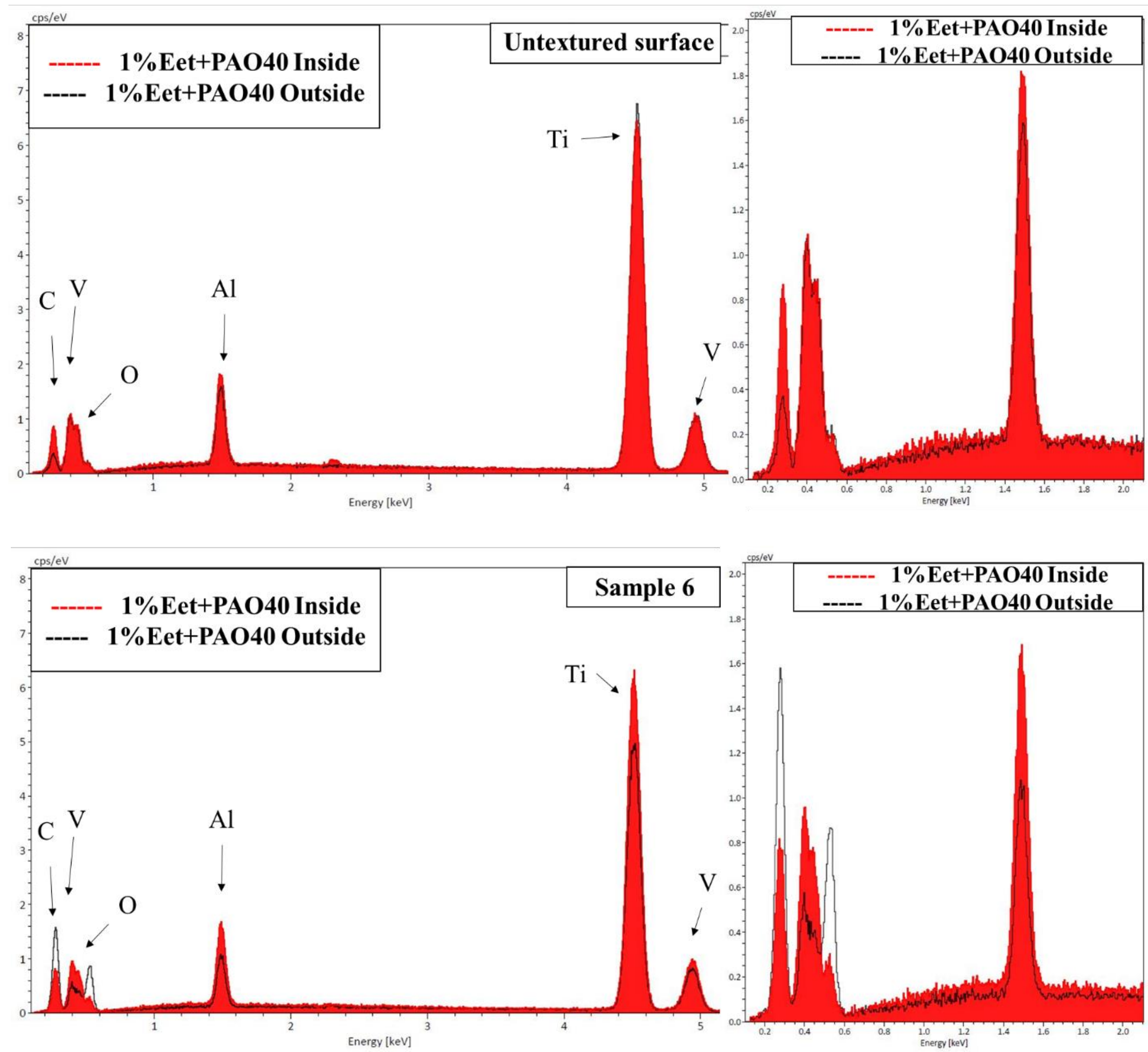
In order to analyze the question about the dependent relationship between the laser micro-texturing parameters and the wear mechanism of the sliding wear tracks and sample 6 with the smallest distance between dimples and the wear track of untextured surfaces have been analyzed by SEM and EDX.

As can be seen from the SEM images in Figure 22, the wear track on the untextured surface has plastic deformation along the borders, compared to the track on the textured surface. Additionally, the abrasive marks can be observed inside the wear tracks, no matter on untextured surface or textured surface, which is different from the results in other research that no abrasive marks were obtained on textured surface. The reason for the abrasion effects on the textured surface may be due to the harder wear debris fell off from the oxidation layer of Ti6Al4V [114].

From SEM pictures, wear particles, which might fall off from war debris can be observed to adhere on both tracks of contact surfaces. This phenomenon can be assumed that adhesion effects happened during sliding process. Meanwhile, three-body abrasion mechanism (3BA) caused by the relative motion of small particles from harder modified oxidation layers and the sliding ball are also detected.



(a)



(b)

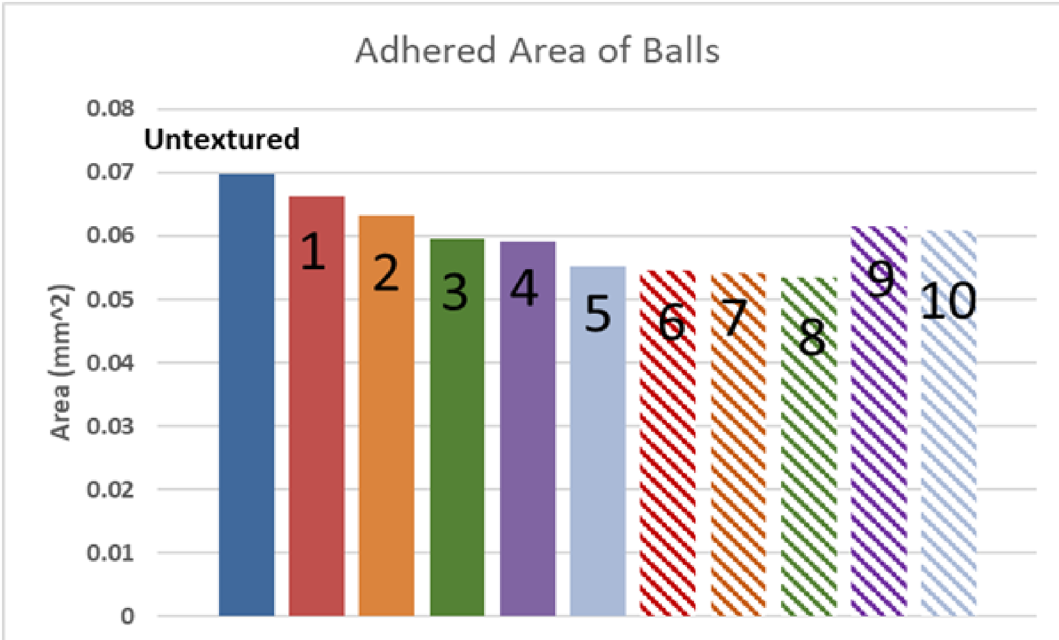
Figure 22. The results of SEM (a) and EDX (b) for untextured surface, sample 1 and sample 6

Table 12 summarized the element difference of inside and outside of wear track measured by EDX. This result exhibits a significant increment of carbon (C) content, mainly due to removed material from spherical balls (ceramic), original components of the alloy and lubricant diffusion phenomena. Because of the laser heat during laser process, thermal oxidation of Ti alloy takes place in the outer layers, which was removed by tribological process. This is the reason why a decrease of oxygen atom percent was discovered in the wear track compared to the outside of wear track.

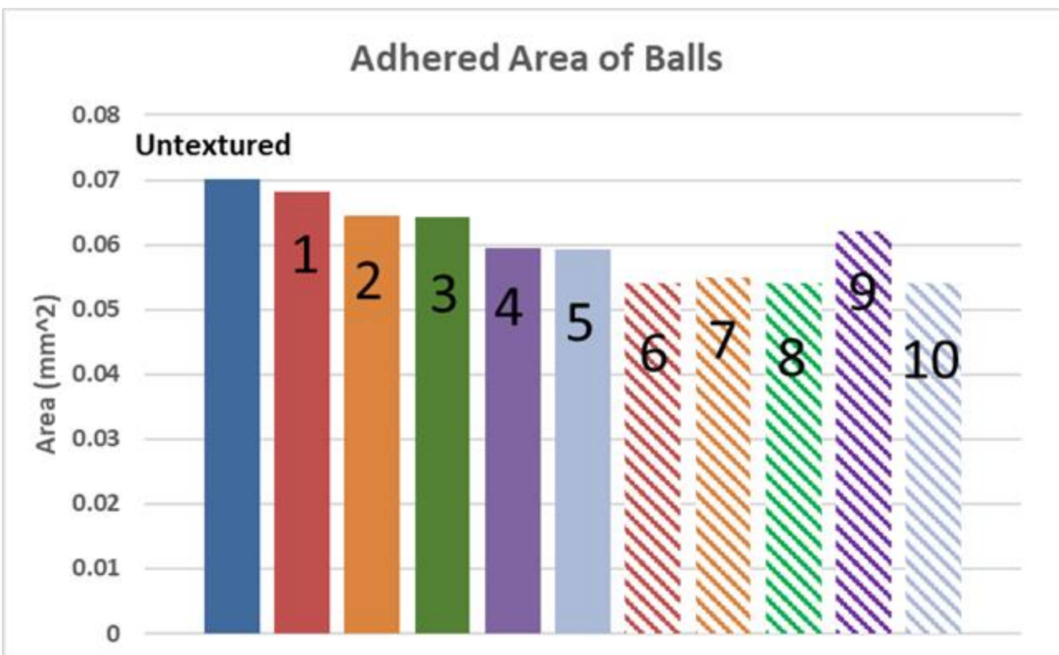
Table 12. The difference of elements between inside and outside wear tracks for untextured surface, sample 1, and sample 6 lubricated by the PIL mixture

	Difference of Inside of Outside (At %)		
Element	**Untextured surfaces**	**Sample 1**	**Sample 6**
C	37.80	1.34	-3.3
O	-5.46	-9.96	-21.30
Ti	-28.48	8.03	22.11
Al	-3.24	0.40	2.28
V	-0.62	0.20	0.08

6.4 Effect on the tungsten carbide ball



(a) Lubricated by PAO40



(b) Lubricated by the PIL mixture

Figure 23. The area of materials adhered on the ceramic balls under different lubricant conditions

The characterization of surfaces of ceramic balls utilized during the sliding process plays an important role to identify the adhesive wear mechanism of the harder component of the contact pair. In Figure 23, the adhered areas of materials on the ceramic ball have been summarized, where the variations of energy density and distance between the dimples are proved to strongly affect the adhered area. Compared to the untextured surface, the adhered material area of textured surfaces is generally decreased no matter lubricated by PAO40 or the PIL mixture. When observing the results of sample 1 to sample 5, the adhered material area is decreased with the decrement of energy density of micro textures, but no specific trend can be observed on the sample 6 to sample 10.

6.5 Conclusions

In this work, laser surface texturing technology has been proved an efficient and eco-friendly way to generate micro textures on metal surfaces. Applying with this technology, modified layer with special topographies for specific applications are induced. The dimensions and geometrical features of textures on the Ti6Al4V surfaces depend on the different laser processing parameters. In this work, the distance between dimples is shown as one of the most important parameters that determine the geometrical properties of the laser modification of micro textures. Compared the variations of energy density selected in this research, the varying distance has a more significant influence on the tribological performance of Ti6Al4V.

Micro dimples created by laser can enhance the ability of lubricant retention on surfaces, which lead to the improvement of wear performance compared to untextured surface. Meanwhile, surface-lubricant interaction can be increased by micro dimples of textured surfaces for reducing friction coefficient. The sample with the smallest distance shows the biggest reduction of wear rate. When utilizing different lubricants including the base oil and the PIL mixture, the results of friction coefficient are behaved differently, where all samples achieved lower friction coefficient compared to untextured surfaces lubricated by the PIL mixture. But the friction behavior of samples is barely changed lubricated by PAO40. This improvement is ascribed that the generation of ordered layer of protic ionic liquid is facilitated on the laser micro-texturing surfaces. Although the wear loss did not show the significant difference as expected when applying PAO40 and the PIL mixture as the lubricant, it is believed that the usage of protic ionic liquid can help the titanium alloy with laser micro textures achieve better frictional behavior, which might expand the applications of the titanium to satisfy different requirements. The more detailed reason for these results needs to be further discussed.

Adhesion effect and abrasion marks have been detected as crucial factors to explain the mechanisms related to the tribological process of the sliding textured Ti6Al4V – ceramic contact under lubricant condition. The energy density of the pulse (J/mm2) and distance between micro-dimples are the key parameters that dominate the formation of modified material top surfaces with varying characteristics and properties influencing the tribological behavior.

7.0 FUTURE RESEARCH

This work has proved the positive effect of laser parameters and protic ionic liquid on the tribological performance of titanium alloy. However, there are few key questions which need to be considered in the future.

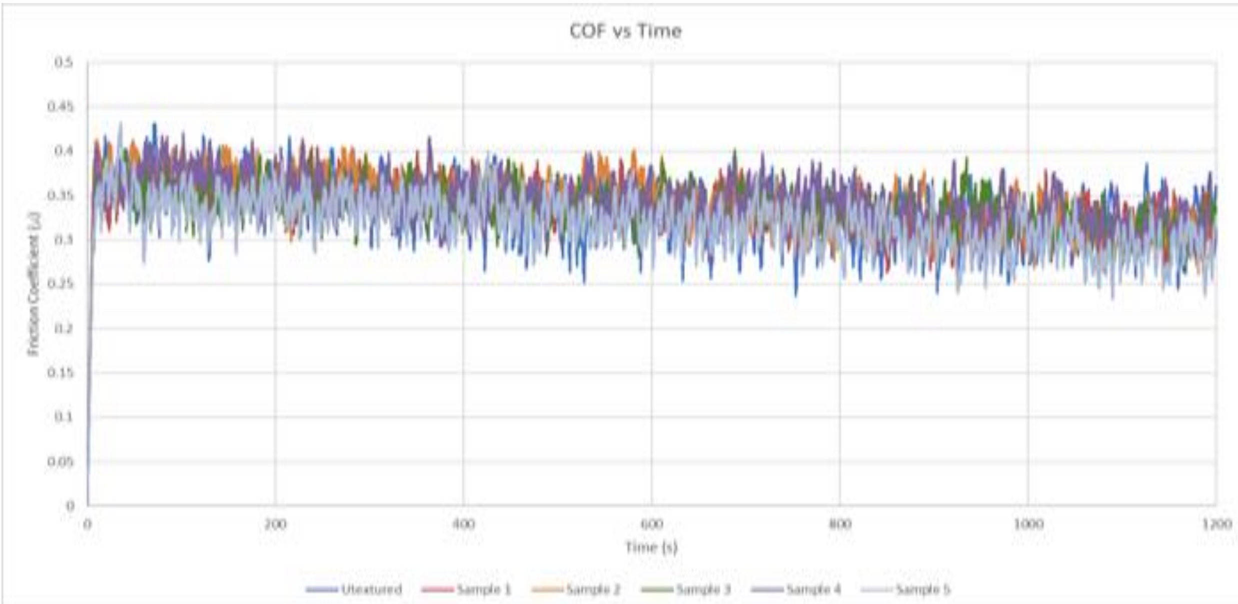
1: The wear rate of mechanical pair lubricated by protic ionic liquid mixture isn't improved visibly. If we can apply different kinds of ionic liquid with different acids or base, the results may be totally changed.

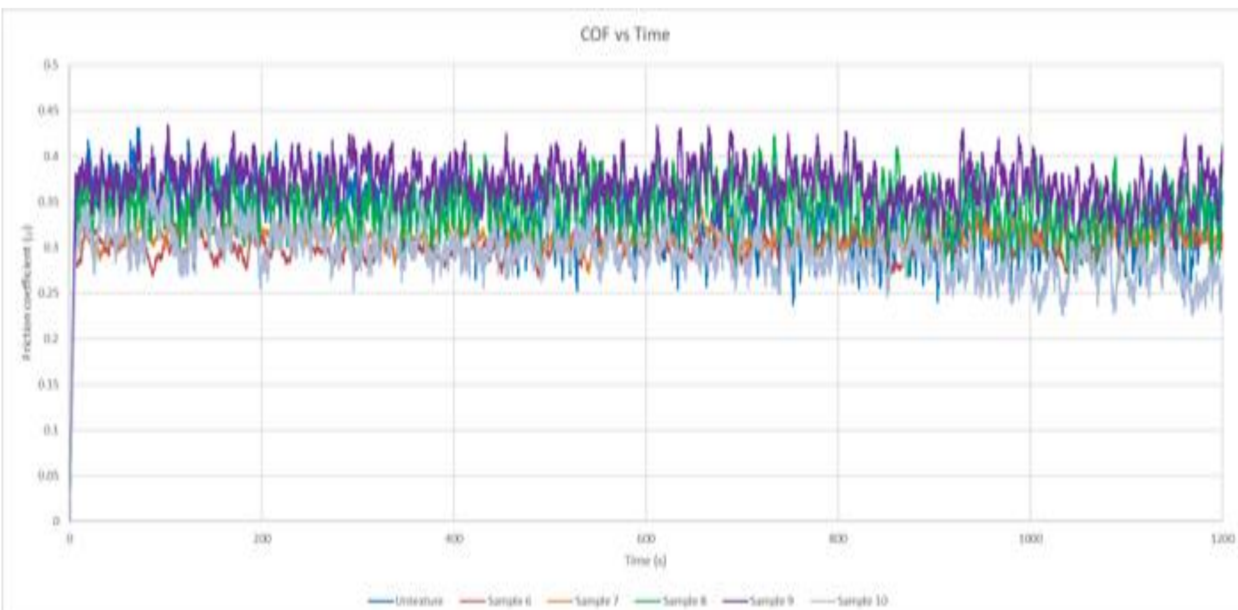
2: Targeting to the aforementioned problem, to try another base oil is worthwhile to study instead of PAO40.

3: The effect of dimple depth controlled by laser micro-texturing technology on the tribological performance of moving pairs can gain interesting results, where the bigger reduction of friction and wear rate might appear.

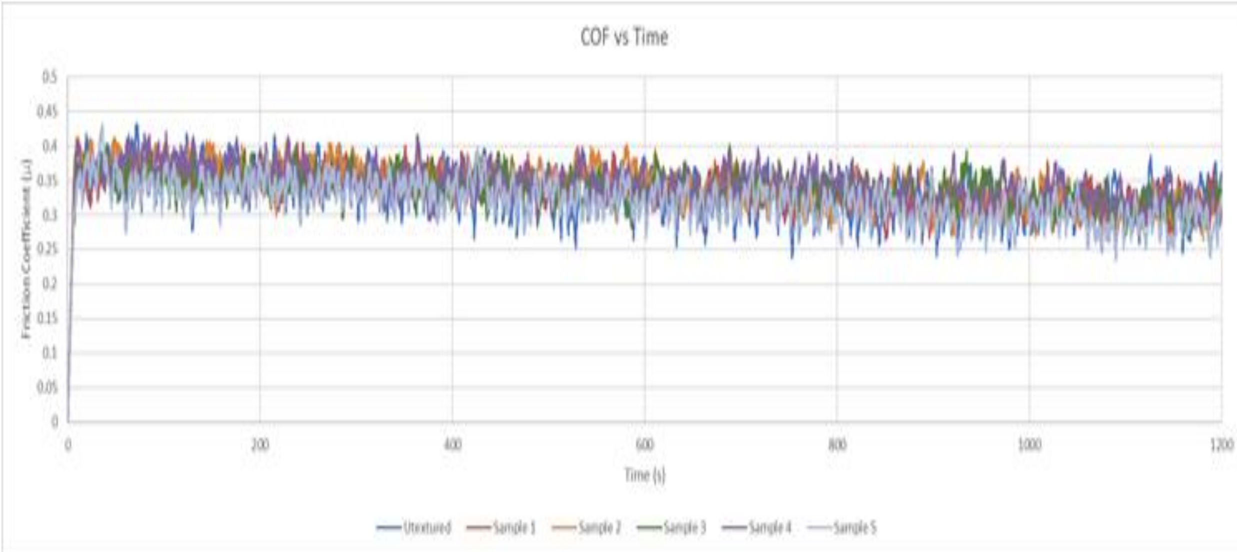
8.0 APPENDIX

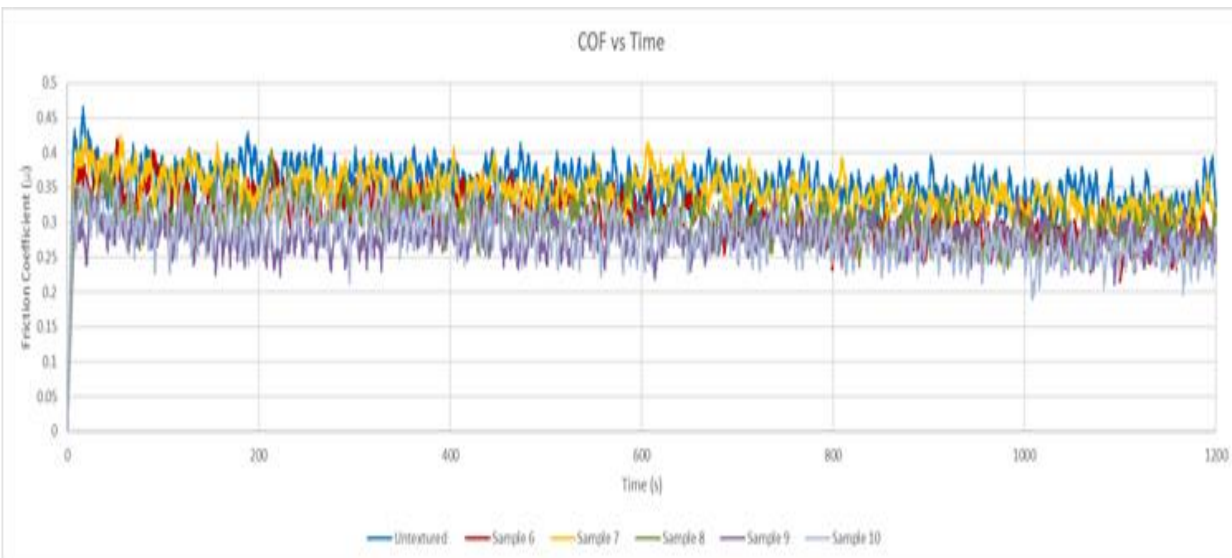
The graphs of friction coefficient vs time have been summarized below.





(a) Lubricated by PAO40





(b) Lubricated by the PIL mixture

Figure 24. Fiction coefficient verse time of sample 1 to sample 10 under different lubricant conditions

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