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Tribological Performance of Gd-DLC and Eu-DLC Coatings in the Presence of Ionic Liquid Additives Under Different Temperatures

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Dissertation under the Joint European Master's Degree in Surface Tribology and Interfaces guided by Doctor Fabio Emanuel De Sousa Ferreira presented to the Department of Mechanical Engineering of the Faculty of Science and Technology of the University of Coimbra.

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Tribological Performance of Gd-DLC and Eu-DLC Coatings in the Presence of Ionic Liquid Additives Under Different Temperatures

Submitted in Partial Fulfilment of the Requirements for the Degree of European Joint European Master in Tribology of Surfaces and Interfaces.

Desempenho tribológico de revestimentos de Gd-DLC e Eu-DLC na presença de aditivos à base de líquidos iônicos sob diferentes temperaturas

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Dedication

I dedicate this piece of my work to:

To our Prophet Muhammad (PBUH), whose teachings continue to inspire humanity. His message of seeking knowledge and sharing it with others resonates deeply within me. As in AL-Tirmidhi (107) it is beautifully stated, "Seek knowledge and teach it to other people."

To my beloved mother and supportive family, whose unwavering prayers, guidance, and blessings have been instrumental in shaping my path.

Additionally, I find it fitting to reflect on the profound significance of the word "IQRA," which marks the very first revelation of the Quran to Prophet Muhammad (peace be upon him). The divine commandment to "read" signifies the importance of seeking knowledge and engaging in continuous learning. It serves as a reminder of the power and transformative potential that knowledge holds. In dedicating this work, I strive to embody the spirit of "IQRA" and contribute to the pursuit of knowledge in our society.

Acknowledgments

I would like to express my deepest gratitude and appreciation to all those who have contributed to the successful completion of my Joint European Master’s Degree in Tribology of Surfaces and Interfaces. This journey would not have been possible without the support, guidance, and encouragement of numerous individuals and institutions.

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In conclusion, the successful completion of this Master's thesis is a testament to the collaborative efforts, unwavering support, and invaluable contributions of the aforementioned individuals and institutions. Their guidance and assistance have left an indelible mark on my academic and personal development, and for that, I am deeply grateful.

Thank you all sincerely.

Abstract

This Master's research thesis investigates the tribological performance of diamond-like carbon (DLC) coatings doped with rare earth metals (Europium and Gadolinium) as well as pure DLC lubricated with ionic liquid additives (trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate {[P_{66614}][DEHP]} and 1-ethyl-3-methylimidazolium diethyl phosphate {[EMIM][DEP]}) in Polyalphaolefin 8 (PAO8). The study aims to examine the effect of temperature on the interaction between the coatings and additives by conducting tribological experiments using a block-on-disk setup at temperatures of 60 °C, 80 °C and 100 °C. The primary objective is to evaluate the performance of doped DLC coatings compared to pure DLC coatings with ionic liquid additives in the lubricant in boundary lubrication conditions at various high working temperature environments. The experiments reveal that doped DLC coatings with ionic liquid additives exhibit superior tribological performance compared to pure DLC coatings. The rare earth metal dopants play a positive role in the formation of a tribofilm on the surface of the coatings as it interacts with ionic liquids, resulting in a lower coefficient of friction (CoF). Temperature influences the performance of the coatings and additives. The CoF increases with temperature for pure DLC coatings, while for doped DLC coatings it was significantly less. These findings highlight the influence of temperature on the tribological behaviour of DLC coatings. Overall, this study contributes valuable insights into the impact of rare earth metal dopants and ionic liquid additives on the tribological performance of DLC coatings under different temperature conditions. The results demonstrate the potential of utilizing doped DLC coatings with ionic liquid additives as an effective approach to enhance the performance of mechanical systems.

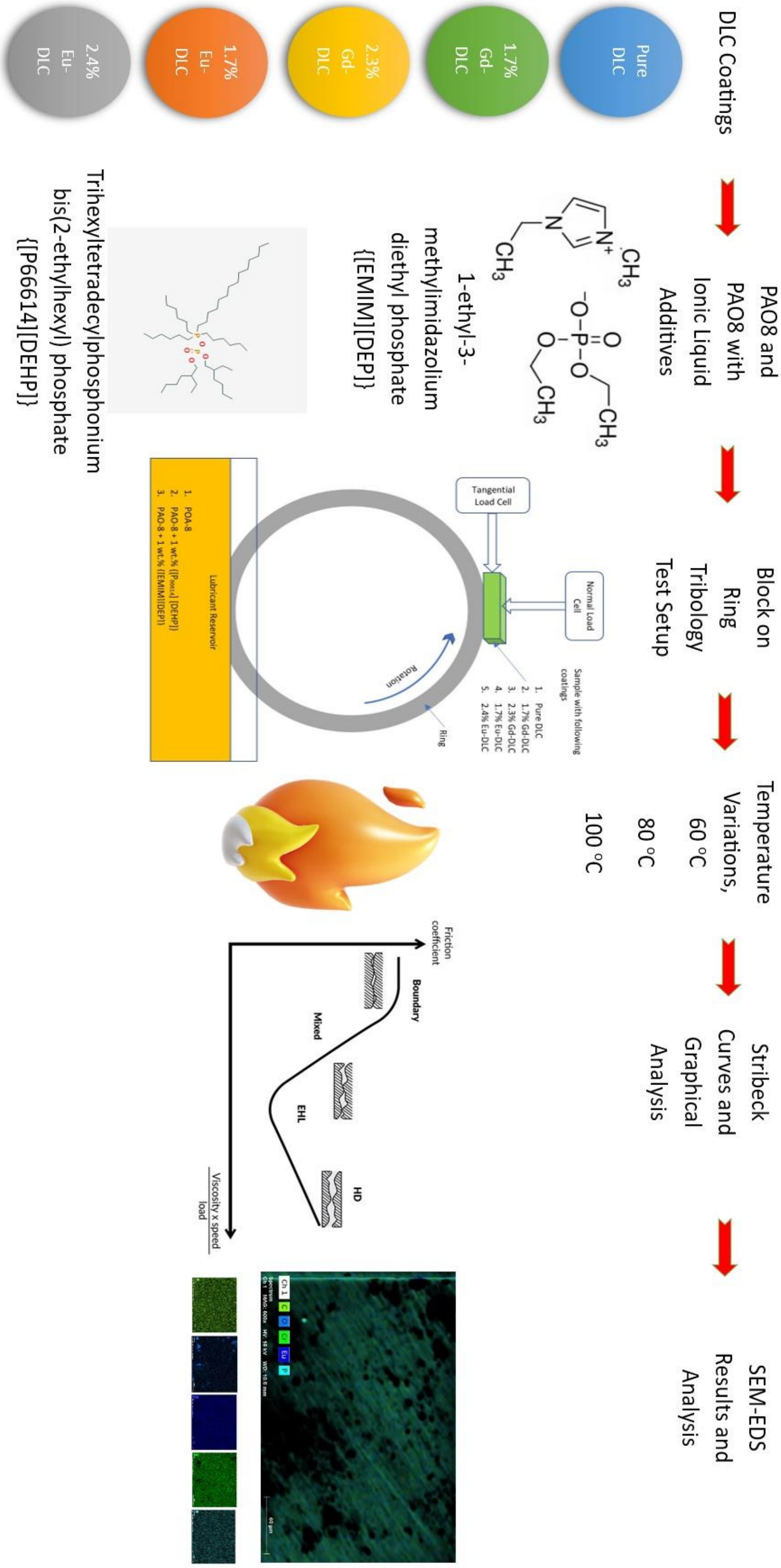
Keywords: Ionic liquids; diamond-like carbon coatings; doped-DLC; tribology; temperature.

Resumo

Esta dissertação de mestrado investiga o desempenho tribológico de revestimentos de carbono tipo diamante (DLC) dopados com metais de terras raras (Európio e Gadolínio), bem como DLC puro lubrificado com aditivos líquidos iônicos (*trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate* {[P_{66614}][DEHP]} e *1-ethyl-3-methylimidazolium diethyl phosphate* {[EMIM][DEP]}) em Polialfaolefina 8 (PAO8). O estudo visa examinar o efeito da temperatura na interação entre os revestimentos e aditivos por meio da realização de testes tribológicos usando uma configuração bloco sobre disco a temperaturas de 60 °C, 80 °C e 100 °C. O objetivo principal é avaliar o desempenho de revestimentos DLC dopados em comparação com revestimentos DLC puros na presença de aditivos à base de líquidos iônicos no lubrificante em condições de lubrificação limite em vários ambientes de alta temperatura de trabalho. Os testes revelam que revestimentos DLC dopados na presença de aditivos à base de líquidos iônicos exibem desempenho tribológico superior em comparação com revestimentos DLC puros. Os dopantes de metais de terras raras desempenham um papel positivo na formação de um tribofilme na superfície dos revestimentos, pois interagem com líquidos iônicos, resultando em um menor coeficiente de atrito (CoF). A temperatura influencia o desempenho dos revestimentos e aditivos. O CoF aumenta com a temperatura para revestimentos DLC puros, enquanto para revestimentos DLC dopados foi significativamente menor. Essas descobertas destacam a influência da temperatura no comportamento tribológico dos revestimentos DLC. No geral, este estudo contribui com informações valiosas sobre o impacto de dopantes de metais de terras raras e aditivos à base de líquidos iônicos no desempenho tribológico de revestimentos DLC sob diferentes condições de temperatura. Os resultados demonstram o potencial da utilização de revestimentos DLC dopados na presença de aditivos à base de líquidos iônicos como uma abordagem eficaz para melhorar o desempenho de sistemas mecânicos.

Palavras-chave: Líquidos iônicos; revestimentos de carbono tipo diamante; DLC dopado; tribologia; temperatura.

Graphical Abstract



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List of Abbreviations

Abbreviation	Meaning
DLC	Diamond Like Carbon
IL	Ionic Liquid
Gd	Gadolinium
Eu	Europium
CoF	Coefficient of friction
PAO8	Polyalphaolefin 8
$[P_{66614}]$ [DEHP]	Trihexyltetradecylphosphonium Bis(2-Ethylhexyl) Phosphate
[EMIM][DEP]	1-Ethyl-3-Methylimidazolium Diethylphosphate
DEP	Diethylphosphate
AFM	Atomic Force Microscope
GLC	Graphite Like-Carbon
ISO	International Organization for Standardization
PVD	Physical Vapor Deposition
PECVD	Plasma-Enhanced Chemical Vapor Deposition
HiPIMS	High-power impulse magnetron sputtering
BO	Base Oil
TGA	Thermogravimetric Analysis
h_0	Film Thickness
R’	Reduced Radius
η_0	Lubricant Viscosity at Atmospheric Pressure
W	Applied Load
E'	Reduced Young's Modulus
U	Sliding Speed
k	Ellipticity Parameter
η_p	lubricant viscosity at pressure p

λ	Tallian Parameter
σ_A	Surface roughness of body A
σ_B	Surface roughness of body B
α	pressure-viscosity coefficient
CNT	Carbon nano tube
DIW	Deionized water
BF4	tetrafluoroborate
EDS	Electron dispersive spectroscopy
GNP	Graphene nanoplatelets
LST	Laser surface texturing
LVM	Low vacuum melting
MA	Mechanical alloying
MWCNT	Multiwall carbon nanotube
PCA	Process control agent
PE	Polyethylene
SCF	Short carbon fibres
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
SS	Stainless steel
XRD	X-Ray diffraction

1 Introduction

Climate change has raised concerns about the impact of fossil fuels on the environment, leading to a search for sustainable alternatives [1]. Frictional losses account for a significant portion of energy wastage, with around one-third of total energy production lost to friction, wear, and tear of components [2]. Reduction of frictional losses can result in decreased energy consumption, increased productivity, and monetary savings. Diamond-Like-Carbon (DLC) coatings, known for their superior tribological and mechanical properties, such as high wear resistance, hardness, and low coefficient of friction (CoF), have emerged as a promising solution [3–5].

DLC coatings are a type of self-lubricating coatings [6–9]. These coatings can be classified as diamond-like carbon (DLC) or graphite-like carbon (GLC) from the carbon fractions of sp^2 and sp^3 in coatings. DLC coatings predominantly contain the sp^3 carbon fraction, while graphite-like carbon coatings have a dominant sp^2 fraction [10]. DLC coatings are governed by the ISO 20523:2017 which was established by the International Organization for Standardization (ISO) to provide guidelines for classifying, designating, and naming carbon-based films. These films may contain other elements such as hydrogen or metals. Metal carbides can be included as constituents in the films. ISO 20523:2017 only applies to films where carbon is the main component if additional elements are present [11].

The push to minimize the use of lubricants in mechanical systems poses a challenge for engineers to operate under boundary lubrication conditions. DLC coatings have been found to exhibit the lower CoF, and their chemical structure can be tuned for various industrial applications [12–15]. However, pure DLC coatings are inert and do not react with conventional lubricants to form a protective tribofilm, leading to wear and tear [14]. Conventional lubricants are not sustainable and may not perform well with DLC coatings. Ionic liquids (ILs) have emerged as a promising solution due to their high thermal stability, low vapor pressure, low flammability, and tuneable properties for specific applications [16–21]. Phosphorus-based ionic liquids in particular, have shown promising results in reducing friction under boundary lubrication conditions by forming a tribofilm [22–24]. ILs are liquid salts composed of organic substances, characterized by a low melting temperature, high combustible temperature, low vapor pressure, superior thermal stability, low volatility, and high miscibility with organic substances [25]. They offer several advantages in lubrication systems, including reduced energy consumption, protection against friction and wear, and improved longevity [25–29]. ILs can be tailor-made to meet specific requirements by varying the combination of cations and anions [30].

The cationic structure of ILs contributes to their exceptional properties, such as high miscibility with lubricants, low melting point, superior thermal stability, and unique molecular structure [31]. The spherical shape of the ions and the variations in alkyl chains and quadrilateral structures enhance the lubrication properties of ILs, making them suitable for high-performance lubricants [32]. The anionic structure of ILs, such as hexafluorophosphate (PF6) and tetrafluoroborate (BF4), contributes to the formation of protective films that improve the wear resistance of the lubricated surfaces [33–38]. The tribological efficiency of ILs depends on the nature of the anion and cation. Hydrophobic ILs generally perform better in tribological applications compared to hydrophilic ILs [39].

ILs have demonstrated remarkable tribological behaviour as both neat lubricants and additives [40]. They can form lubrication films on interacting surfaces, resulting in reduced friction and wear. ILs have been investigated for their potential to enhance the tribological properties of traditional lubricant systems as additives [41]. The electrical charge of the DLC surface and the adsorption ability of the lubricant played significant roles in friction control [42,43]. The electrical conductivity of the lubricant (ionic liquid) affected the transport of additives to the surface, ultimately impacting friction. Higher electrical conductivity in IL-additivated lubricants resulted in faster transport kinetics and lower friction [44].

Many studies have been conducted on the interaction between base oils, lubricant additives, and doped DLC coatings over the past 30 years, but there is no consensus yet, moreover there is little to no research on the interaction of doped DLC and ionic liquids [45–50]. To overcome this limitation, doping with metals such as tungsten, zirconium, titanium, chromium, and silver has been done and it is successful in improving their thermal stability, corrosion resistance, and adhesion to the substrate, but the coefficient of friction still remains comparatively high [51–59]. Additionally, the lubrication mechanism and performance of new additives, developed to improve energy efficiency in moving mechanical components, when used with DLC films, are still unknown. The researchers have explored the tribological behavior of DLC coatings doped with rare earth metals like Gd and Eu, which showed significant improvement in the reaction with ionic liquids and doped DLC [60]. Research done by Omiya et al. and Sadeghi et al. has shown that as the concentration of dopants (Eu and Gd) increases in the DLC their affinity towards the ionic liquid additivated lubricant increases [61,62].

In this study, we will be using trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate [P_{66614}] [DEHP], which has been shown to react with iron surfaces and form an iron phosphate tribofilm layer [63–65]. In situ atomic force microscopy (AFM) by Li et al. has confirmed the adsorption of [P_{66614}] [DEHP] on the iron surface through its phosphate anions, resulting in reduced nanoscale friction [66]. Another ionic liquid lubricant additive, 1-Ethyl-3-methylimidazolium diethylphosphate ([EMIM][DEP]), has shown low wear rate and CoF due to its phosphorus-based anions [67–71]. DEP has also been recognized as a green and sustainable solvent for a sustainable future [72–74]. The phenomenon of chemical wear, resulting in reduced CoF and increased wear volume, has been observed with DEP [71]. The ionic liquid additives in PAO8 will henceforth be reported as either Ionic Liquid #1 or IL#1 for PAO 8 + 1 wt.% {[P_{66614}][DEHP]} and Ionic Liquid #2 or IL#2 for PAO 8 + 1 wt.% {[EMIM][DEP]}.

Despite the importance of these studies, only a few have focused on the benefits of using DLCs lubricated by ILs (ionic liquids) as a lubricant or oils that contain ILs with anti-wear additives. Therefore, for our experimental investigation, we will be employing Europium and Gadolinium as dopants of rare earth elements in DLC coatings to study their interaction with ionic liquids as additives in Polyalphaolefin 8 (PAO8). The rare earth elements are unexplored in the field of doping of DLC. Ionic liquids have been in use as solvent for the extraction of Europium and Gadolinium due to its affinity towards them [75]. Prior research has shown that ionic liquids can enhance the luminescence properties of rare earth metals and are used in their extraction processes [76–79]. The trivalent oxidation state of lanthanide ions makes them attractive for tribological processes with ionic liquids and their impact on tribolayer formation will be investigated. The tribological processes, where ILs serve as anti-wear additives, are expected to be influenced using lanthanides, according to these indications. Non rare earth metals have been used in doping and they have improved their thermal stability, corrosion resistance, and adhesion to the substrate, but the coefficient of friction still remains comparatively high or there are some caveats. Khanmohammadi et al. did experiments on silver which improved the properties, but CoF was high, whereas tungsten showed good results but was limited to low temperature with glycol-based water lubricant [80]. In another study researchers conducted a study on Cr-doped coatings made of diamond-like carbon (Cr-DLC) using PVD and PECVD methods [81]. The lubrication performance of solid-liquid composite lubrication systems was studied using two ionic liquids (ILs) as lubricants. The findings indicated that the friction coefficient was reduced but it corroded the surface [81].

Therefore, to assess the tribological performance, a comprehensive study was conducted to examine the behaviour of lanthanides, specifically gadolinium (Gd) and europium (Eu), as reactive elements on the surface of diamond-like carbon (DLC) coatings. The DLC coatings were prepared using a deposition technique known as High Power Impulse Magnetron Sputtering (HiPIMS). The objective was to evaluate the lubrication effectiveness of these coatings when subjected to sliding against steel surfaces, in the presence of lubricants with ILs as additives compared to regularly used base oil (BO). Comparing the samples lubricated with ILs and base oil along with various temperatures has allowed for a comprehensive evaluation of the dependency of ILs and the efficacy of the doping process on enhancing the lubrication performance of ILs in tribological applications.

Overall, the combination of doped DLC coatings and ILs showed promising results in improving tribological properties. The addition of doping elements enhanced the performance of DLC coatings, while ILs with their lubricity and thermal stability proved to be suitable for various tribological applications. The combination of doped DLC coatings and ILs was reported to further enhance their tribological properties through the formation of a protective film or tribofilm on the coating surface.

1.1 Aim of the Study

The objective of this master's thesis is to evaluate the tribological performance of doped-DLCs in the presence of different ionic liquids under different temperatures. This will be achieved using the comparative study of doped DLC along with pure DLC, ILs as additives in PAO-8 along with pure PAO-8 at three different temperatures of 60 ^{o}C, 80 ^{o}C and 100 ^{o}C.

- Evaluate the frictional behaviour of diamond like carbon (DLC) coatings doped with Europium and Gadolinium as well as pure DLC with Ionic Liquids as lubricant additive in PAO8 and pure PAO-8.
- Evaluate the lubrication performance of phosphorus based Ionic Liquids as lubricant additive in PAO8 and pure PAO8 with Europium and Gadolinium diamond like carbon (DLC) coatings along with pure DLC coating.
- Evaluate the frictional behaviour as well as lubrication performance at three different working temperatures of 60 ^{o}C, 80 ^{o}C and 100 ^{o}C.

2 State of the Art

It is a grave concern about energy and sustainability which require more efficient industrial systems to be developed. The global energy, which is produced by fossil fuels, have a significant negative impact [1] Transportation vehicles alone consume about 30% of all energy produced, and the worst part is that one-third of that being lost through wear and friction [2]. Efforts are being spent worldwide to improve the efficiency and wear-resistance of mechanical components [82–84].

Along with the growing electric vehicles, it is necessary to meet requirements for CO_2 emissions in the major cities [85–87]. The panacea to reduce friction in sliding components and to decrease damage can be done through lubricants, which mostly mineral or synthetic. To increase the certain properties of lubricant, additives are added to them. They react with the surface to form a tribofilm and to reduce friction, friction modifiers are added and similarly to reduce wear, anti-wear additives are added.

Zinc dialkyldithiophosphates (ZDDPs) are the most widely used lubricant additives [88] and it does its job, but the downside is that it is very reactive and corrosive, it blocks the filters in the engines and the main concern is that it is very harmful to the environment. ZDDP therefore has an extensive guideline on its safety and handling standards in ACC (American Chemistry Council) [89]. For this reason, researchers have been searching for a worthy alternative to it and ionic liquids seems to be the perfect candidate for it. Ionic liquids are molten salts made up of cations and anions which have lubricating properties along with excellent high thermal stability, low flammability and negligible vapour pressure. There are many studies conducted on the ionic liquids and specially on the phosphorous based ILs on the steel surface [90] but there is little or no research on the DLC coated surfaces. The control and optimization of phosphorus in ionic liquids can be carefully done. By creating lubricants with the minimum necessary amount of phosphorus to achieve the desired performance, we can further reduce the potential impact on the environment. In our case, we limit the additive to just 1%, making the phosphorus content in the lubricating oil negligible. Furthermore, in certain situations, using phosphorus in ionic liquids can be a safer option compared to other lubricants that have more dangerous additives. By incorporating phosphorus-based compounds in ionic liquids, we may be able to replace lubricants that contain toxic or environmentally harmful substances, resulting in a decrease in overall environmental risks [91–94].

DLC coatings have excellent wear resistance as well as they have high hardness [95,96] but they have very low reactivity with the lubricants used currently in machines [97]. There has been research to dope DLC with metals and nonmetals like tungsten and silicon [57,98] which improves the compatibility of DLC with lubricants but the use of DLC along with the ionic liquids is still unexplored. Moreover, the use of rare earth metals as dopant in the DLC coating is the novel research to find out the interaction between them.

In this chapter there's an overview of the thin film coatings, more specifically about DLC coatings, doped DLC coatings and then about lubricants, in which the main focus will be on the Ionic Liquids as additives in lubricants.

2.1 Thin Film Coating

Thin film coatings are characterized by thickness in the range of nanometres to few micrometres. It can be made up of single or different elemental compositions, layers, phases which can give us composite or homogenous coatings. Coatings are generally applied to increase the performance of the substrate without interfering with the properties of the bulk material. Thin film coating is an effective and cost-efficient technique for surface engineering and modification.

Thin film deposition can be divided into two categories based on the method of deposition that is chemical or physical vapour deposition. To generalise, chemical vapour deposition (CVD) basically uses liquid or gas chemical reactions to deposit the film whereas, physical vapour deposition (PVD) technique uses evaporation, or sputtering of target material on to the substrate [99].
Thin film coatings are in use for the application of improving the strength, toughness, fatigue, hardness, corrosion, wear and tear. It is used in the automobile industry, chip manufacturers for superconductor machines [100], microprocessors [101], electromagnetic machines [102], hard coatings and visual coatings for optics [103,104]. DLC coatings are a type of thin film.

2.1.1 DLC Coatings

DLC coatings as of now are widely studied and one of the main coatings under analysis in University of Coimbra. Tribology is made up of three parts, that is friction, wear and lubrication. Therefore, studying DLC and its interdependence on all these three aspects is of crucial importance. The coefficient of friction and wear are the important parameters of DLC coatings. The important factor to note is that the conventional lubrication makes the DLC coatings increase their coefficient of friction [14].

This can be further analysed, by understanding the interaction of doped DLC as there are some structural differences in the non-doped coatings from the bonding types. DLC is made of sp^2 and sp^3 diamond like bonding along with some hydrogen content or not at all [49,105]. If these DLC are doped with certain other metals, non-metals, rare earth metals, it will give us superior tribological characteristics. Out of this rare earth metals have never been studied and this paves a novel way for us to research.

The thing with DLC is that it is a dry lubricant coating which means it does not require lubricant, so when the two materials slide over each other the hard one will wear out the other material, and DLC has in general higher hardness compared to other materials. But even though DLC have higher hardness they wear out [105]. Under specific circumstances, DLC coatings can act as a solid lubricant. This happens when carbon or other elements from the coating transfer to the surfaces that are sliding or rubbing against each other. This transfer forms a thin film or layer that acts as a lubricant, reducing friction and preventing wear [49].

Now the important factor to look for is that most of machines and systems run on lubricated conditions and it is of utmost importance to study the interaction of DLC coatings with lubricants, this has been done over the years and it has been found that DLC are inert to any sort lubricants compared to bare surface of steel, which can increase friction [106–108]. Whereas, in certain doped DLC with certain lubricants the friction has reduced [109–111].

2.1.1.1 Doping of DLC Coatings

To overcome some of the shortcomings and to increase the desirable properties in the DLC coatings, researchers have studied various doping elements in DLC like Si, F, N, O, and metals, etc [112,113].

Figure 1 shows some of the doping elements introduced into the DLC compositions for achieving improved properties. It has helped to achieve excellent hardness, thermal stability, tribological properties, surface energy, internal stresses, etc. DLC coatings have very low coefficient of friction and high hardness which it gives it the excellent characteristics of very low wear rates, but this comes at the cost of high internal stresses which are one of the main hurdles in the pure DLC coatings and it is irrespective of the technique used in thin film growth like pulsed laser deposition, magnetron sputtering or ion beam deposition, etc. This high compressive stresses in the DLC coatings makes the film to bulge and then come out of the surface, hence the researchers found the way out by using other metallic and non-metallic elements as dopants in the DLC coatings to improve its properties. Doping in DLC is a modification technique to release their internal compressive stresses, to increase the reaction of lubricant with the surface, to increase their adhesive properties (by incorporating Si, N, metals), modify their surface energy (by incorporating O, N, F, Si), and it can also increase its biocompatibility (by incorporating Ca, Ti, Si) [114]. In *Figure 1* we can see some of the doping elements and the improvement in the properties.

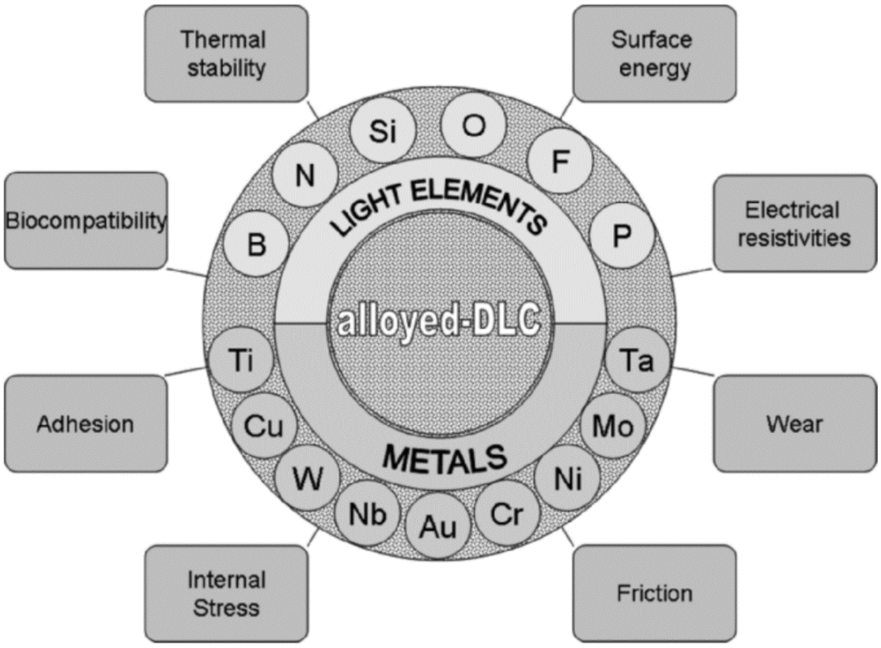


Figure 1. Doping elements achieving improved properties in DLC [113]

If the metal doping is above 30-40% it causes an increase in the hard carbide and metallic phases which in return increases the coefficient of friction with higher abrasion and adhesive wear. The metal doping elements are very versatile with low internal stresses and coefficient of wear, and it is more used in the industries than its pure DLC counterpart. This is mostly due its gradual transition from the metal to ceramic which provides higher load support and adhesion strength. It should be taken under consideration that doping provides various characteristic properties and, in some cases, it might work in certain circumstances but is ineffective in the other, this requires a thorough tribological and field test to be done. After this analysis is achieved, the dopant and doped DLC can give us desired tribological properties with steady state wear and friction rates [114].

For our experimental purposes we will be using Europium and Gadolinium as rare earth element dopants in the DLC coatings, and we will find out their interaction with ionic liquids as additive in PAO8 and pure PAO8.

The rare earth metals group has not been explored much to increase the reactivity of the DLC surface. Lanthanide ions have a high attraction to ILs because they are in the trivalent oxidation state [75]. This has been shown in studies where ILs were used to extract rare earth metals [76,78,115] and improve their luminescent properties [79]. It is believed that using lanthanides can affect the tribolayer formed during tribological processes where ILs are used as anti-wear additives.

2.2 Regular Liquid Lubricants

The lubricants have a natural property of being lubricious, which protects the surfaces against wear and tear. Their properties can be of significant importance and can vary from surface protection to heat dissipation characteristics. They provide a smooth sliding and rolling motion in the machine components with reduced friction and noise. They interact directly with the surface and asperities on it to form a tribofilm. Lubricants with a desired property are actually a mixture of the base stock with certain types of additives. The percentage of additives is according to the necessity of the desired property, and it is in the range of 1 to 25%. The classification of the lubricants can be seen in the Figure 2. Base oils are most commonly of three types, viz. mineral oils, vegetable oils and synthetic oils. The mineral oils are extracted from the crude oils by fractional distillation process. But due to its toxicity and very poor biodegradability, we need to find a better way and abundant way. Vegetable oil lubricants can be a solution, but they have poor viscosity index [116–118]. In *Figure 2* we can see the simplified classification of the lubricants and where does ionic liquids belong.

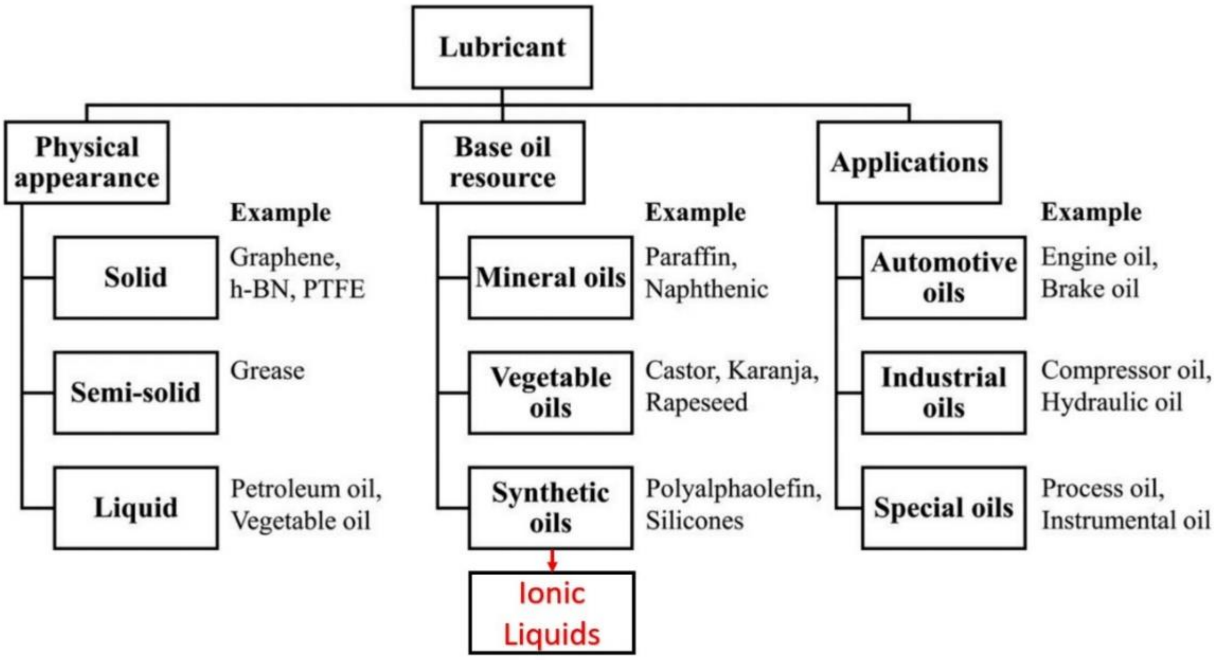


Figure 2. Classification of lubricants [117]

2.2.1 Functions of lubricants

Function of lubricants depends on the desired property required in the machine or component. The main aim of the lubricant is to protect the surfaces from wear and tear and to dissipate the heat. Various other functions of lubricant are, sweep away the contaminations, prevent corrosion, lower the vibration and noise, act as seal for gases, to separate the interacting surfaces, to remove heat and transfer power [117].

2.2.2 Synthetic Lubricants

In simple terms, synthetic lubricants are the artificial made lubricants which has enormous benefits unlike the mineral oils, it has extended the machine safety along with the duration we need to change the lubricant is enhanced. Synthetic lubricants are made from the synthetic base oils and comes from the chemical reactions of one or many products, which may be combined with various additives to enhance the properties of the lubricants. Synthetics base oils are mostly derived from the polyphenyl esters, synthetic hydrocarbons, phosphatic esters, silicones, polyalkylene glycols, fluorosilicones, organic esters, and others [119].

The base oil which we will be using in our experiments is Polyalphaolefin 8 (PAO 8). Polyalphaolefin (PAO) are the most widely used synthetic lubricant which has synthetic hydrocarbons to give us higher and wider operating temperature range along with being less volatile [120]. PAO oils offer greater creep resistance and water washout. It has superior lubricity on various substrates of metal-to-metal and metal-to-plastics. PAO 8 is an extremely branched isoparaffinic Polyalphaolefin, which has higher volatility, oxidative stability and it has superior viscosity index along with best low temperature viscosities. It also has a superior pour point [121].

All these superior properties of PAO 8 make it the most preferred lubricant for extreme situations and operating circumstances in extreme cold start up or in extreme temperature conditions. PAO 8 is odourless and colourless, moreover it is not toxic or corrosive to the component as it does not have any sulphur and aromatic compounds in it [122]. It acts as the excellent base oil for the addition of additives and will be used with ionic liquids in our experiments.

2.2.3 Ionic Liquids

The development of biodegradable, environmentally friendly lubricants with lower toxicity levels is imperative. Within the realm of green chemistry, effective lubrication decreases energy consumption in mechanical applications, thereby reducing energy loss due to friction. The utilization of quality lubricants also protects all materials from friction and wear while promoting longevity. Additionally, employing an exceptional lubrication system aid in conserving energy, reducing energy loss, and minimizing raw material usage [25]. Recently, ionic liquids (ILs) have emerged as promising lubricant options for various applications. ILs, liquid salts composed of organic substances, are characterized by a low melting temperature, high combustible temperature, low vapor pressure, superior thermal stability, low volatility, and high miscibility with organic substances [25–29].

Ionic liquids basically mean a liquid with ions, and it is true to its name as it contains anions and cations [30,123]. Detailed research about the history of ionic liquids is done by Welton [124]. Many scientists explain ionic liquids as salts that are liquids below 100 °C, but it is misguiding as there are now many high temperature applications where liquids above 100 °C are required [125]. Ionic liquids are very ancient and were first reported by Gabreil in 1888. Ionic liquids are constituted by the combination of organic cations and inorganic or organic anions, and as a result, the physicochemical characteristics of these liquids can be modified by varying the combination of cations and anions. This allows for the design of customized ionic liquids that are tailored to meet specific requirements [30]. So, ionic liquids are the liquids which are composed of only ions and no other molecular species present but with certain exceptions [125].

2.2.3.1 Methods of production

Ionic liquids come under the category of synthetic lubricants; therefore, they are artificially made by humans in the laboratory with experiments. Merck, Aldrich, Acros, etc are the commercial manufacturers of the ionic liquids in large quantities whereas, several research labs around the world manufacture them for their R&D. As ionic liquids have commercial success for their use as a solvent they are mostly favored for the same. There is still ongoing research for the use of ionic liquids as lubricants and it is quite promising with results.

There are many types of ionic liquids and with the permutation and combination of different ions it gives us more than million different ionic liquids, practically infinite! As of the current research exploration, ionic liquids mostly revolve around the imidazolium salts [126]. The methods of production for our 2 ionic liquids are explained below, the procedure varies according to required properties and chemistry.

1-Ethyl-3-methylimidazolium diethylphosphate ([EMIM][DEP])

A uniform mixture of 1-Methylimidazole (25.0000 g, 0.30 mol) and triethyl phosphate (50.0000 g, 0.30 mol) was subjected to stirring at 80 °C for 8 h under reflux, after which the reaction mixture was further stirred at 150 °C for 10 h. The resulting ionic liquid was cooled to room temperature and subjected to washing with diethyl ether (4×30 mL). The ionic liquid was then subjected to evaporation under reduced pressure at 75 °C for 4 h to remove all volatile residues, and subsequently vacuum-dried at 80 °C for 48 h to yield a light-yellow liquid identified as 1-Ethyl-3- methylimidazolium diethylphosphate ([EMIM]DEP) [30].

Trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate [P_{66614}] [DEHP]

The synthesis of Trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate ([P_{66614}][DEHP]) was carried out by adding 8.96 g [P_{66614}]Br and 5.13 g bis(2-ethylhexyl) phosphate (HDEHP) to a 100 ml beaker. The mixture was then subjected to the addition of 20 ml of Deionized water (DIW) and 25 ml of hexane. After stirring for a few minutes, the mixture separated into two layers, the upper yellow organic phase and the lower water phase. The ion exchange reaction between [P_{66614}]Br and HDEHP was completed when the yellow organic phase turned colorless after some time. A solution of NaOH (0.64 g NaOH dissolved in 17 ml DIW) was added to the beaker, and the mixture was vigorously stirred for 4 h to remove the by-product of the ion exchange reaction (HBr). The resulting white emulsion was then centrifuged at 8000 r/min for 5 min to separate the NaBr aqueous solution (bottom of the centrifuge tube) and the [P_{66614}][DEHP] phase (upper part of the centrifugal tube). The [P_{66614}][DEHP] phase was collected and washed four times with DIW to remove any remaining NaBr. The hexane was then removed by rotary evaporation, and the product was dried under vacuum at 70 °C overnight. The [P_{66614}][DEHP]-G gel was prepared by grinding 200 mg graphene with 1 ml [P_{66614}][DEHP] in an agate mortar with a pestle for 30 min. After the mechanical grinding treatment, the structure and physicochemical properties of the resulting product were aligned [127].

2.2.3.2 Characteristics

Ionic Liquids are recently trending for their peculiar characteristics and being associated as green lubricants. A green lubricant, also known as an environmentally friendly or eco-friendly lubricant, refers to a lubricating substance that is formulated with a focus on reducing its impact on the environment compared to traditional lubricants. The majority of researched ionic liquid lubricants contain imidazolium alkyl cations and either hexafluorophosphate or tetrafluoroborate anions[128–142]. As the ionic liquids can be tailor made, which can be infinite, and their properties can vary significantly, the more common characteristics for which it is usually preferred are non-volatility, versatile solubility, and thermal stability [126].

One of the main characteristics of ionic liquid is that it is green and sustainable, but if some contains phosphate, which is already an environment depleting element, so how it is sustainable? To answer this question, phosphate is commonly employed as lubricating oil additive [143–151]. The creation of an ionic liquid exhibiting superior lubrication and anti-wear characteristics while posing no corrosion issues to metallic friction pairs can be achieved by coordinating phosphate with cations that are resistant to hydrolysis. Drawing inspiration from this concept, a series of alkylimidazolium cation and phosphate anion-based ionic liquids were synthesized, and their tribological properties as lubricants were thoroughly studied [152].

2.2.3.2.1 Cationic structure and Anionic structure

Ionic liquids are composed of anions (ions carrying negative charge) and cations (ions carrying positive charge) [153]. Within an ionic liquid, the cationic structure often incorporates organic compounds, including ammonium or imidazolium, accompanied by alkyl chains and diverse substituents [154,155]. As for the anionic structure, it can be either inorganic or organic, exhibiting distinct sizes, shapes, and functional groups [154]. The properties of the ionic liquid, such as viscosity, conductivity, and solubility, are determined by the specific combination of cations and anions. Through the design of the cationic and anionic structures, the properties of ionic liquids can be tailored for various applications [156]. Furthermore, long alkyl chain substituents increase the tribological efficiency of cationic and anionic ILs but decrease their thermal stability. Hydrophobic ILs typically exhibit better tribological performance compared to hydrophilic ILs [39].

2.2.3.2.2 Thermal stability

Thermal stability is a pivotal characteristic that impedes the degradation of lubricant within the working temperature range. At elevated temperatures, the lubricants are susceptible to chemical degradation, leading to fluid evaporation and viscosity reduction [157,158].

To evaluate the thermal stability of ILs dissolved in oils under nitrogen, thermogravimetric analysis (TGA) was conducted extensively. Air is a crucial and practical medium for assessing the lubricating efficacy of ILs, wherein oxidation is inevitable. Typically, ILs exhibit greater thermal stability relative to hydrocarbon oils that decompose around 250°C. Previous studies have indicated that phosphonium-carboxylate and ammonium-phosphate ILs display inferior thermal stability when compared to phosphonium-phosphate ILs. Conversely, imidazolium- and pyridinium-based ILs exhibit remarkable thermal stability, even in the presence of cationic alkyl chains [159].

In contrast to mineral oil and water, ILs exhibit negligible evaporation [157,158].The thermal stability of a highly promising candidate for combustion engine utilization, ionic liquid is notably exceptional, exhibiting minimal mass loss even at temperatures up to 225 °C. Thus, the performance of ILs is deemed to surpass that of high-performance motor oils with regards to thermal stability

[160]. Thus, they are deemed environmentally benign compared to conventional lubricants.

2.2.3.2.3 Corrosion behavior of ionic liquids

To be applied in industry, ionic liquids must fulfil several conditions and a thorough test to check its potential corrosion behaviour towards equipment materials. The deterioration of materials can jeopardize reliability, decrease productivity, trigger shutdowns of the system, decrease yields, taint manufactured goods, lead to overdesign expenses and necessitate expensive maintenance procedures [161].

One of the first comprehensive studies on this issue for flow-induced localized corrosion (erosion corrosion) cases was performed using the rotating cage technique and results showed that the tosylate and dimethyl phosphate anions have detrimental impacts. When diluted or contaminated with water, numerous anions utilized in the production of ionic liquids could undergo hydrolysis, leading to the creation of acids such as sulfuric and phosphoric acid. This process leads to an acidic environment which causes corrosion [161]. However, the focus of this research did not include the examination of localized attacks or flow-related analyses of ionic liquids. These areas warrant further investigation [161].

In a similar study with rotating cage setup, a screening was conducted of various ILs with differing ion structures to evaluate their corrosiveness behavior. The outcome of the study reveals a significant dependence of the corrosion behavior on the particular chemical structure of the ionic combination. It was observed that the vast majority of the tested ILs displayed a low level of corrosiveness in interaction with steel, particularly stainless steel [160]

Corrosion inhibitors refer to substances that are added to the operating fluid in minimal quantities and chemically or mechanically interact with the metal surface to impede any further metal degradation and reduce corrosion [162–165]. Several studies have investigated the potential of ILs as corrosion inhibitors [162,166,167].

Therefore, based on the literature, while ionic liquids (ILs) can act as corrosion inhibitors, they can also promote corrosion in some cases. The corrosive behavior of ILs can depend on various factors, including the chemical structure of the IL and the metal surface, as well as the environmental conditions. These studies suggest that ILs can potentially act as corrosion promoters depending on their chemical structure and the conditions in which they are used. Therefore, it is important to carefully consider the specific IL and conditions when using them in industrial applications.

2.2.3.2.4 Hygroscopicity

Lubricant free from impurities works as desired but water being an impurity for lubricants is an inevitable parameter which generally sips into the system from the environment. So, water is not good for lubrication because it can actually damage the lubricant. Water can cause a process called hydrolysis, which breaks down the molecules in the lubricant and makes it less effective. Therefore, it is imperative to maintain hygroscopic stability in a lubricant to uphold its physical and chemical properties. The hydrolysis process can produce harmful by-products that can inflict permanent damage to the lubricant and reduce its quality [168].

Several studies have reported that ILs possess a broad range of physical properties when exposed to water and works in favor in some conditions. The physical properties of fluids significantly impact their lubrication properties, including their cooling capabilities. The ability of a coolant to minimize temperature is heavily dependent on its heat transfer properties such as convective heat transfer coefficient, specific heat capacity, thermal conductivity, and specific heat of evaporation. Various formulations and physical properties of ILs have been explored by several researchers [169–175]. In comparison with normal water-based and mineral oil-based coolants, ILs offer a broad range of physical and thermal properties.

2.3 Tribology

Tribology is the study of surfaces moving relative to one another, which includes the three most important things that is friction, wear, and lubrication. Tribology comes from the Greek word tribos, which means rubbing. The resistance to relative motion is called as friction whereas, wear is the loss of material from the relative motion and nevertheless lubrication is the use of lubricating liquid or solid to decrease the wear and friction. Tribology plays an important role in the machine components as total one third of the energy is lost in the friction and it is a driving need of every industry to reduce frictional losses and increase the efficiency for higher production and monetary benefits but along with this it has a very importance for the environmental sustainability [176].

To facilitate the understanding of our project we need to understand the three major aspects of the tribology. In which friction is the resistance to motion and this resistance is turn a material function and is related to the geometries and surface roughness or surface features in contact. It is also dependent on the environmental and operating conditions. The most common notion is that as the load and surface roughness increases, along with no or decreased lubrication it causes an increase in the friction. Now due to the increase in the friction it will cause the increase in the wear of the sliding bodies and can lead to the failure of the machine, therefore lubrication is used in between the parts to reduce the friction and to separate the two interacting bodies to prevent the friction and wear. Lubrication also has some other major functions to dissipate the heat and remove wear and debris from the contact [176]. Lubricants can be of mineral, synthetic or biological origin and have certain additives to give them specific properties. They can also be in the form of solids or gases but are generally in liquid form.

2.3.1 Tribology of DLCs

The tribological characteristics of the DLC coatings is of great importance as they have the some of the lowest coefficient of friction [177]. The DLC coatings when they lose hydrogen through the annealing at high temperatures the coefficient of friction increases in the UHV but not in the humid surrounding. The wear and friction characteristics of the DLC coatings can be influenced by the transfer layer from the friction. Carbon materials, such as graphite, non-graphitic carbon, carbon-carbon composite, and non-hydrogenated amorphous carbon, have their friction and wear affected by gases in the environment when sliding. These materials generally have higher friction and wear in environments without lubrication. The same effect can be seen when these materials are exposed to water vapor or oxygen. Even small amounts of water vapor, as little as 100 ppm in nitrogen, can effectively lubricate these materials [177]. Oxygen, depending on the humidity in surrounding can behave as lubricant or it can behave as a tribochemical wear agent.

The tribological behaviour of DLC is typically controlled by a transfer layer that is formed during sliding of the surfaces in contact. This transfer layer can have a lubricating effect and its formation may be increased by hydrogen but can be limited in the presence of water or oxygen. It has been noted that the friction coefficient of hydrogenated DLC films increases in humid air, which is thought to be due to the increased van der Waals bond strength of hydrogen bonding to adsorbed water molecules [177].

When examining the tribological properties of DLC, consideration must be given to the material of the surface that is in contact with it. This has been studied by various authors. A significant difference was observed in the wear rates of steel, silicon nitride, and DLC when they were sliding against DLC. In dry air, the wear of silicon nitride and steel against DLC was found to be unmeasurable due to the formation of a protective DLC transfer layer. In humid air, the DLC transfer layer did not adhere well to the solids, and the wear of both silicon nitride and steel was greater than in dry air. However, the wear of DLC against itself was found to be unmeasurable. These results are thought to be caused by friction-induced transformation of the surface layer of DLC. The transformed layer is believed to have low shear strength and to transfer to the counter-surface during rubbing. It is speculated that humidity increases the shear strength of the transformed layer and weakens the adhesion between DLC and the surface of the counterpart, thus increasing the wear of the pins [178].

2.3.1.1 Tribology of doped diamond-like carbon coatings and ionic liquids

In a study by Hamid K. et al., three DLC coatings (DLC, W-doped DLC, and Ag-doped DLC) were deposited on stainless steel substrates, and their friction properties in dry and lubricated conditions using water-based lubricants were investigated [44]. Three different ILs and a known organic friction modifier (dodecanoic acid) were used as additives. The doped coatings demonstrated superior mechanical integrity, toughness, and adhesion compared to undoped DLC. Among the coatings, the Ag-doped DLC had the best mechanical properties. Tungsten carbide precipitates were formed by W in the DLC coating. Friction was controlled by two different additive-adsorption mechanisms: a triboelectrochemical activation mechanism for Ag-DLC and an electron-transfer mechanism for W-DLC, resulting in the largest friction reduction [44]. The friction of DLC (diamond-like carbon) is influenced by the electrical charge of the surface and the lubricant's ability to adsorb to the surface. The electrical conductivity of the lubricant (ionic liquid) drives the transport of additives to the surface and impacts friction. The higher the lubricant's electrical conductivity, the lower the friction. Additionally, the Zeta-potential of DLC surfaces in aqueous solutions is negative, resulting in no change in friction with the addition of negatively charged molecules [42,43]. The higher electrical conductivity in IL-additivated lubricants leads to faster transport kinetics of the cation and anion moieties to the surface, resulting in lower friction [44].

Arshad M. et al. explored the potential of enhancing the lubrication properties of tungsten-doped diamond-like carbon coatings by incorporating a 1,3-dimethylimidazolium dimethylphosphate ionic liquid into glycerol base oil. The researchers conducted tribological tests under varying loads (5 N, 10 N, 20 N) and elevated temperature (100 °C). They found that the friction coefficient was significantly reduced by approximately 50% when 1 wt% IL was included. They also discovered that the formation of a thin tungsten phosphate (WPO) based tribofilm on the surface of the coatings played a crucial role in friction reduction. A temperature-induced tribochemical reaction occurred with the ionic liquid additivated with glycerol and DLC, which formed a phosphate-based tribofilm on the surface. The study provides insights into the lubrication mechanism and offers implications for the development of improved lubricants for tribological systems [179].

Another investigation was conducted by Arshad M. et al. to examine the interaction between coatings of tungsten-doped diamond-like carbon (WDLC) and three phosphate-based ionic liquid (IL) additives. Among these additives, two contained the anion dimethylphosphate, while the third contained the hydrolytic trifluorophosphate anion. The tests were carried out under boundary-lubrication conditions. The findings indicated that IL additives containing dimethylphosphate anions exhibited reduced friction on the surface of WDLC, whereas the IL with trifluorophosphate anion displayed poor performance. Analysis of the surface revealed the formation of a tribofilm based on phosphate on the WDLC surface when dimethylphosphate additives were present, resulting in friction reduction. The WDLC coatings demonstrated remarkable resistance to wear [180].

Researchers conducted a study on Cr-doped coatings made of diamond-like carbon (Cr-DLC) using PVD and PECVD methods [81]. The lubrication performance of solid-liquid composite lubrication systems was studied using two ionic liquids (ILs) as lubricants. The findings indicated that the friction coefficient was reduced by about 40% when compared to dry conditions, and the composite system displayed an effective synergistic lubrication effect. The Cr-DLC coating showed superior tribological, mainly because of its improved physicochemical film formation during friction and the dense microstructure of the Cr-DLC coating. The ILs' viscosity, corrosiveness, and coating microstructure influenced the composite systems' synergistic effect [81].

Rare earth metals like Gd and Eu can be added to DLC to improve its reactivity with ILs. Testing shows that low atomic concentration of Eu or Gd (1-3%) doped-DLC films have a slightly higher CoF but low wear rates and high hardness, making them suitable for many applications [60].

The study examined the effect of a silicon-doped diamond-like coating on tribological behavior in IL-lubricated friction pairs [181]. Tests showed that the coating, when used with the ionic liquid, reduced both coefficient of friction and wear. The study concluded that using DLC coatings lubricated with the ionic liquid helps improve tribological properties of sliding surfaces under friction [181].

Ti-doped DLC coatings were prepared on steel substrates and analyzed using Raman and TEM. Two types of ILs were synthesized and evaluated as lubricants for Ti-DLC/steel contacts, with excellent friction-reducing properties. These coatings with ILs lubricating systems have potential as lubricants in vacuum and space moving friction pairs [182].

A study examined how the concentration and type of electrolyte in the solution affects the adhesion of hydrophobic material to silicon-doped DLC surfaces [183]. As electrolyte concentration increased from 0 to approximately

0.01 M, there was a small but significant increase in contact angle. An increase in Si content in the DLC coatings increased the change in contact angle for all types of electrolytes. These results suggest that adding electrolytes to the surrounding solvent reduces adhesion to Si-doped DLC surfaces due to increased ion adsorption and greater surface hydrophilicity [183]. These results can also be translated to the work of ionic liquids.

Limited research has been conducted on the tribological properties of doped DLC coatings with ionic liquids (ILs), and their combined effect has been found to be highly beneficial. The addition of doping elements has demonstrated to improve the tribological properties of DLC coatings significantly. ILs, with their exceptional characteristics such as excellent lubricity and high thermal stability, are deemed ideal for various tribological applications. Through the formation of a protective film or tribofilm on the surface of the coating, the combination of doped DLC coatings and ILs has been reported to elevate their tribological properties further.

2.3.2 Tribology of Ionic Liquids

Ionic liquids (ILs) have been widely implemented in lubrication systems, either as an additive or a neat lubricant. Researchers have demonstrated the remarkable outcomes of IL-based lubricants due to their exceptional properties and the potential to customize or substitute for traditional lubricants, thereby achieving superior results or improved output performance. Furthermore, the ability to vary the combination of cations and anions confers a significant advantage in the formulation of ILs for specific engineering and manufacturing applications. The physical properties of ILs and their potential have been extensively studied, primarily in the context of anti-wear and lubrication properties. The collective performance of ionic liquids reveals that when bio-based oil is mixed with ILs, the minimum coefficient of friction is achieved. The enhanced tribological performance of oil in the presence of ILs is attributable to the dipolar structure of ionic liquids, which adsorbs on the interacting surfaces and produces a lubrication film [41]. However, the use of ILs as lubricants raises concerns regarding thermal oxidation, toxicity, corrosion, oil miscibility, and cost. Recent research has focused on developing thermally stable, non-corrosive, and oil-soluble ILs, which has been the subject of much discussion among researchers. The primary research on ILs in lubrication has shifted from utilizing them as both lubricant additives and neat lubricants to developing halogen and phosphorus-free ionic liquids as energy-efficient and environmentally friendly lubricant additives for steel-based engineering surfaces. The focus is to establish the correlation between the anion structure and the tribophysical properties of ILs. Halogen-free ionic liquids, such as borate-based ionic liquids, are of particular importance for lubricant applications in the present and future.

2.3.2.1 Ionic Liquids as a neat lubricant

Numerous research studies have been conducted on the use of ionic liquids as neat lubricants [40]. Specifically, the use of three types of ionic liquids, namely 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide and ethyl-dimethyl-2-methoxyethylammonium tris(pentafluoroethyl)trifluorophosphate, in steel-to-steel contact has been investigated [184]. The results obtained from the studies show that the ionic liquid [BMP][NTf_2] exhibited the lowest friction coefficient [184]. The effect of alkyl chain components on the chemical changes of various types of methylimidazolium salt was studied [185–187]. The presence of tribofilms in samples lubricated was confirmed by X-ray photoelectron spectroscopy, while only neat ionic liquid without interaction with the surface could be detected inside the wear scar of the sample lubricated, which suggests their usability as straight and neat lubricants.

2.3.2.2 Ionic liquids as an additive

The use of ionic liquids as lubricants presents a promising option for improving the cost-effectiveness of traditional lubricant systems. While the high cost of ionic liquids currently limits their use as neat lubricants to specialized applications, their incorporation as additives in small quantities in the base oils has gained interest due to their potential to enhance tribological properties [188]. By this it will be a good starting point for the use of ionic liquids in lubricants until a commercially viable cheap solution is devised. Therefore, a continuous drive for improved friction and wear performance for common tribo-pairs, as well as the need to facilitate lubrication in difficult-to-lubricate systems, necessitates the development of additive-based lubrication systems.

In addition to lubrication applications, research has shown that the use of ILs as lubricant additives and corrosion inhibitors can effectively reduce friction and wear. ILs have also been found to form electric double layers in water, allowing for the effective adsorption of additives on ceramic surfaces and improving tribological properties [189]. However, the use of water-based lubricants is limited under elevated test temperatures due to their high volatility and low cooling point, and the development of tribofilms on ceramic substrates is often thin. Compared to ILs, water-based lubricants may exhibit higher coefficients of friction and greater attachment of surface-clean alkyl phosphate [188].

2.3.2.3 Tribochemical reaction properties

Ionic liquids have opened new doors in the tribology as it works as a lubricant. Scientists did some tests to see how ILs affect friction when different metals are rubbed together [190–192]. They found that ILs work well with every metal, but the gases that get released when they decompose depend on the metal. Chemical reactions like adsorption, chemisorption, and tribochemical reactions play an important role in creating a boundary layer on the surface of the metal. When the metal is rubbed, a positive charge is created on the surface of small bumps, and the ILs stick to the surface because of their electrostatic charge, this helps to reduce friction and wear [193,194].

Scientists are using computer simulations to study how ionic liquids work as lubricants. They found that the way the liquid interacts with the solid surface is important for how it flows and lubricates. The simulations also showed that the ionic liquid can change from a liquid to a solid-like state under different pressure and movement. Studies also show that water can change the way ionic liquids behave when they are near solid surfaces [195].

As the size of the alkyl chains in fatty acid ionic liquids increases, the ionic liquids become better at reducing wear and friction[196]. It was found that an ionic liquid called with a long chain can make a stable liquid-based magnetic fluid that can be used as a lubricant [197]. Studies have shown that when ionic liquids and glycol ether mixtures are used on titanium surfaces, the friction force decreases as the normal load increases [198]. Research has been done on how ionic liquids can be used to make lubricating molecules move more smoothly. Using acid-based ionic liquids as additives in glycerol solution improves its ability to prevent corrosion and be used as a lubricant. Studies have been done on how using a combination of certain ionic liquids and an organic friction modifier can reduce friction. There is new research being done on the use of ionic liquids in different ways [199–202]. Ionic liquids made from biomaterials, such as amino acids and choline, have been found to have good properties as lubricants for steel surfaces. Ionic liquids have also been used as additives to reduce wear. Studies have shown that using certain ionic liquids can make surfaces have less friction and be protected from wear. Research has also been done on using a specific ionic liquid called trifluoromethyl sulfonyl amide as a lubricant and as an additive in polar oil [203–206].

Ionic liquids are being used more and more as lubricants. They are being tested in labs to see how well they work. The goal is to make them hydrophobic, which means they don't mix with water, to make them work better and last longer. Researchers are also trying to find ways to improve their anti-wear properties and reduce friction and corrosion. There is still a lot of work to be done to make new and better ionic liquids. They can be used in space and in high-temperature situations where there is a risk of fire. They can also be used in clean rooms where there are strict rules about harmful gases.

2.3.2.4 Ionic liquids as extreme temperature lubricants

Ionic liquids can be used as lubricants in extreme temperatures. Researchers have studied the surface properties of metals lubricated with ILs at 300 °C. They found that ILs react with steel/iron substrates. New types of ILs have been developed, such as those with polyethylene glycol and functionalized dicationic, which exhibit excellent thermal stability and are reliable lubricants [207]. Some ILs, like imidazolium-based dynamic liquids, have high degradation temperatures which is greater than 400 °C, making them suitable for extreme temperature lubrication [190]. There are also different types of ionic fluid, such as polyacylater and polyifuoracillil, which have bridging moieties and can be tailored to have specific lubrication properties [190]. Thus, ionic liquids have a characteristic to maintain their properties at extreme temperature and pressure which makes them suitable for such conditions.

3 Materials and Methods

3.1 Specimens

There is a total of five DLC coatings which are selected, namely Pure DLC, 1.7%-Gd DLC, 2.3%-Gd DLC, 1.7%-Eu DLC, and 2.4%-Eu DLC. The study utilizes steel substrates (AISI M2) that are 25 mm in diameter and 8 mm thick. Before mirror-polishing the steel substrates, using a diamond paste (Ra≈0.1 µm), the samples were tempered at 200 °C, achieving a hardness of around 60 HRC. Subsequently, the samples are cleaned by placing them in an ultrasonic bath filled with acetone and ethanol for 15 to 20 minutes.

After cleaning, the M2 samples are attached to an aluminium holder using silver glue and placed in the deposition chamber. The DLC coatings are deposited using the sputtering method with a DOMS power supply and a pure graphite target. Pellets containing Europium and Gadolinium are used in the target to achieve the desired composition. The chamber is then vacuumed and maintained at a pressure of 3×10^{-4} Pa using a turbomolecular pump. Before depositing the DLC coatings, the substrate and target are cleaned to remove any surface oxides for 10 minutes using a DOMS (Deep Oscillation Magnetron Sputtering) power supply of 600 W at a pressure of 0.4 Pa. Next, a Chromium interlayer is deposited to enhance adhesion on the substrate using direct-current magnetron sputtering. A 400 nm thick CrN layer is then deposited with an $Ar:N_2$ gas flow ratio of 1:3 for 7 minutes at 0.3 Pa.

Finally, the DLC coatings are deposited by HiPIMS for a duration of 57 minutes under a pressure of 0.4 Pa. This process results in the formation of the desired DLC coatings on the steel substrates, which can be further analysed and characterized for their properties and performance in the study. The wear rate of the coatings can be enhanced by the specific type and quantity of doped metals, thereby implying that the ionic liquid (IL) has the potential to improve their wear resistance characteristics [61]. Furthermore, it was observed by Omiya et al. that an increase in the atomic concentration of the doped metal led to a greater reduction in friction, particularly in Gd-doped diamond-like carbon (DLC) coatings compared to Eu-doped DLC coatings [61]. *Figure 3* shows the various DLC samples before the SEM analysis.

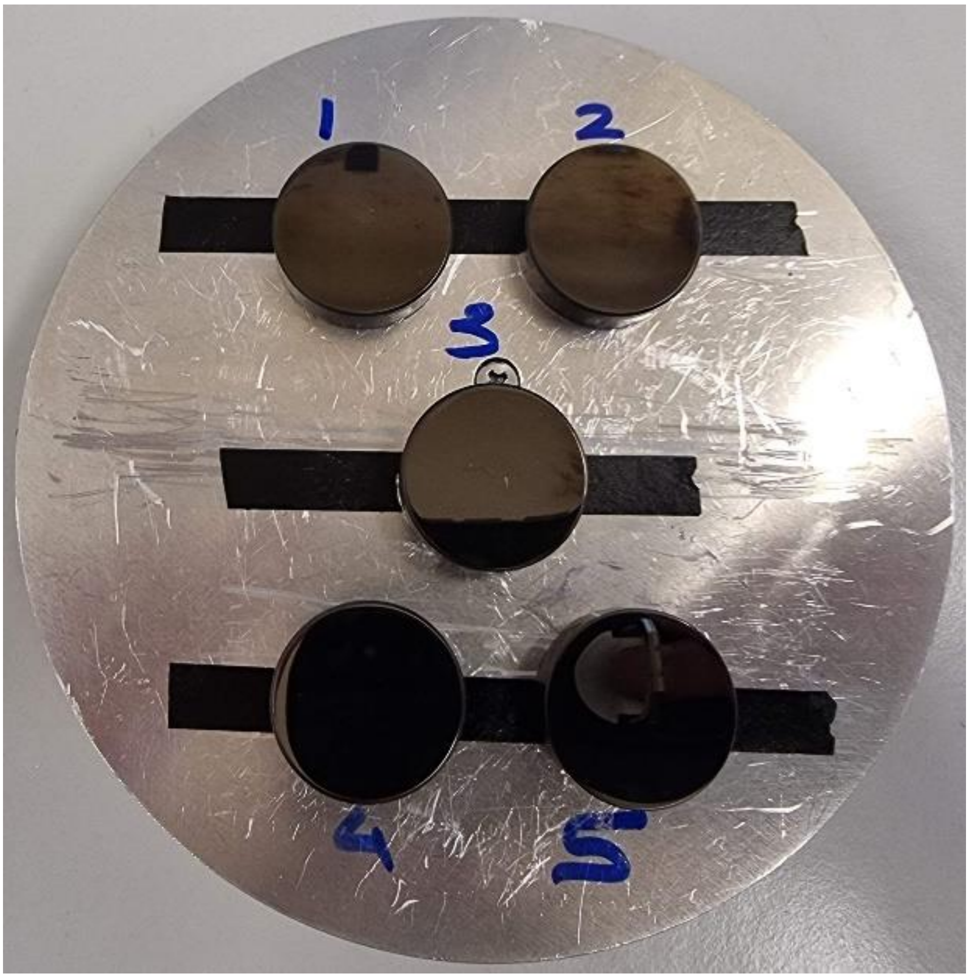


Figure 3. 1) Pure DLC, 2) 1.7%-Gd DLC, 3) 2.3%-Gd DLC, 4) 1.7%-Eu DLC, and 5) 2.4%-Eu DLC

3.2 Lubricants

The base lubricant used was PAO8. Synthesis of trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate [P_{66614}][DEHP] was conducted according to the procedure described in [208]. In brief, trihexyl(tetradecyl)phosphonium bromide (with a purity of 95%, obtained from

Strem chemicals) was combined with methanol and treated with Amberlite IRN78 (with a purity of 99.9%, obtained from Alfa Aesar) to obtain trihexyl(tetradecyl)phosphonium hydroxide. The resulting mixture was then filtered and subjected to a 3-day reaction with bis(2-ethylhexyl) hydrogen phosphate (obtained from TCI). Methanol and other volatile compounds were subsequently removed under reduced pressure (approximately 1070 Pa) and at a temperature of around -50 °C. The water content in [P_{66614}][DEHP] was determined to be 0.07 % (equivalent to 700 ppm). The estimated purity of [P_{66614}][DEHP] was ≥ 92 % based on nuclear magnetic resonance (NMR) spectroscopy analysis. To prepare the lubricant containing PAO 8 and 1 wt.% of [P_{66614}][DEHP], 1 g of [P_{66614}][DEHP] was mixed with 99 g of PAO8 using an analytical balance [61].

3.3 Tribological Tests

The five DLC coated specimens undergo testing utilizing a block-on-ring configuration tribometer, under unidirectional sliding motion. The stationary block, consisting of the DLC coated specimens, is subjected to a constant applied load during the test and pressed against a rotating ring. The rotating ring is constructed of alloyed carbon steel (3415, AISI) with a hardness of 237 HV_{10} (kgf/mm^2) and has a dimension of Ø150 × 12 mm. The rotating ring is positioned at a 90° angle relative to its axis of rotation and has an initial surface roughness of Ra = 0.01 µm. A schematic diagram of the block-on-ring configuration can be seen in Figure 4.

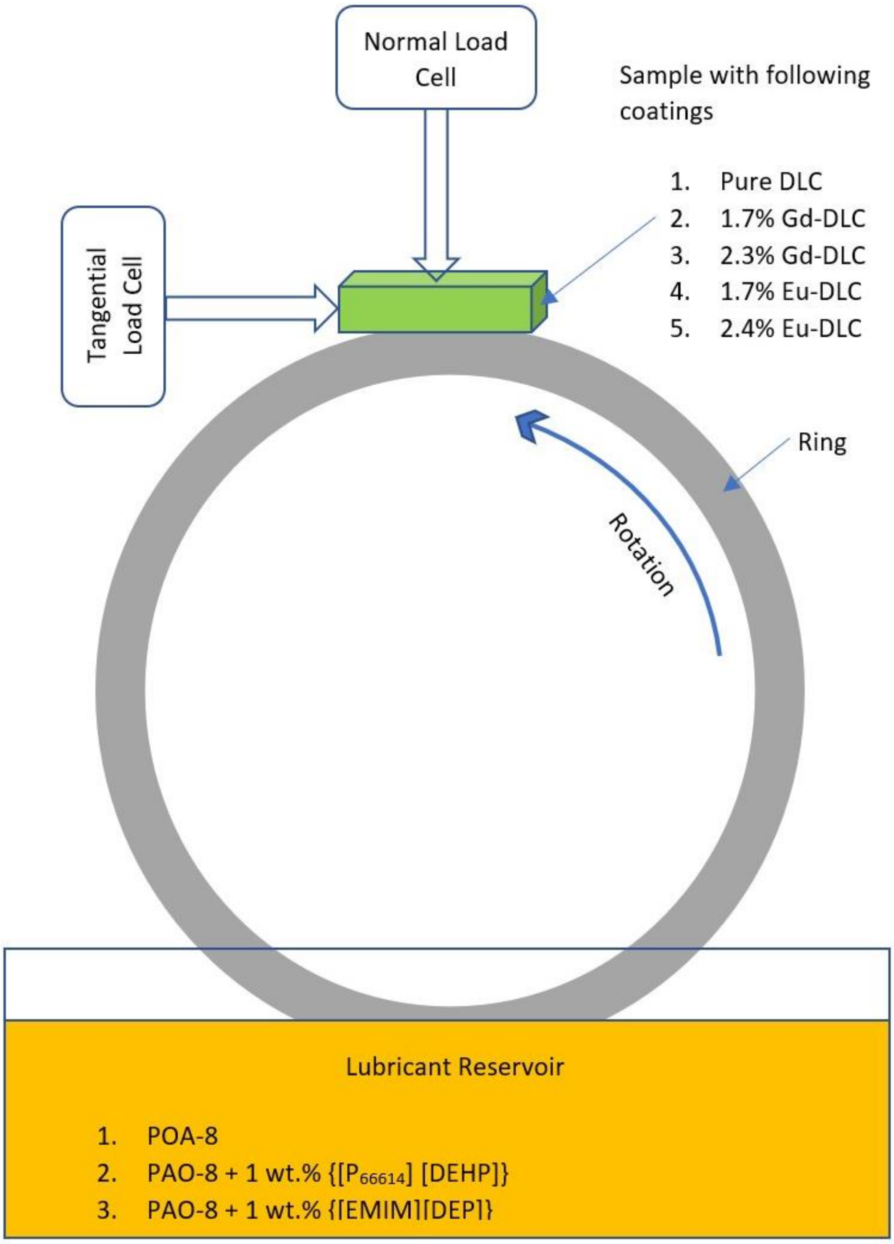


Figure 4. Schematic diagram of block-on-ring friction tribometer

The normal applied load and friction force between the block and the ring were continuously monitored throughout the testing process using two load cells, which facilitated real-time computation of the friction coefficient. A normal load of 25 N was applied during the test. The normal force load cell served as the input for normal force (F_N) and a tangential force load cell measured the friction force (F_f). The coefficient of friction (μ) was calculated by dividing F_f by F_N. A lubricant reservoir was utilized to keep the contact lubricated with lubricating oil. A radiation heating system was utilized for temperature control during the tests, enabling the execution of tests at various high temperatures in oil, which were 60 °C, 80 °C, and 100 °C in the study. The test setup can be seen in the Figure 5.

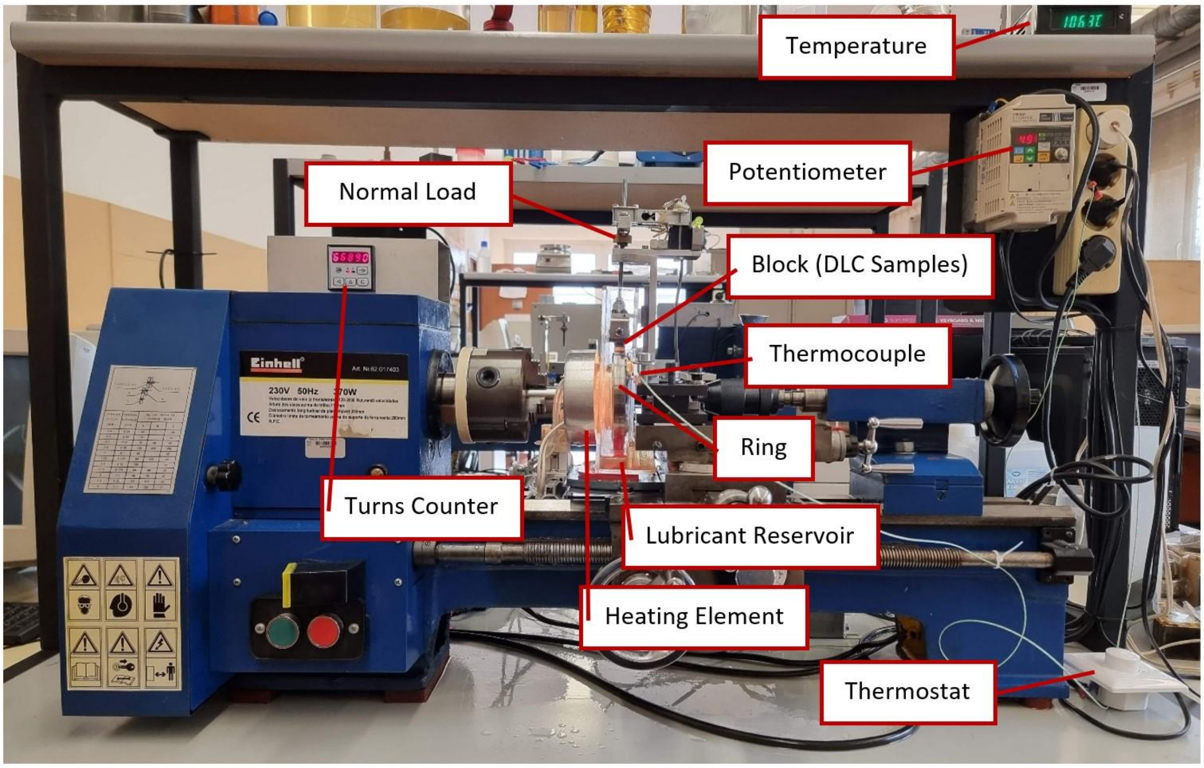


Figure 5. Block on ring test setup with all instruments

During tribological testing, three different lubricants were utilized, which were established as fully flooded with a homogenous film of lubricant that wetted the contact region. The rotation of the ring within the lubricant, created a constant and uniform film of several millimetres in thickness on the surface of the ring, with the oil being picked up by the rotating disk and supplied to the contact before flowing back to the lubricant housing. The tribometer utilized in this study, which is particularly suitable for low speeds, employed a lubrication supply system. Prior to the testing procedure, the surfaces of both the block and the disk were cleaned through ultrasonic cleaning in ethanol and dried in air. The standard deviation from the curves was utilized to calculate the error bars for the friction coefficient versus sliding distance.

The minimum film thicknesses were determined for the isothermal elastohydrodynamic lubrication conditions using the Hamrock and Dowson equation [209,210] given below (equation 1), which applies to linear contacts and various material combinations up to maximum pressures of 3 to 4 GPa [211].

$$\frac{h_0}{R'} = 3.63 \left(\frac{U\eta_0}{E'R'}\right)^{0.68} (\alpha E')^{0.49} \left(\frac{W}{E'R'^2}\right)^{-0.073} \left(1 - e^{-0.68k}\right) \qquad (1)$$

Where α is the pressure-viscosity coefficient, R' is the reduced radius of curvature, η_0 is the lubricant viscosity at atmospheric pressure and temperature, W is the applied load, E' is the reduced Young's modulus, U is the sliding speed, and k is the ellipticity parameter which is given by the ratio of semiaxis in the transverse direction to the semiaxis in the direction of motion, k is infinite for a line contact as in the case of a block-on-ring configuration. These were the parameters taken into consideration in the calculation of the film thickness. The lubricant fluid was assumed to be compressible, and its viscosity-pressure behaviour was described by the Barus law given below (equation 2) in which the lubricant viscosity η_p at pressure p and temperature θ was considered in the calculations.

$$\eta_p = \eta_0 e^{\alpha p} \qquad (2)$$

To consider the effect of the surface roughness of both materials on the calculation of the film thickness, Tallian introduced a new parameter given below (equation 3) [212], which characterizes the ratio between the minimum film thickness and the combined surface roughness, represented by the symbol λ. The parameter λ is calculated as the ratio of the minimum film thickness to the composite surface roughness, where the surface roughness (Root Mean Square) of body A and body B is represented by σ_A and σ_B, respectively.

$$\lambda = \frac{h_0}{\sqrt{(\sigma_A{}^2 + \sigma_B{}^2)}} \qquad (3)$$

The criterion for lubrication regime determination values are summarized below [213,214]. The analysis of the λ value reveals distinct regimes and their corresponding lubrication conditions:

λ > 5: Complete hydrodynamic lubrication

- This regime indicates a lubrication condition where the lubricant film thickness is sufficient to entirely separate the surfaces, resulting in minimal wear and friction.

3 < λ < 5: Asperity smoothing, minimum wear

- In this regime, the lubricant film thickness is moderate, allowing some contact between the surfaces. However, the pressure is high enough to deform the asperities, reducing wear and promoting smoother operation.

1.5 < λ < 3: Asperity smoothing

- This regime represents a lubrication condition with a relatively thin lubricant film, allowing some contact between the surfaces. However, the pressure is insufficient to prevent direct contact between the asperities.

1 < λ < 1.5: Asperity smoothing, delamination

- Similar to the previous regime, this regime involves asperity smoothing but with an additional factor of delamination. Delamination refers to the separation of thin surface layers under specific conditions.

λ < 1: Macro-Plastic deformation

- The regime indicates a lubrication condition where the lubricant film thickness is extremely thin or absent, leading to direct contact between the surfaces. This regime is characterized by significant plastic deformation of the contacting asperities.

As previously discussed, increasing the lubricant viscosity leads to a transition from boundary to mixed and hydrodynamic lubrication regimes at lower speeds.

The acquisition of hardness and reduced Young's modulus was achieved through the process of nano-indentation, utilizing a Berkovich diamond indenter within the nano indenter device. To guarantee that the indentation depth would not exceed 10 % of the coating thickness, a maximum load of 10 mN, in accordance with the standard parameters of the CEMMPRE laboratory, was applied. The mechanical properties were determined by calculating the mean and standard deviation based on sixteen measurements that were conducted on each sample.

The various conditions of block on ring tribological test at different sliding speeds and sliding times can be found in Table 1. Conditions for block on ring tribological test. These conditions are specifically selected to plot the points for Stribeck curve. The rules are stated in the ASTM G77-17/98 (Standard Test Method for Ranking Resistance of Materials to Sliding Wear Using Block-on-Ring Wear Test).

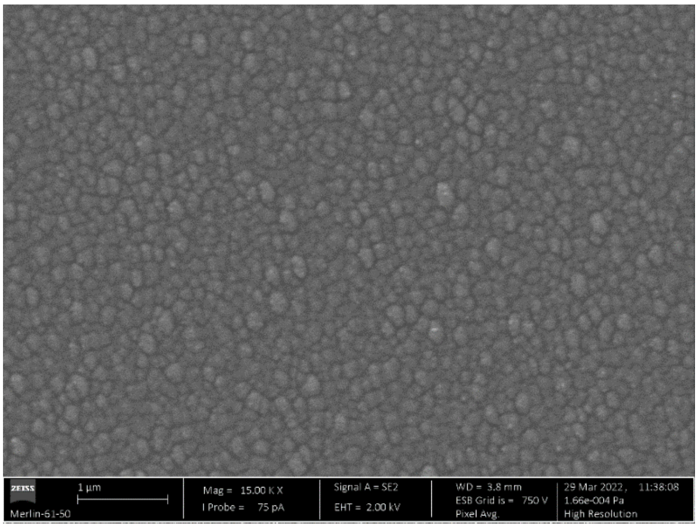
Table 1. Conditions for block on ring tribological test

		1	2	3	4	5
Conditions	Potentiometer	1.6	4.9	11.2	24.7	45.5
	Sliding Speed (m/s)	0.02	0.07	0.18	0.40	0.74
	Rotational speed (rpm)	4	13	32	64	127
	Rotational speed (rps)	0.07	0.21	0.53	1.06	2.12
	Number of turns	100	250	500	1000	1000
	Sliding time (s)	1500	1181	943	942	471

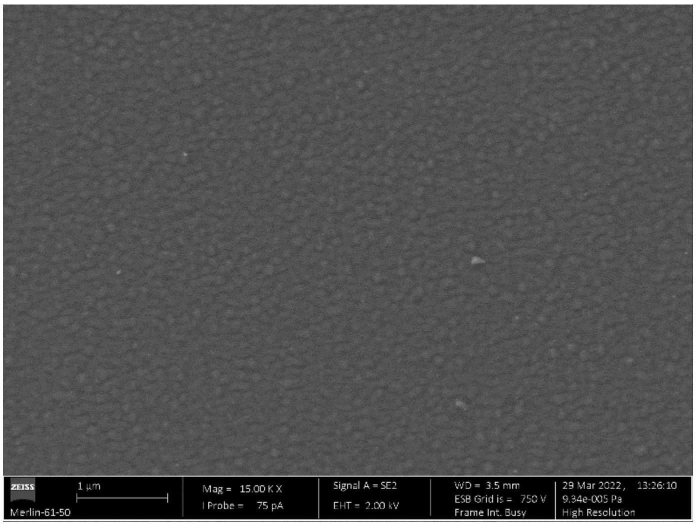
4 Results and Discussion

4.1 DLC Coating Analysis

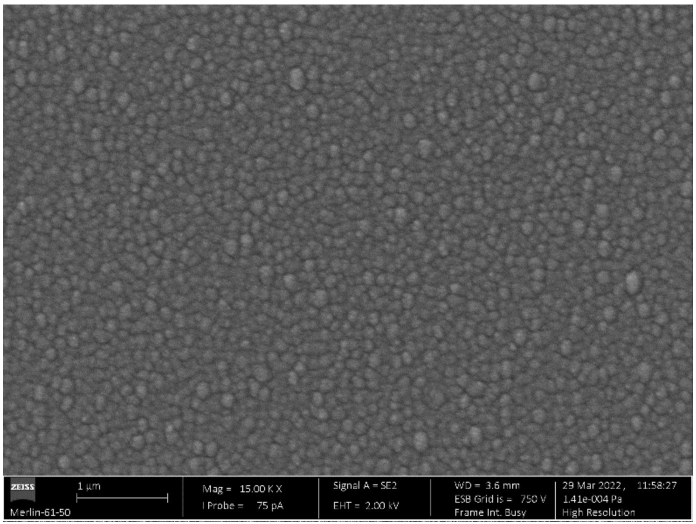
The HiPIMS deposition technique was used to coat the samples, and the aspect of the DLCs coatings is shown in the Figure 6. Carbon clusters or a cauliflower-like structure can be observed in all five samples, which is a common characteristic of DLCs coatings. These clusters do not represent the actual grain structure, but rather the carbon-amorphous regions (we know it is carbon from the EDS analysis) [215–219]. It is evident that the size and shape of the carbon clusters depend on the deposition technique. Additionally, these regions with a high carbon content indicate the density of the film. Therefore, a denser film is achieved when the carbon clusters are smaller [220–222]. Consequently, all five samples (pure DLC, 1.7%-Gd DLC, 2.3%-Gd DLC, 1.7%-Eu DLC, and 2.4%-Eu DLC) exhibit a similar structure and thickness, indicating the uniform coating achieved through our HiPIMS process.



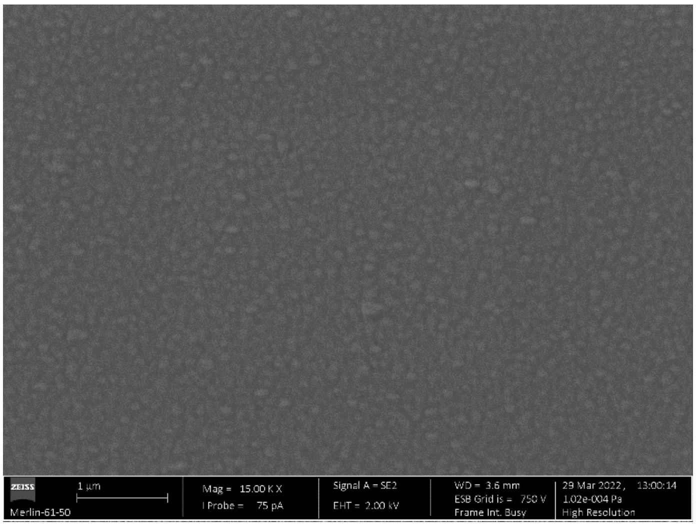
(a)



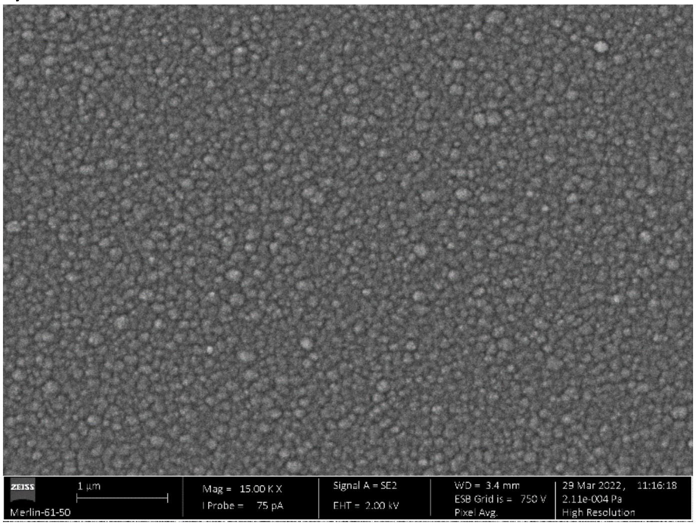
(b)



(c)



(d)



(e)

Figure 6. Examination of DLC coating structure under SEM.: (a) 2.3% Gd-DLC; (b) 2.4% Eu-DLC; (c) 1.7% Gd-DLC; (d) 1.7% Eu-DLC; (e) Pure DLC

To examine the detailed morphology of the coating's cross-section, SEM was used with a magnification of 25kX which can be seen Figure 7. The cross-sectional view revealed columnar and dense structures. At the top of these columnar structures, there are dome-shaped bumps resembling hats, which indicate the morphology of the cross-section. The adhesion between the substrate and the coating is improved by a chromium interlayer, which forms a compact structure. The thickness of all the coatings is similar, with the total film and interlayer thicknesses measuring approximately (1.7 ± 0.1) µm and (0.45 ± 0.05) µm, respectively, based on the measurement scale.

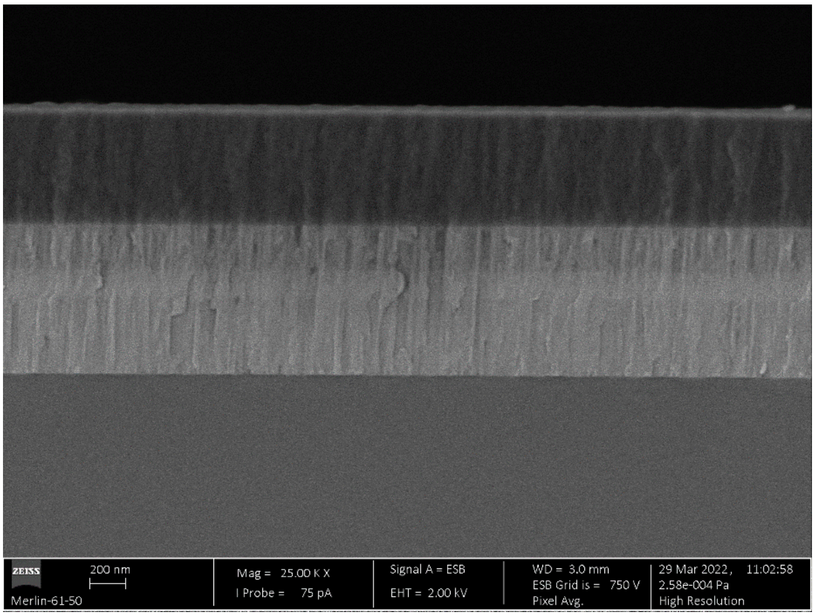


Figure 7. Examination of cross-sectional morphology of DLC coating under SEM

4.2 Viscosity of lubricants

To investigate the temperature responses of various ILs, a viscosity test was conducted from 100 °C to ambient temperature of 25 °C on both the lubricants with ionic liquids as additives. Different ionic liquids have distinct temperature responses due to variations in their structural features, including the size, symmetry, and presence of specific functional groups. Understanding these temperature-dependent behaviours is essential, therefore, In the study of lubricated contacts, the viscosity is considered a crucial factor as it influences the tribological characteristics of the lubricants [223].

Figure 8 and Figure 9 below shows the viscosity/temperature relation of both the lubricants with ionic liquids as additives. In this investigation, variations in viscosity were observed due to the utilization of differing temperatures in the tests as well as due to the different composition of ionic liquid additives.

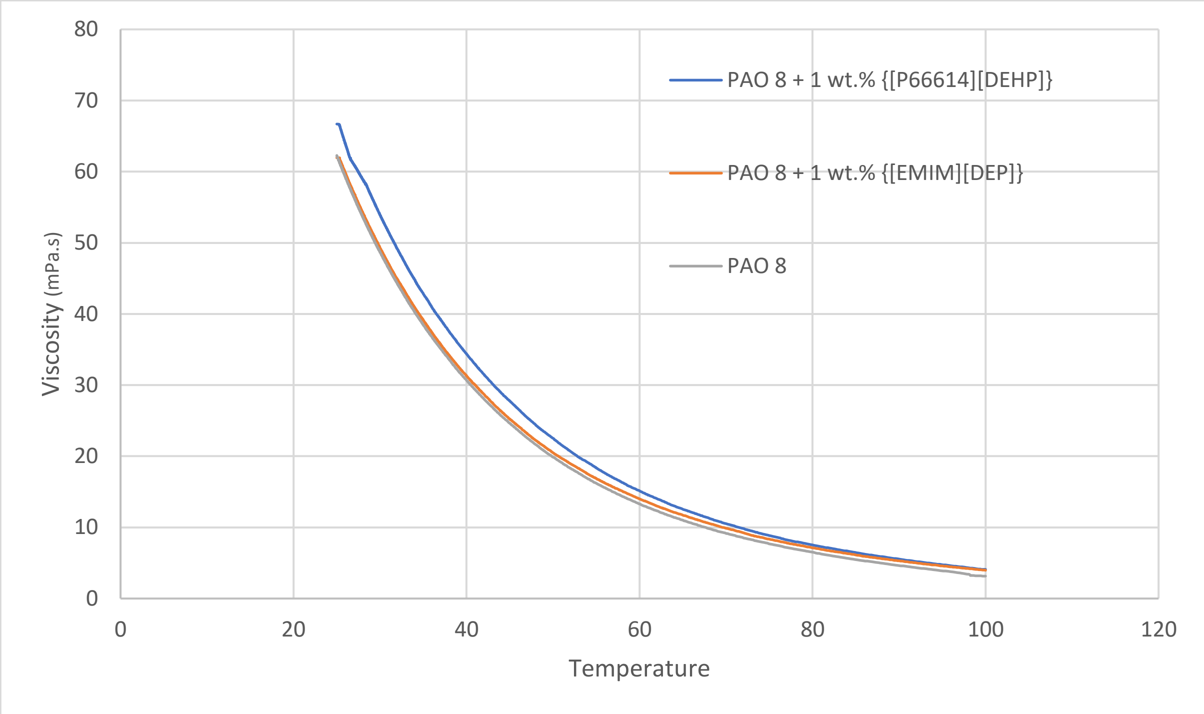


Figure 8. Dynamic viscosity/temperature graph of PAO 8, PAO 8 + 1 wt.% {[P$_{66614}$][DEHP]} and PAO 8 + 1 wt.% {[EMIM][DEP]}

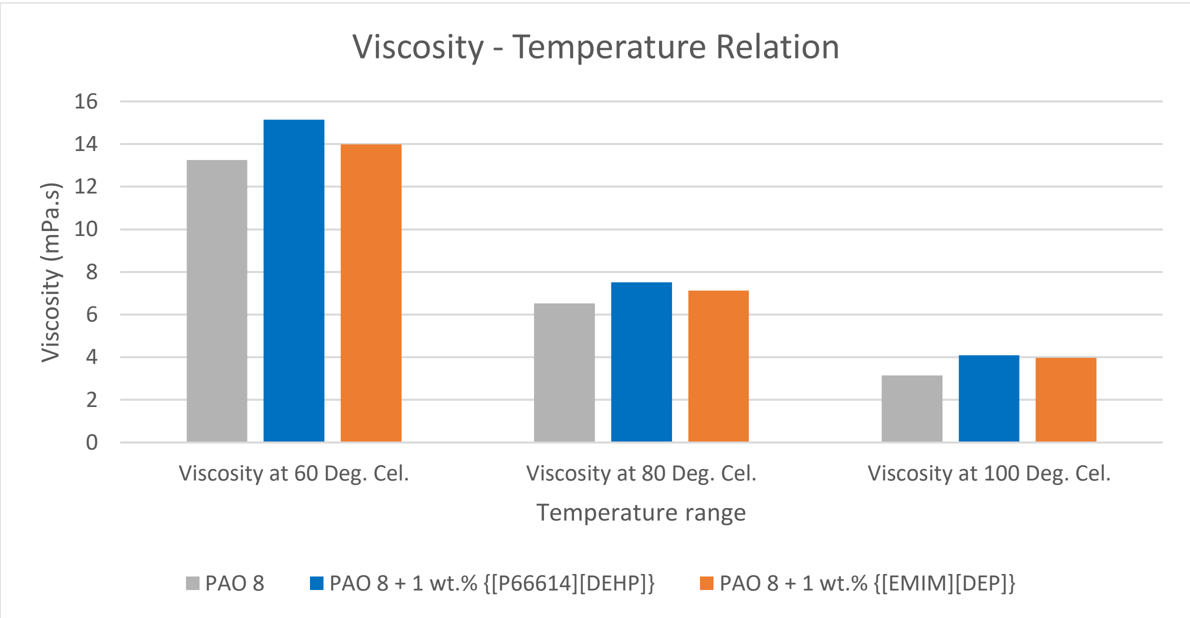


Figure 9. Dynamic viscosity/temperature of all three lubricants

Comparatively, the viscosity of PAO 8 is 8% to 20% lower than its counterpart with the addition of ionic liquids {[P$_{66614}$][DEHP]} and {[EMIM][DEP]}. Even though just being at 1% the weight of the lubricant, it has some significant change in the viscosity and the action of lubricant of the surface. Of all the lubricants, {[P$_{66614}$][DEHP]} has highest viscosity, followed by {[EMIM][DEP]}. This is due to the different viscosities of the ionic liquids themselves. The viscosity of the ionic liquid is influenced by its structural characteristics. The viscosity is enhanced as the side chain lengthens or as the cation's symmetry increases. Additionally, an increase in the number of branches leads to a corresponding increase in the viscosity [224].

Ionic liquid {[P_{66614}][DEHP]} has 7.6% higher viscosity at 60 °C compared to {[EMIM][DEP]} but the difference reduces to being negligible as the temperature increases. A slightly higher viscosity from the ionic liquids {[P_{66614}][DEHP]} and {[EMIM][DEP]} has benefited by extending some portion of the Stribeck curve in the mixed lubrication regime which will be discussed in the further section of Stribeck curves. The analysis revealed that different ionic liquids exhibit diverse temperature responses, primarily due to the structural variations of their constituent ions [225]. ILs with smaller, more symmetrical cations and anions tend to have higher melting points and exhibit less temperature dependence. In contrast, ILs composed of bulkier, asymmetric ions generally display lower melting points and a greater sensitivity to temperature variations [225].

Furthermore, the presence of specific functional groups in the IL structure can influence the temperature response [226]. For example, ILs containing hydrogen bond acceptors and donors exhibit increased ionic conductivity and can display significant changes in properties with temperature variations, including viscosity and solubility [226]. Additionally, the type and strength of intermolecular interactions within the IL, such as ion-ion interactions, ion-dipole interactions, and hydrogen bonding, contribute to the temperature-dependent behavior [227]. These interactions affect the ordering and dynamics of the ions, influencing the overall response to temperature changes.

4.3 Mechanical characterization (Hardness and Young's Modulus)

Figure 10 and Figure 11 show, respectively, the hardness and Young's modulus for the five different DLC coatings. As seen in the Figure 5, the highest result of hardness was obtained for Gd-DLC with an atomic concentration of 1.7%, exhibiting a mean value of approximately 23 GPa, while the mean value for Eu-DLC with an atomic concentration of 2.4 % was found to be around 19 GPa and that of 2.3 % Gd-DLC is 20 GPa. The reduced Young's modulus of the DLC coatings was observed to be between 180 and 195 GPa and can be seen in Figure 6. These values of hardness and Young's modulus were determined to be comparable to those of pure DLC coatings produced using the same technique by Ji Cheng et al. [228]. Consequently, it was concluded that despite the addition of dopant elements, the mechanical properties of the coatings were not affected.

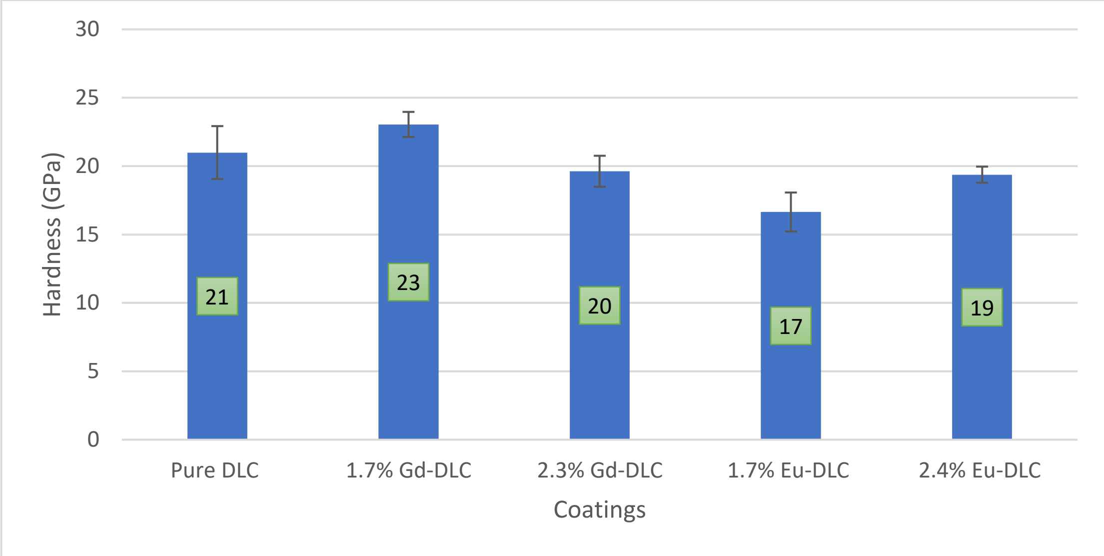


Figure 10. Hardness of coatings

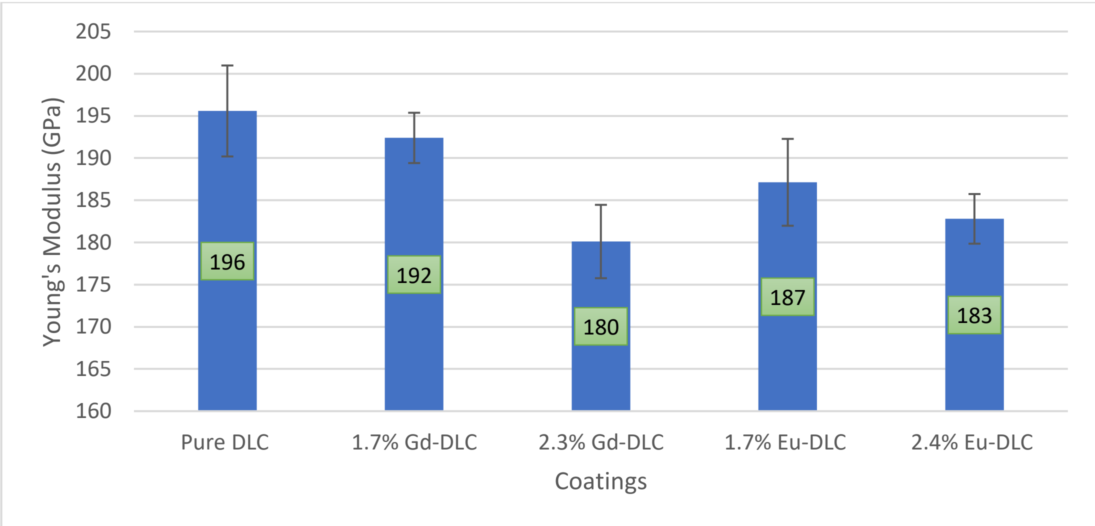


Figure 11. Young's Modulus of coatings

The variations in hardness and Young's modulus can be attributed to morphological type, sp^2 or sp^3 hybridization, and structural evaluation through density analysis. The high hardness in DLC coatings can be achieved with a high proportion of sp^3 hybridization in the amorphous carbon matrix and a dense and compact structure in the DLC coating [229–232]. Nevertheless, a decrease in the sp^3/sp^2 ratio results in a reduction of the hardness of DLC coatings [233].

4.4 Tribological Test (Influence of the Temperature)

The results of the block on ring tribotest are divided into three groups based on the temperature (60 °C, 80 °C and 100 °C). In these three temperature groups we can find the specific coating along with which lubricant was tested. The calculation of the Hersey parameter was performed by multiplying the viscosity of the lubricating oil at various temperatures by the sliding speed applied during the tests and dividing the result by the normal force (25 N) per unit length (12 mm). The Stribeck curves were generated from the values of the coefficient of friction obtained from tests conducted at different sliding speeds and temperatures with different DLC coatings. The standard deviation values, as we will see, were found to be minimal for all points and showed a tendency to decrease with increasing sliding speed, thus only the average data set was presented. Analysis of these curves revealed the existence of three lubrication regimes: boundary, mixed, and hydrodynamic lubrication.

4.4.1 Temperature of 60 °C

Table 2 presents the Tallian parameter along with the film thickness calculated from the Hamrock and Dowson equation for 60 °C. It is possible to observe that the PAO8 + 1 wt.% {[P_{66614}][DEHP]} presents the highest film thickness and lambda parameter. This is followed by PAO8 + 1 wt.% {[EMIM][DEP]}.

Table 2. Tallian parameter and film thickness at 60 °C

		60 °C				
	Velocity - u (m/s)	0.0241	0.0765	0.1916	0.3835	0.7671
PAO 8	Film Thickness - h_0 (m)	1.8E-08	3.94E-08	7.37E-08	1.18E-07	1.89E-07
	Tallian Parameter- λ	0.2946	0.6463	1.2067	1.9348	3.0997
PAO 8 + 1 wt.% {[P_{66614}][DEHP]}	Film Thickness - h_0 (m)	1.97E-08	4.32E-08	8.06E-08	1.29E-07	2.07E-07
	Tallian Parameter - λ	0.3226	0.7077	1.3213	2.1184	3.3939
PAO 8 + 1 wt.% {[EMIM][DEP]}	Film Thickness - h_0 (m)	1.87E-08	4.1E-08	7.65E-08	1.23E-07	1.96E-07
	Tallian Parameter - λ	0.3058	0.6710	1.2528	2.0086	3.2180

Figure 12. PAO 8 at 60 , presents the evolution of the coefficient of friction with Hersey number (Stribeck curve) for the different DLC coatings under different lubricating conditions at 60 °C.

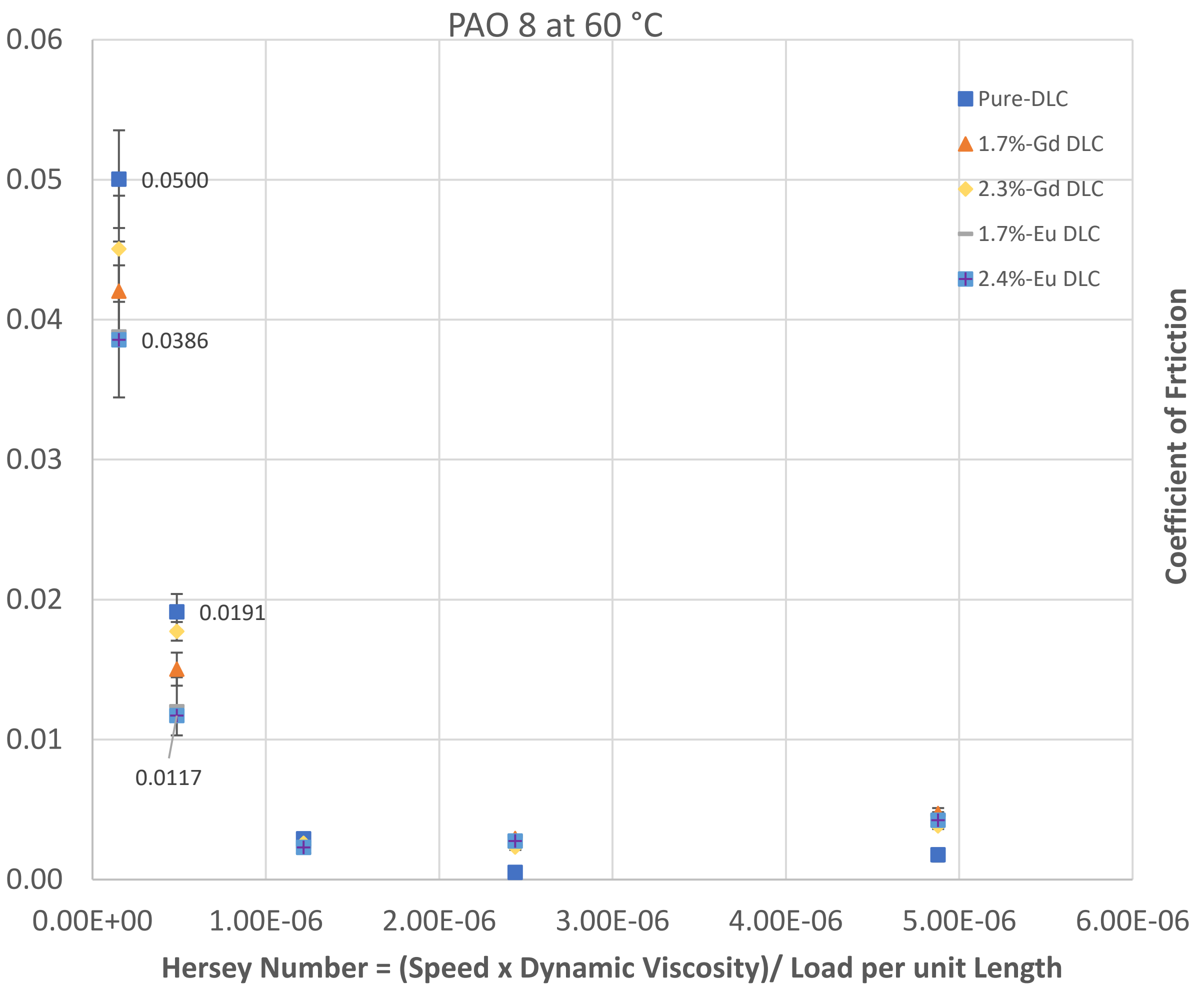


Figure 12. PAO 8 at 60 °C

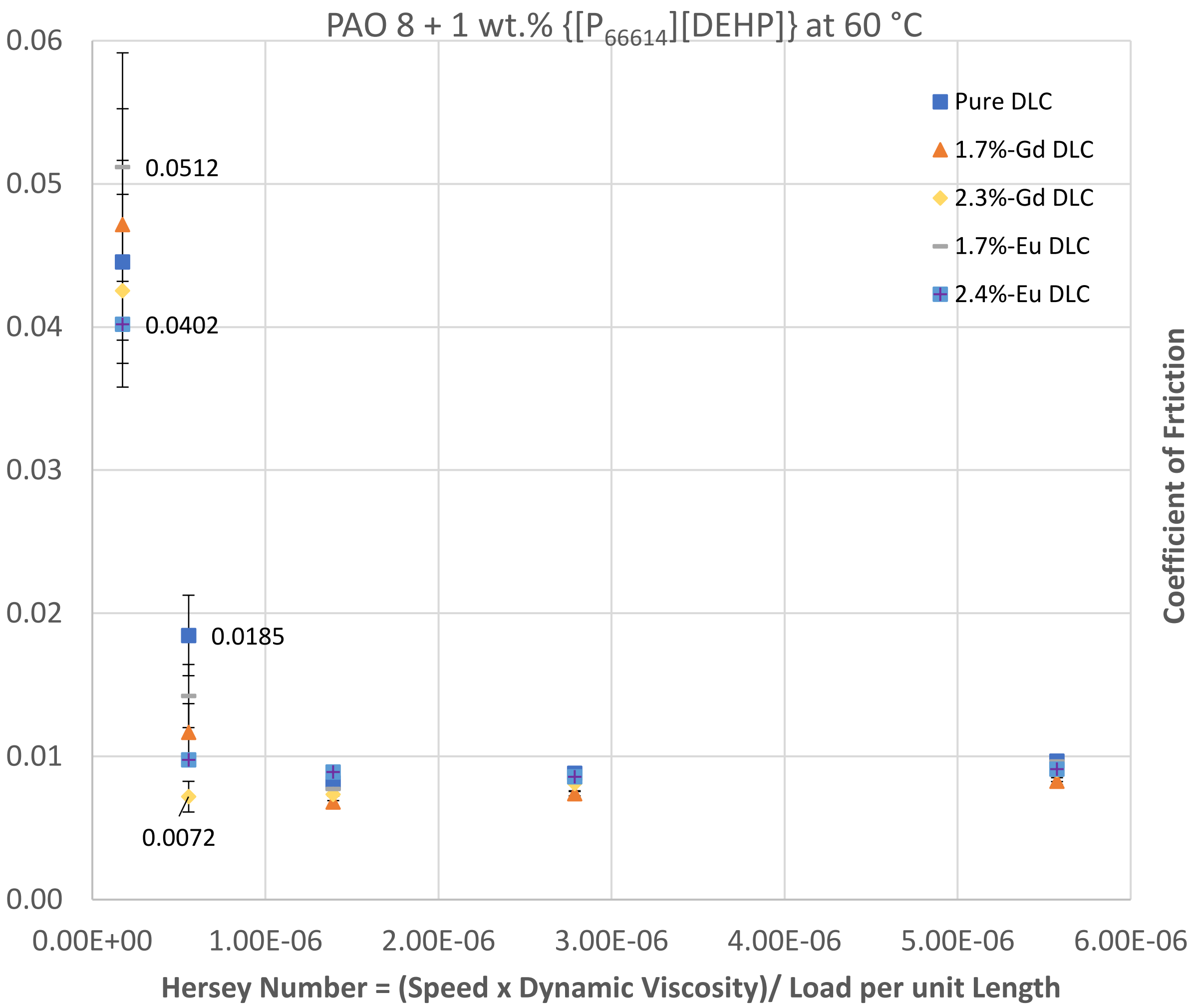


Figure 13. PAO 8 + 1 wt.% {[P_{66614}][DEHP]} at 60 °C

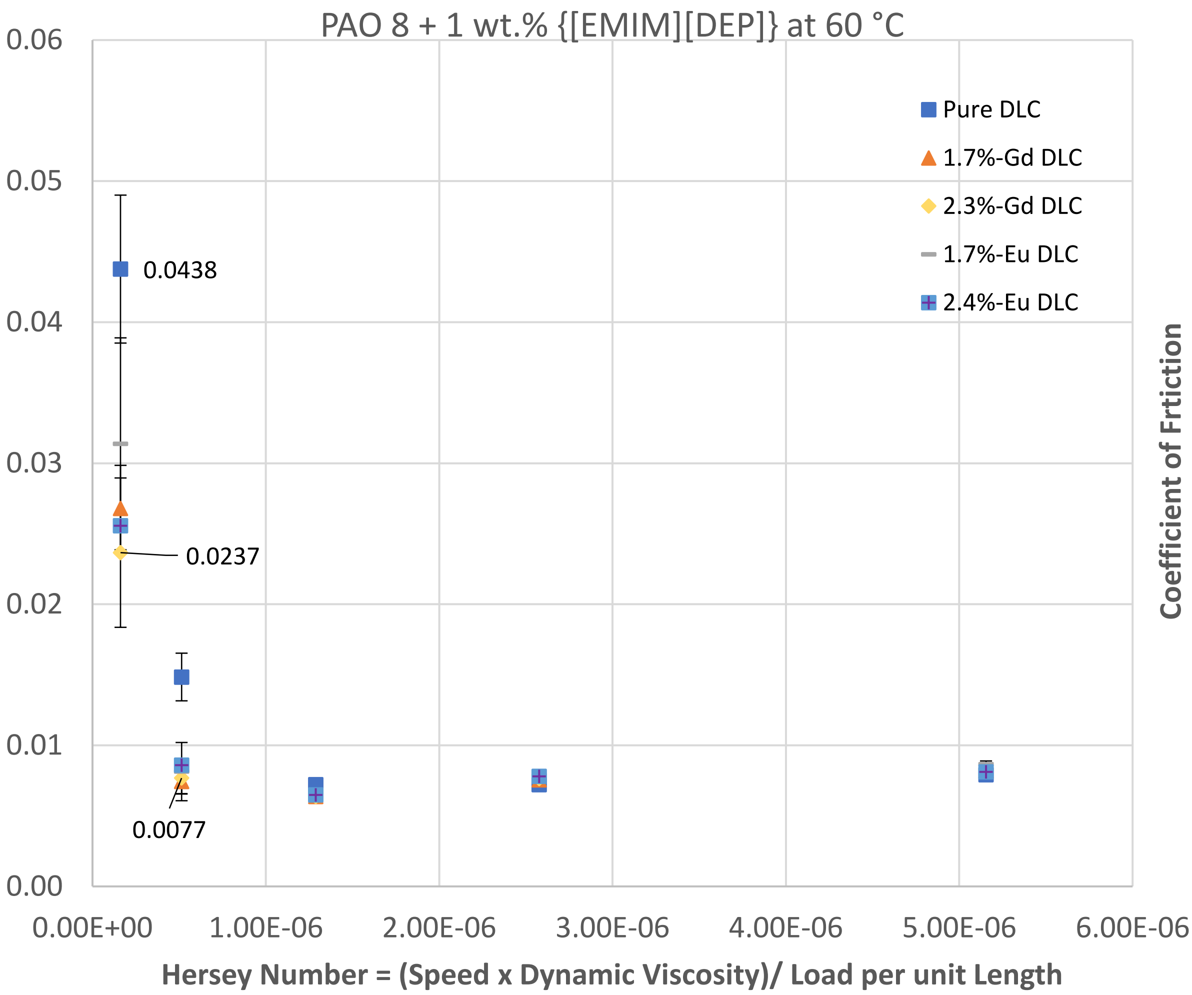


Figure 14. PAO 8 + 1 wt.% {[EMIM][DEP]} at 60 °C

There is 46.86 % of reduction in the coefficient of friction using ([EMIM][DEP]) as ionic liquid additive in PAO8 and the doped DLC with Gadolinium at a very low speed of (0.02 m/s) in boundary lubrication condition compared to the Pure DLC with PAO 8 + 1 wt.% {[P_{66614}][DEHP]}. Specifically, ([EMIM][DEP]) has shown a significant consistency in lowering the friction levels. Pure DLC and ionic liquid additives comparatively show a contrasting behaviour with high CoF (0.0446), which is 47 % higher compared to the doped DLCs in similar conditions of 60 °C. This proves that the ionic liquid, along with the doped elements, have some interaction between them which creates a tribofilm and is preventing the asperity-asperity contact on the surface.

In elastohydrodynamic region, all the points converge, which suggests a uniform lubrication film thickness. The distinctive points are the first two, which are in boundary lubrication condition. The thickness of the lubrication film in the elastohydrodynamic regime (3 < λ < 5) is thinner than the hydrodynamic regime (5 < λ), and in the results, we don't find any point of λ parameter greater than 5, therefore it is in elastohydrodynamic regime. Consequently, the maintenance of an uninterrupted hydrodynamic film necessitates the elastic deflection of the surfaces. Therefore, when studying elastohydrodynamic region, it becomes imperative to consider these deflections [234,235]. In the hydrodynamic lubrication regime, characterized by a lambda ratio greater than 5, the load is entirely supported by the lubricant film, and there is no contact between the asperities on the sliding surfaces [236,237].

In both the elastohydrodynamic and hydrodynamic regimes, as the speed escalates, the lubricating film may fail to match the pressure variations promptly, impeding the lubricant from adequately flowing into the contact area and forming a sufficiently thick fluid film. Consequently, this situation leads to an increase in friction [50,238]. Additionally, the viscosity of the lubricant commonly decreases as the temperature rises, which can occur occasionally during high sliding speeds due to the generation of heat resulting from friction, this will be represented further below for 80 and 100 °C.

4.4.2 Temperature of 80 °C

Table 3. Tallian parameter and film thickness at 80 °C

	80 °C					
	Velocity - u (m/s)	0.0241	0.0765	0.1916	0.3835	0.7671
PAO 8	Film Thickness - h_0 (m)	1.11E-08	2.44E-08	4.55E-08	7.29E-08	1.17E-07
	Tallian Parameter- λ	0.1819	0.3991	0.7451	1.1946	1.9139
PAO 8 + 1 wt.% {[P_{66614}][DEHP]}	Film Thickness - h_0 (m)	1.22E-08	2.68E-08	5.01E-08	8.03E-08	1.29E-07
	Tallian Parameter - λ	0.2002	0.4393	0.8202	1.3151	2.1070
PAO 8 + 1 wt.% {[EMIM][DEP]}	Film Thickness - h_0 (m)	1.18E-08	2.59E-08	4.83E-08	7.74E-08	1.24E-07
	Tallian Parameter - λ	0.1931	0.4237	0.7910	1.2683	2.0319

In Table 3 at 80 °C, there is no more elastohydrodynamic lubrication regime in both the lubricants. PAO 8 + 1 wt.% {[P_{66614}][DEHP]} outperforms other with highest film thickness (1.29E-07 m) and Tallian parameter (2.1070) which is followed by PAO8 + 1 wt.% {[EMIM][DEP]} at (2.0319). In this case of 80 °C there will be mostly delamination and asperity smoothing. As the velocity will further decrease it will result in macro plastic deformation.

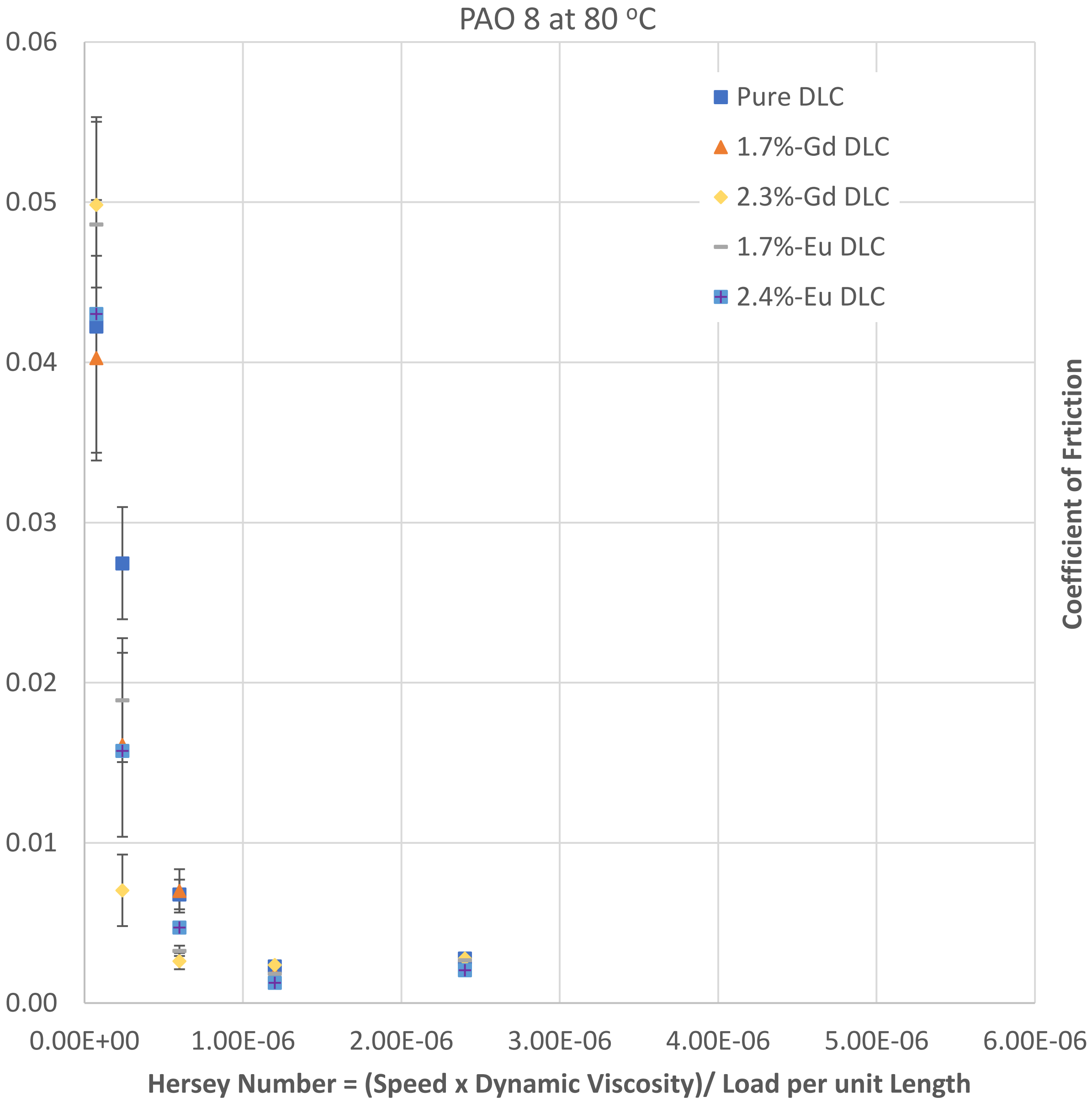


Figure 15. PAO 8 at 80 °C

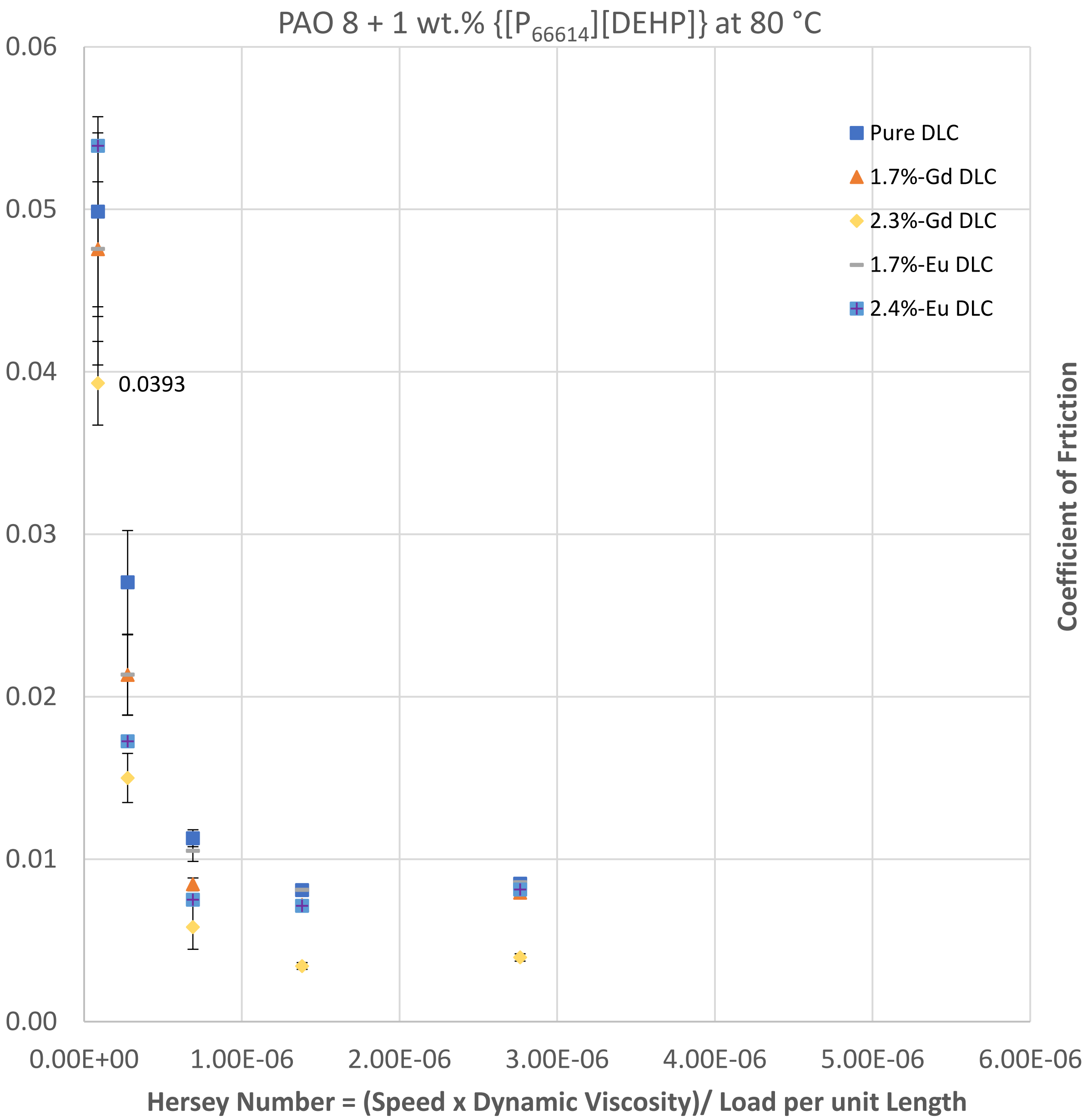


Figure 16. PAO 8 + 1 wt.% {[P_{66614}][DEHP]} at 80 °C

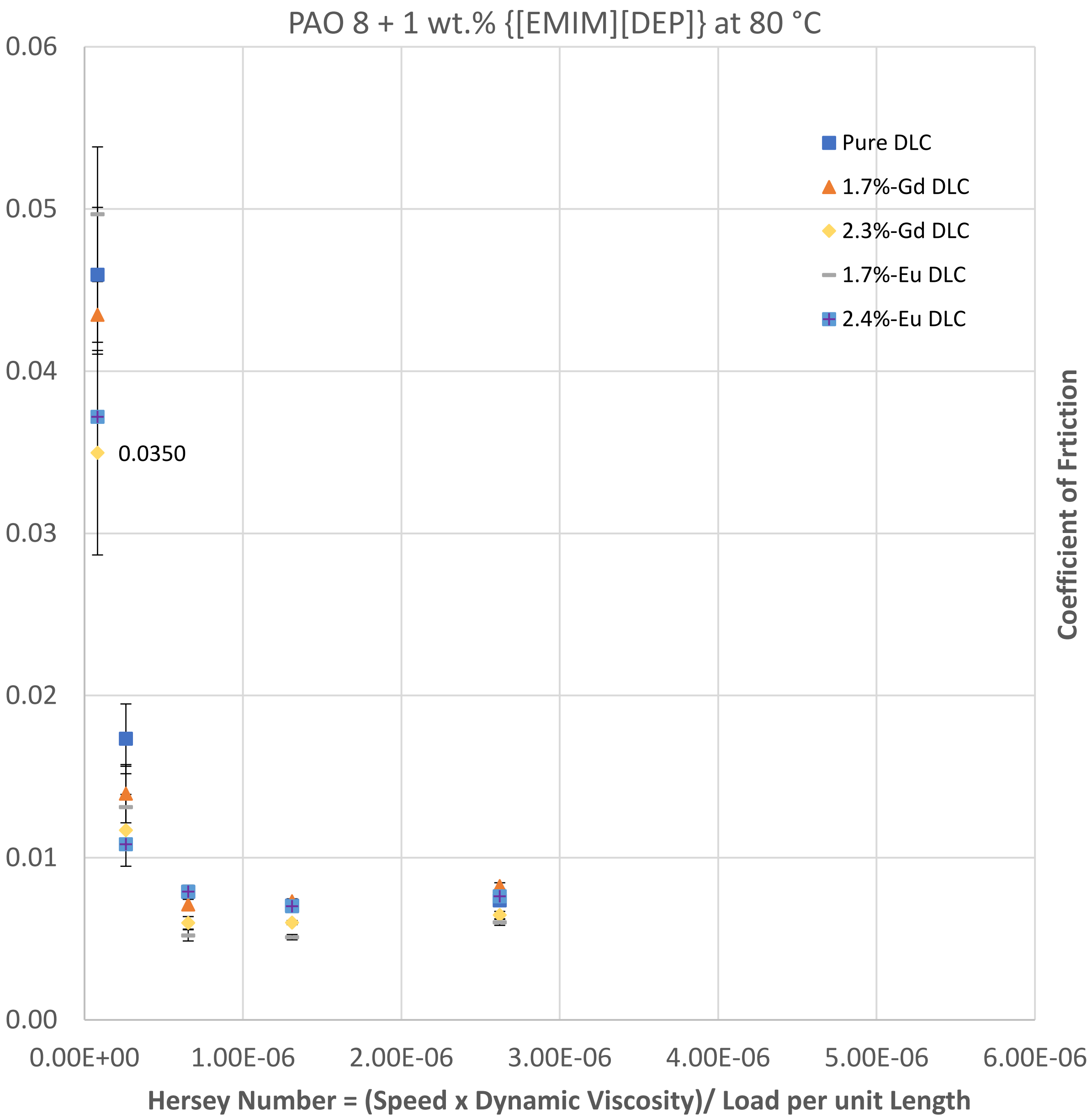


Figure 17. PAO 8 + 1 wt.% {[EMIM][DEP]} at 80 °C

From above figure it is possible to observe that the curves are shifted towards the left side. As the temperature is increasing the Stribeck curve is shifting towards the mixed lubrication regime. The significant role played by the mixed lubrication regime ($1 < \lambda < 3$) in numerous close clearance machines cannot be understated. It encompasses a fusion of characteristics from both elastohydrodynamic lubrication and boundary lubrication. This signifies that while certain sections of the contact area are coated with a film of lubricant, other regions witness the sliding of peak asperities on the moving surfaces due to the absence of a separating liquid film. Engine components like piston rings, cams, and engine bearings frequently experience mixed lubrication. For system engineers, a comprehensive understanding of mixed lubrication is of utmost importance, as it represents the most demanding lubrication regime to accurately predict friction. This complexity arises from the intricate interplay between surface topography and the thickness of the oil film [234,239,240].

Gadolinium doped DLC with PAO 8 + 1 wt.% {[EMIM][DEP]}. At 80 °C, the CoF has shown a 30 % substantial decrease if compared to Pure DLC. The tribosystem composed of 2.4% Europium doped DLC also showed a similar result. 2.4% Gadolinium doped DLC with PAO 8 + 1 wt.% {[P_{66614}][DEHP]} perform better than the Europium doped DLC. PAO 8 + 1 wt.% {[EMIM][DEP]} shows consistent results with all 5 DLC coatings with 2.3% Gd DLC and 2.4% Eu DLC being the best performing coatings. PAO 8 + 1% {[P_{66614}][DEHP]} and PAO 8 + 1% {[EMIM][DEP]} perform better with 20% extended Stribeck curve in mixed lubrication regime as compared to pure PAO 8.

4.4.3 Temperature of 100 °C

It is an extreme condition with all the points in boundary lubrication regime with just last point on the brink of mixed lubrication which can be seen from the calculated Tallian parameters in Table 4. Certainly, in this case there will be asperity-asperity contact with macro plastic deformation on the surface.

Table 4. Tallian parameter and film thickness at 100 °C

	100 °C					
	Velocity - u (m/s)	0.0241	0.0765	0.1916	0.3835	0.7671
PAO 8	Film Thickness - h_0 (m)	6.77E-09	1.49E-08	2.77E-08	4.45E-08	7.12E-08
	Tallian Parameter- λ	0.1109	0.2433	0.4543	0.7284	1.1670
PAO 8 + 1 wt.% {[P_{66614}][DEHP]}	Film Thickness - h_0 (m)	8.1E-09	1.78E-08	3.32E-08	5.32E-08	8.52E-08
	Tallian Parameter - λ	0.1327	0.2911	0.5435	0.8714	1.3961
PAO 8 + 1 wt.% {[EMIM][DEP]}	Film Thickness - h_0 (m)	7.92E-09	1.74E-08	3.25E-08	5.2E-08	8.34E-08
	Tallian Parameter - λ	0.1298	0.2848	0.5317	0.8525	1.3658

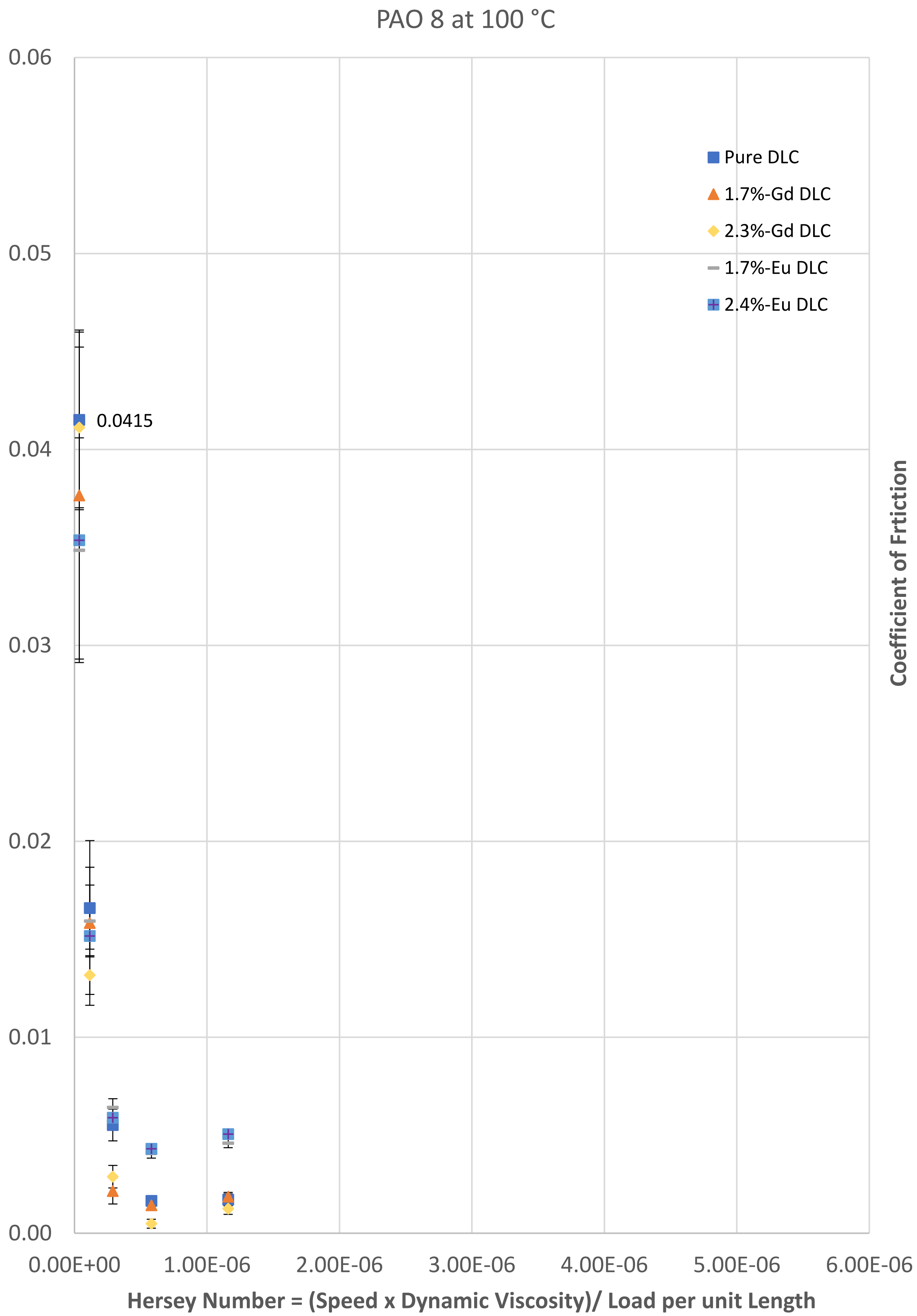


Figure 18. PAO 8 at 100 °C

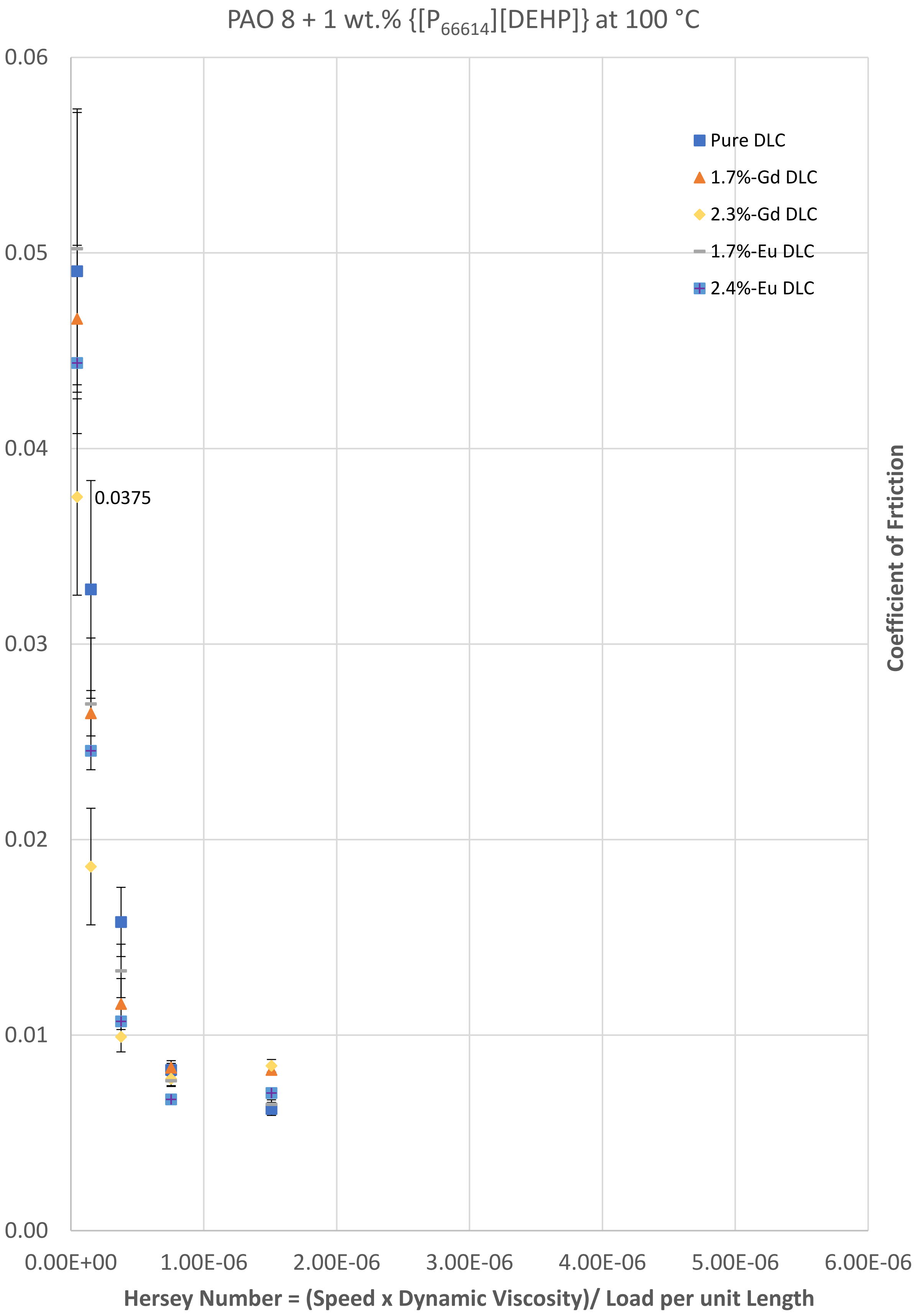


Figure 19. PAO 8 + 1 wt.% {[P_{66614}][DEHP]} at 100 °C

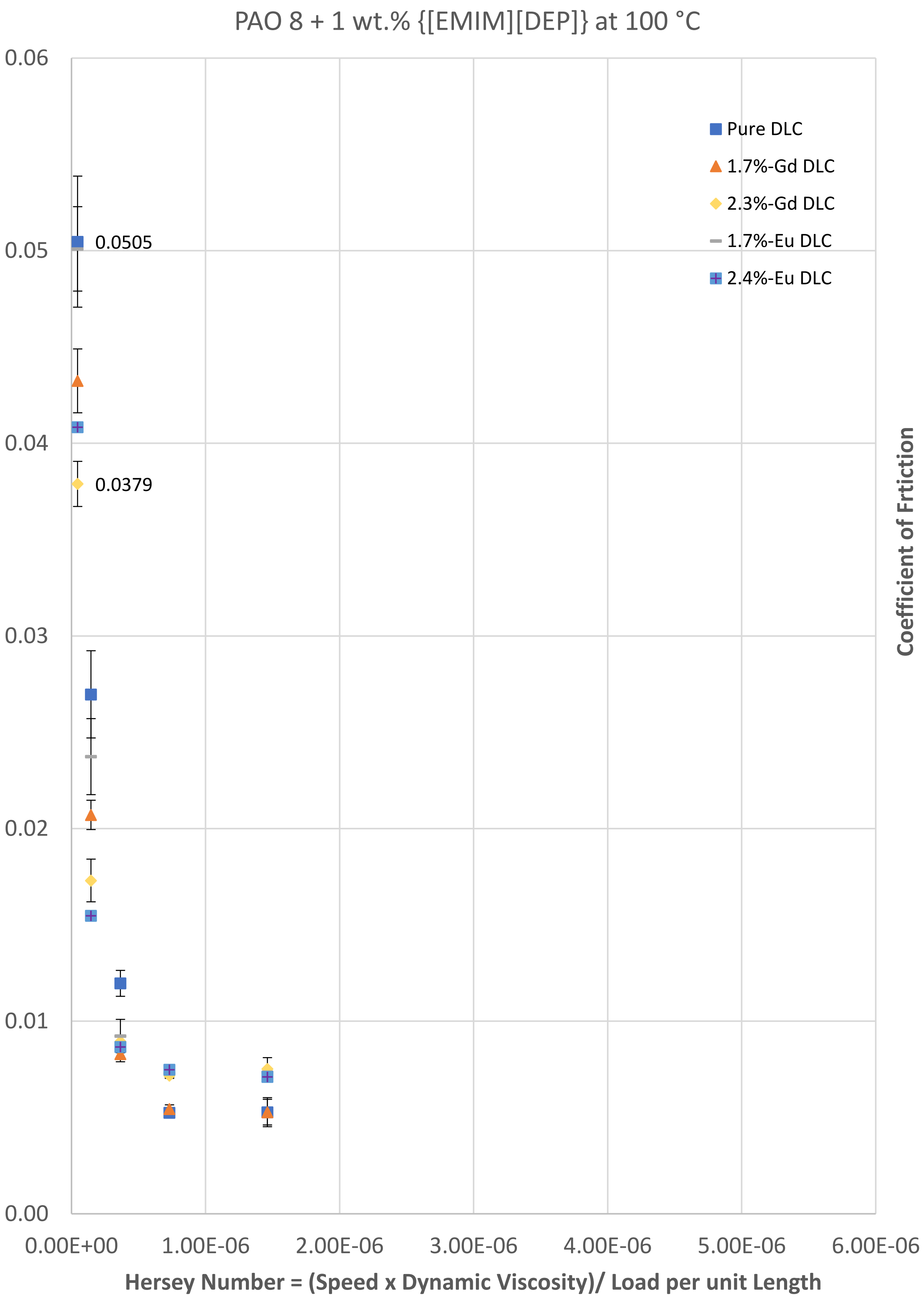


Figure 20. PAO 8 + 1 wt.% {[EMIM][DEP]} at 100 °C

The boundary lubrication regime, with a coefficient λ less than 1, exhibits the feature of load support by the minute surface irregularities, without the presence of a continuous film of lubricant. The interaction between these irregularities can lead to substantial levels of friction and wear, ultimately diminishing the operational life of the system [234,237,241,242] and at 100 ^{o}C it is clearly evident. 2.3 % Gd DLC with PAO 8 + 1 wt.% {[P_{66614}][DEHP]} and PAO 8 + 1 wt.% {[EMIM][DEP]} at 100 °C has boundary friction of just 0.0379, compared that to with Pure DLC which is 0.0505, a total of 25 % improved performance in coefficient of friction with ionic liquids and doping.

2.4 % Eu DLC performs better with PAO 8 + 1 wt.% {[EMIM][DEP]} at 100 Deg. Celsius whereas, pure DLC has the worst performing trend in all the three lubricants. Even at very high temperatures of 100 °C the coefficient of friction has no drastic increase which suggests that the DLC coatings are interacting with lubricants to keep the friction as low as possible. Out of all 2.3 % Gd DLC along with PAO 8 + 1 wt.% {[P_{66614}][DEHP]} has proven to be the best combination with the least coefficient of friction. Ionic liquid additives in PAO 8 + 1% {[P_{66614}][DEHP]} and PAO 8 + 1% {[EMIM][DEP]} extend the Stribeck curve in the mixed lubrication regime by 21% compared to pure PAO 8.

When comparing the Stribeck curves of different films, it was found that adding the ionic liquid to the PAO 8 lubricant generally decreased the coefficient of friction (CoF) at the lowest achievable sliding speed. This effect was particularly significant for the Gd-doped DLC film. The Eu-DLC film exhibited improved performance compared to the pure DLC film when the ionic liquid was present. The primary factor responsible for the reduced CoF in Eu-DLC and Gd-DLC films is the formation of adsorbed layers. These layers facilitate movement between two sliding surfaces due to their low shear. Additionally, the formation of a protective tribofilm on metal surfaces, resulting from chemical reactions between ionic liquids and the contacting surfaces during friction, is another contributing factor discussed [80,243]. As per the proposed mechanism for adsorbed layers, the negatively charged part of ionic liquids is attracted to the positively charged metal surface, causing adsorption on the surface [244]. Another anionic entity can adsorb the cationic component, resulting in the formation of single- or multi-layered adsorbed structures on the surface. These structures generate a film on the metal surface and possess weak bonding between the layers, which aids in decreasing friction and facilitating movement between the surfaces in contact [80,243,245,246].

4.5 Wear Mechanism Characterization

SEM-EDS was used to assess the impact of incorporating an ionic liquid (IL) as an additive on the characteristics of diamond-like carbon (DLC) thin films. SEM-EDS images of Gd-DLC and Eu-DLC films are depicted in Figures 21-27. These maps reveal that the thin film was partially removed in certain regions, and the presence of chromium, originating from the interlayer, was detected. At the location of wear, we can clearly see the distinction of the elements from each other.

Figure 21 and Figure 22 shows, the EDS X Ray mapping which gives us the details of the elements for 2.3% Gd DLC sample with PAO8 + 1 wt.% {[P_{66614}][DEHP]}. The sample was kept constant for the lubricant and was rotated at 45-degree angle for the three temperature ranges, this method was adopted to maintain the steady state conditions. The SEM-EDS analysis was done at the end of performing all the experiments, but it is difficult to contemplate the temperature regions. Therefore, the sample results represent an overall view of the entire temperature range.

In the results we can see, Chromium (purple) is the interlayer of CrN and Carbon (yellow) is from the DLC coating, Gadolinium (pink) is the dopant, Phosphorous (green) is from the ionic liquid. Calculation of the wear rate is not possible as the wear is not uniform and is difficult to identify a wear track. However, from a general overview in the SEM, Gd-DLC has some significantly visible wear, whereas Eu-DLC has less to no wear on the samples. A study done by M Sadeghi. et al. shows the similar results found in the optical microscopy images of different lubricant films along with SEM-EDS images, the wear reduction is clearly evident by using ionic liquids as additives and doping of DLC coatings [62].

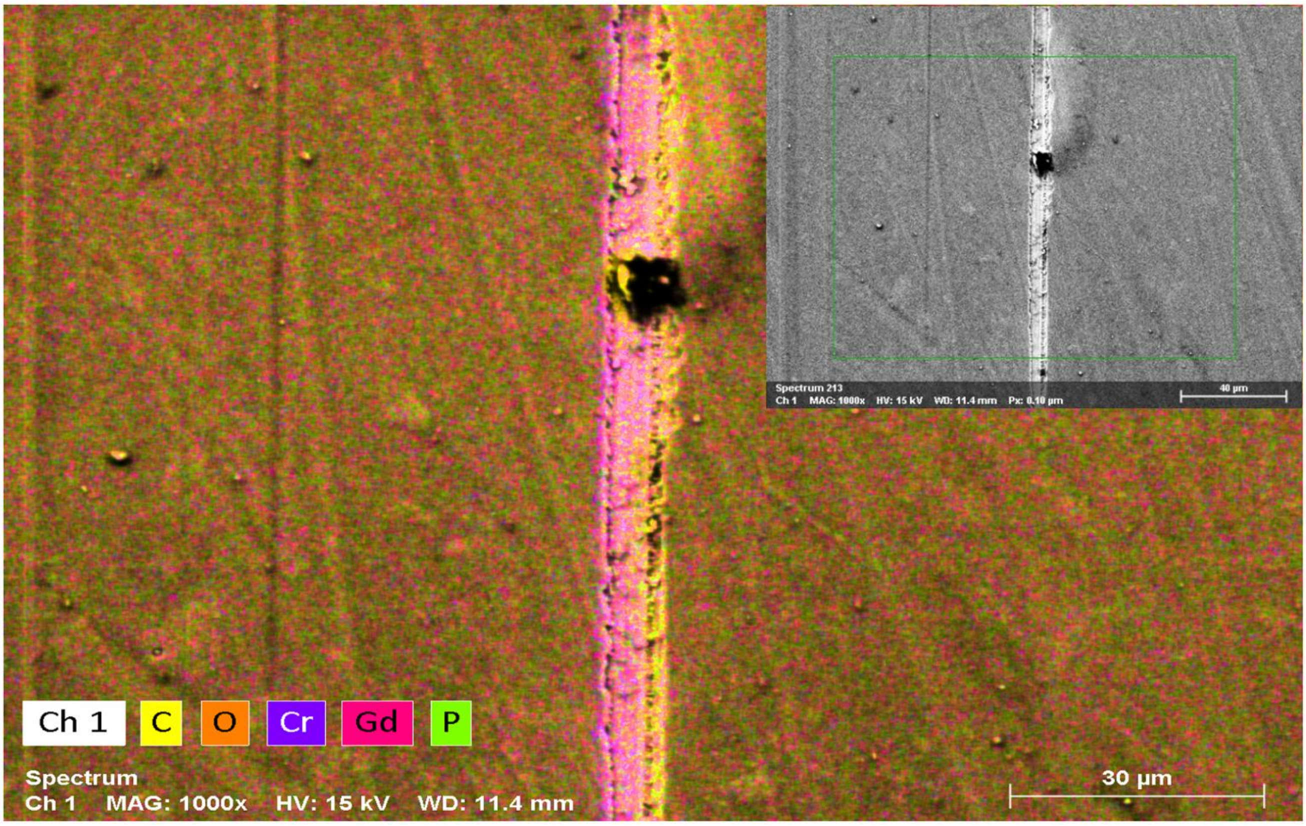
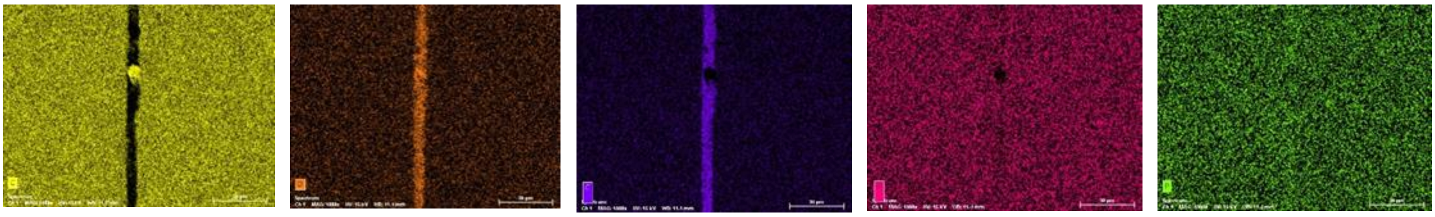


Figure 21. EDS of 2.3% Gd-DLC with PAO 8 + 1 wt.% {[P_{66614}][DEHP]} and SEM image of the same in top right corner



(a) (b) (c) (d) (e)

Figure 22. Element mapping of the Gd-DLC thin film paired with PAO 8 + 1 wt. % {[P_{66614}][DEHP]} : (a) C; (b) O; (c) Cr; (d) Gd and (e) P

The 2.4% Eu DLC with PAO8 + 1 wt.% {[EMIM][DEP]} have significantly performed better with the least CoF even at the extreme conditions of 100 °C, it can also be seen in Figure 23 the SEM image that the coating has no wear but a light bruise/scratch.

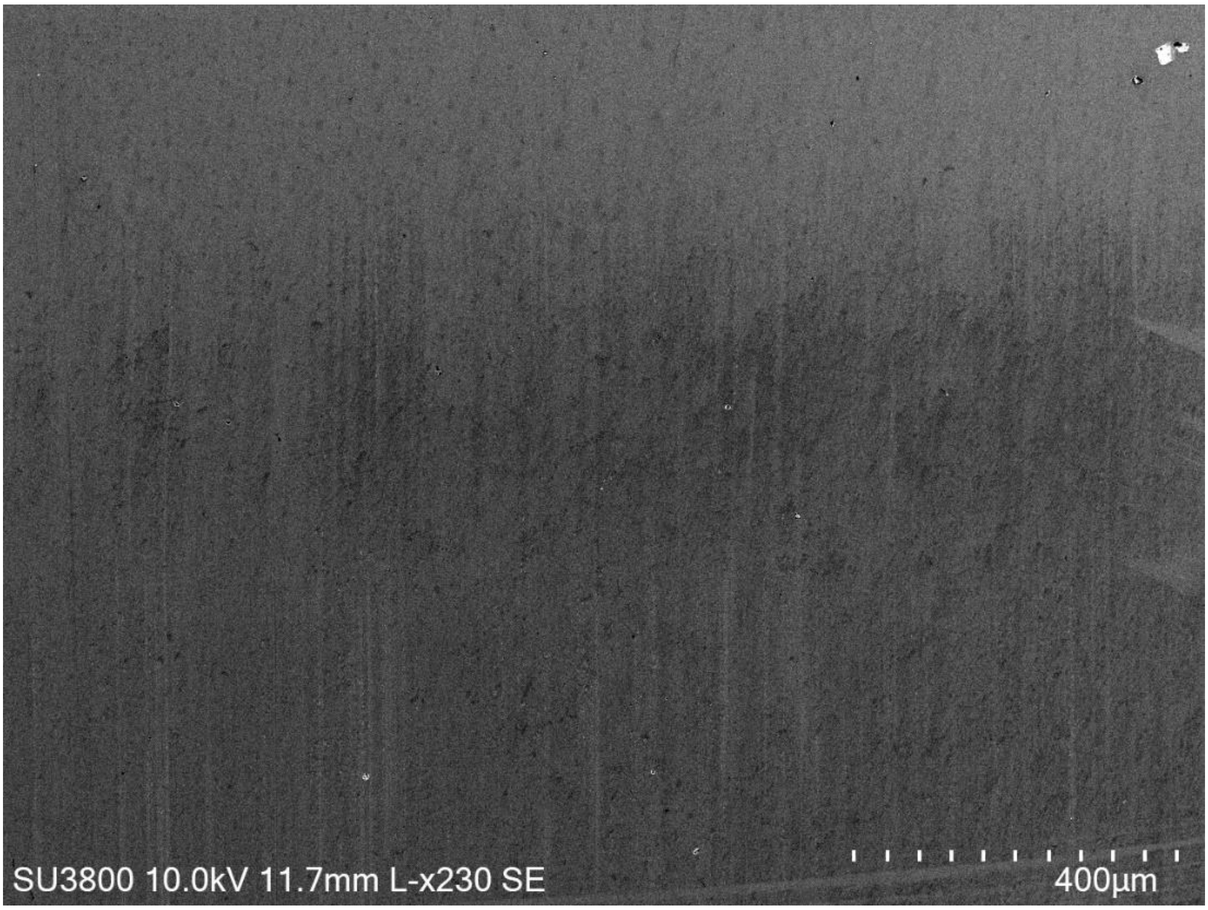


Figure 23. Scratch/Wear pattern on 2.4% Eu DLC coating with PAO 8 + 1 wt.% {[EMIM][DEP]}

The SEM-EDS technique was used to assess the impact of IL with 2.3% Gd-DLC and 2.4% Eu-DLC. On 2.4% Eu-DLC with PAO 8 + 1 wt.% {[P_{66614}][DEHP]} sample, oxides were found on the surface and there were no significant wear marks. This suggested the formation of tribofilm through oxides, although there is no direct evidence of tribofilm. In a study by Barnhill et al. [1], it was discovered that the lubricants containing [P_{66614}][DEHP] had a tribofilm containing oxygen and phosphorus. This finding suggests that the tribofilm originated from the [P_{66614}][DEHP]. In EDS X ray map in Figure 24 and Figure 25, we can distinctly see the oxygen and a very slight presence of phosphorous, from which we can conclude that phosphorous based ionic liquid reacted with the surface of the Europium doped DLC coating to a form a tribofilm.

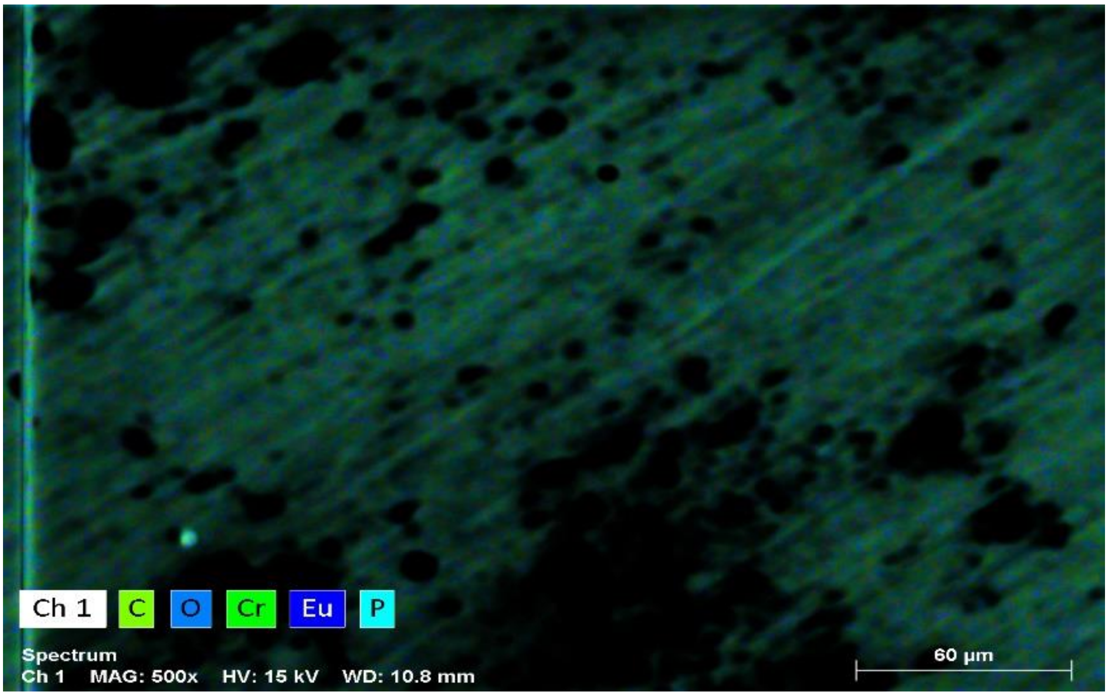
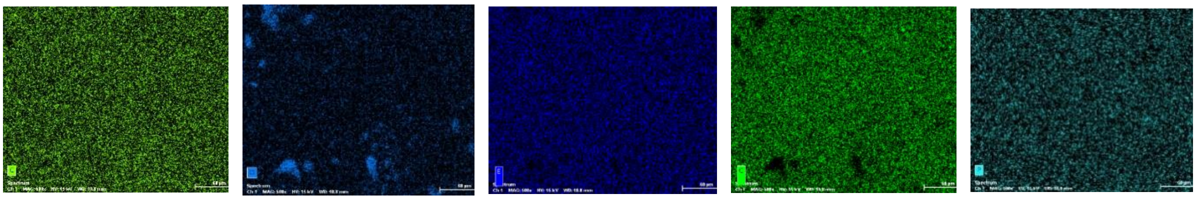


Figure 24. EDS image of oxides on the 2.4% Eu-DLC surface PAO 8 + 1 wt.% {[P_{66614}][DEHP]}



(a) (b) (c) (d) (e)

Figure 25. EDS X Ray map of oxides on the 2.4% Eu-DLC surface PAO 8 + 1 wt.% {[P_{66614}][DEHP]} surface: (a) C; (b) O; (c) Eu; (d) Cr; and (e) P

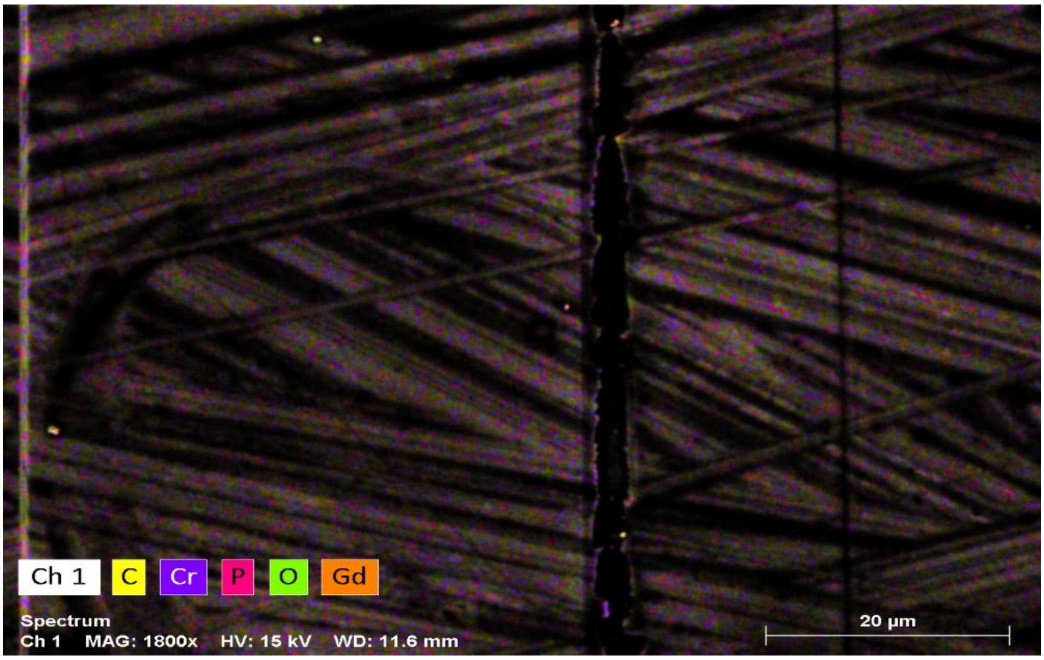


Figure 26. EDS image of oxides on the 2.3% Gd-DLC with PAO 8 + 1 wt.% {[EMIM][DEP]}

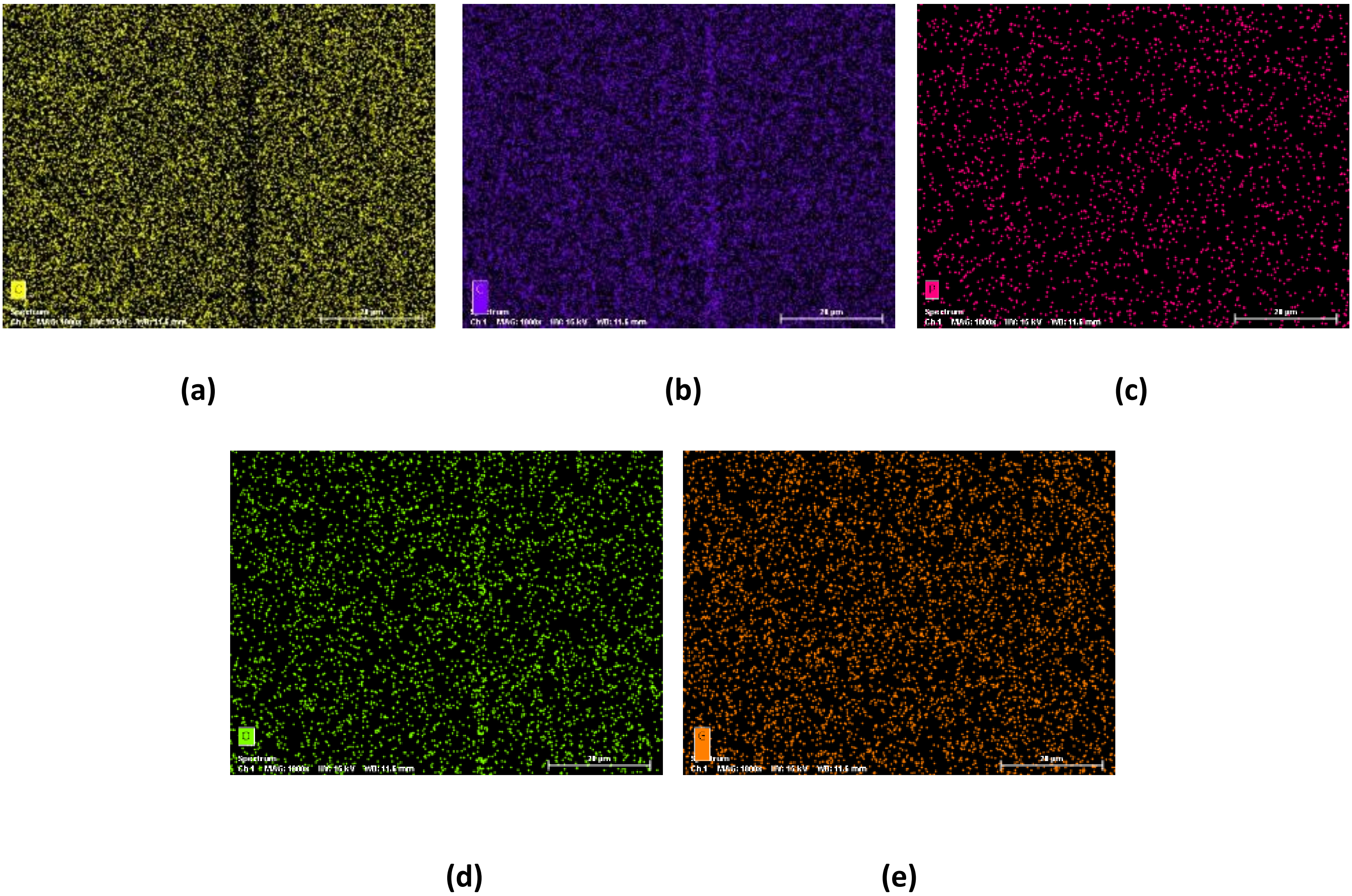


Figure 27. EDS X Ray map of oxides on the 2.3% Gd-DLC with PAO 8 + 1 wt.% {[EMIM][DEP]} surface: (a) C; (b) Cr; (c) P; (d) O; and (e) Gd.

Gd-DLC also forms a tribofilm which can be inferred from EDS X ray map in Figure 26 and Figure 27, oxides were found on the surface near the wear marks. This suggests the formation of tribofilm through oxides. In EDS X ray map we can distinctly see the oxygen and presence of phosphorous, from which we can conclude that phosphorous based ionic liquid reacted with the surface of the Gadolinium doped DLC coating to a form a tribofilm.

Research was conducted by Qu J. et al. on [P_{66614}][DEHP] and its interaction with a steel surface. The study, carried out using TEM by Qu J. et al., displayed a cross-section of the region just below the wear mark, which was lubricated by PAO+IL. The cross-section revealed a two-layer structure consisting of a top film at the boundary (120-180 nm) and a deeper zone (0.5-0.8 µm) exhibiting plastic deformation and a refined grain structure. The IL additive is believed to provide anti-scuffing and anti-wear properties through this protective boundary film. When the boundary film was observed at a higher magnification, it exhibited an amorphous matrix containing small nanoparticles (1-10 nm in diameter). The electron diffraction pattern confirmed the presence of a nanocomposite phase structure. EDS element mapping indicated significant concentrations of P, O, and Fe in the boundary film, resulting from the interactions between the IL and the metal surface [247]. Similarly, our EDS elemental mapping shows P, O, and Eu/Gd resulting from the interactions between the IL and the coatings.

5 Conclusions

In summary, this study investigated the tribological performance of rare earth element-doped diamond-like carbon (DLC) coatings in the presence of ionic liquid additives under different temperature conditions. DLC coatings have been considered as a sustainable solution for reducing frictional losses in mechanical systems due to their excellent tribological and mechanical properties. However, pure DLC coatings are inert and do not interact effectively with conventional lubricants, resulting in wear and tear. To address this limitation, doping DLC coatings with metals has shown promise in enhancing their reactivity with lubricants. Ionic liquids have emerged as a potential solution due to their adjustable properties for specific applications and their ability to form protective tribofilms.

The study specifically examined the interaction between Europium and Gadolinium dopants in DLC coatings and ionic liquid additives in Polyalphaolefin 8 (PAO8). Two different lubricants were used in the experimental investigation to evaluate the tribological performance of the coatings under three different temperature conditions.

The results demonstrate that both ionic liquid additives can improve the tribological performance of DLC coatings. However, the optimal temperature range for each coating differs depending on the doping element and the type of ionic liquid used.

At 60 °C, the combination of 2.3% Gadolinium-doped DLC with PAO 8 + 1 wt.% {[EMIM][DEP]} showed the best results with the lowest coefficient of friction (CoF) 52.6% less than pure PAO 8, followed by 2.4% Europium-doped DLC. The addition of {[EMIM][DEP]} resulted in a more significant reduction in the coefficient of friction compared to {[P_{66614}][DEHP]}, although the latter showed a lower wear rate (wear rate from the general overview from the SEM-EDS analysis as the calculation of wear rate is not possible as explained earlier). The 2.3% Gadolinium-doped DLC and 2.4% Europium-doped DLC coatings consistently exhibited superior tribological performance under all conditions compared to the Pure DLC, highlighting the beneficial effects of rare earth metal doping.

Pure DLC can be clearly seen as worst performer in all the graphs at all the temperatures. In PAO 8 + 1 wt.% {[EMIM][DEP]} at 60 °C we can see the clear distinction of Pure DLC and doped DLC coatings. CoF reduction with ionic liquid and doped DLC is 39% lower compared to pure DLC and PAO 8.

Nevertheless, as we move in the higher temperature range, it has significant reduction in coefficient of friction, which is also in line with prior research that on iron/steel substrates, $[P_{66614}]$[DEHP] demonstrates commendable performance at elevated temperatures [63–65].

At 80 °C, both dopants with PAO 8 + 1 wt.% {[EMIM][DEP]} showed a substantial decrease in the coefficient of friction compared to Pure DLC. The lubricant plays a crucial role in providing the necessary film between the contacting surfaces, and the ionic liquid additives enhance the overall performance of the coatings. The 2.4% Gadolinium-doped DLC with PAO 8 + 1 wt.% {$[P_{66614}]$[DEHP]} outperformed the Europium-doped DLC under these conditions. PAO 8 + 1% {$[P_{66614}]$[DEHP]} and PAO 8 + 1% {[EMIM][DEP]} perform better with 20% extended Stribeck curve in mixed lubrication regime as compared to pure PAO 8. Also, the results of Omiya et al. are in good harmony with this study, it also revealed that as the concentration of the dopant increases in the DLC coatings, there is significant improvement with reduction in CoF and wear rate [61].

In extreme conditions of 100 °C, all the points were within the boundary lubrication regime, except the last point, which was marginally in the mixed lubrication regime. The DLC coatings, even at high temperatures, demonstrated low coefficients of friction, indicating their effective interaction with the lubricants. Among all the combinations, the 2.3% Gadolinium-doped DLC with PAO 8 + 1 wt.% {$[P_{66614}]$[DEHP]} exhibited the best performance with the lowest coefficient of friction. Ionic liquid additives in PAO 8 + 1% {$[P_{66614}]$[DEHP]} and PAO 8 + 1% {[EMIM][DEP]} extend the Stribeck curve in the mixed lubrication regime by 21% compared to pure PAO 8. The most feasible answer to these results is that ionic liquids maintain their viscosity index and properties quite well as compared to base oil, moreover from the research done by Fontes et al., it indicated the high performance is derived by using the combination of Eu-DLC and Gd-DLC with the ionic liquids [60].

The SEM-EDS analysis confirms the performance of the Eu-DLC with a very light scratch whereas the Gd-DLC has some wear marks. The element in the EDS also shows the formation of oxides, which strongly suggest that there is interaction between the coatings and the ionic liquids. The prior research of pure PAO 8 as reference and PAO 8 additivated with {$[P_{66614}]$[DEHP]} by M. Sadeghi has shown the similar results with drastic reduction in wear and CoF [62].

Overall, the findings of this study highlight the potential of rare earth element doped DLC coatings and ionic liquid additives for improving tribological performance in various temperature conditions. The results contribute to the understanding of the interactions between DLC coatings, dopants, and lubricants, providing valuable insights for the development of advanced lubrication systems with enhanced friction and wear properties.

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