TRIBOLOGY OF ENGINEERING AND COATED MATERIALS IN THE PRESENCE OF ENVIRONMENTALLY FRIENDLY REFIRGERANT

BY

MOHAMMAD WASIM AKRAM

DISSERTATION

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Mechanical Engineering
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2015

Urbana, Illinois

Doctoral Committee:

Professor Andreas A. Polycarpou, Chair and Director of Research
Professor Emeritus James Economy
Professor Pascal Ballon
Professor Iwona Jasiuk
Assistant Professor Alison Dunn
ABSTRACT

In recent years, considerable effort has been devoted towards finding of alternative refrigerants due to environmental issues related to high global warming potential (GWP). Specifically, developing a system-compatible alternative refrigerant is of prime concern in order to reduce costs associated with design modifications. Among the candidate refrigerants, newly developed Hydrofluoroolefin-based refrigerant (HFO-1234yf) is considered as a direct substitution for the current R-134a refrigerant for possessing similar thermo-physical properties. However, in an actual system, a refrigerant circulates through different tribo-components where it interacts with the interfacial components (such as surface materials and lubricants), altering their tribological behavior. Therefore, the tribological performance of a refrigerant must be evaluated prior to widely use in refrigeration/air-conditioning systems. Along this line, we have investigated the tribological performance of HFO-1234yf refrigerant under aggressive boundary lubrication conditions. Specifically, we have performed controlled tribo-experiments, simulating actual automotive air-conditioning compressor systems, to measure in-situ friction and near-contact temperature. Interestingly, we have observed a run-in instability in the frictional behavior for the case of HFO-1234yf refrigerant, unlike HFC-134a refrigerant. This intermediate instability is associated with decomposition of the reactive HFO-1234yf refrigerant at the contact interface under specific loading conditions. However, beneficial anti-wear tribofilms are shown to evolve throughout this process as revealed via Scanning Electron Microscopic (SEM) analysis. Energy Dispersive Spectroscopy (EDS) in conjunction with X-ray Photoelectron Spectroscopic (XPS) analysis identified the existence of Fluorine on these boundary films, attributing the fluorinated interaction at the contact zone. This fluorination, thus, facilitates formation of FeF$_3$-enriched tribofilms over the cast iron based interface. In addition, we have demonstrated the influence of
the loading conditions and state-or-art lubricants on the tribological compatibility of HFO-1234yf refrigerant. Finally, the tribological performance of newly synthesized aromatic thermosetting polyester (ATSP) blended with 5% polytetrafluoroethylene (PTFE), namely ATSP/PTFE, has been evaluated under unlubricated and boundary lubricated conditions. Current state-of-art polymeric coatings have also been considered for comparative purposes. Tribological and morphological investigations revealed superior tribological performance for ATSP/PTFE. The better performance is attributed to segregated surface morphology associated with ATSP/PTFE.
ACKNOWLEDGEMENT

First and foremost, I would like to express my sincere gratitude to my advisor Dr. Andreas A. Polycarpou for his support, patience, caring, motivation, and profound knowledge. I am also grateful to him for his valuable suggestions and advice not only on my research but also on life and career. I could not have imagined having a better advisor and mentor in my life. Without his unwavering guidance and persistent help this dissertation would not have been possible.

I am immensely grateful to my committee members: Dr. Iwona Jasiuk, Dr. James Economy, Dr. Pascal Bellon and Dr. Alison Dunn for their valuable suggestions and insightful comments.

I would like to extend my sincere thanks to my collaborator: Dr. Kyriaki Polychronopoulou for helping me to perform XPS analysis. I am also grateful to Jacob Meyer who worked with me on the development of coatings. I thank my fellow lab-mates in University of Illinois at Urbana-Champaign and in Texas A&M University for the stimulating discussions and all the funs we have had in the last four years at different stages. Special thanks to Surya Mishra and Seung Min Yeo who trained me on the instruments at micro-tribodynamics Laboratory.

I am thankful to Air-Conditioning and Refrigeration Center, an Industry University Cooperative Research Center at the University of Illinois at Urbana Champaign, for supporting this research work. Special thanks are for Honeywell International and ATSP Innovations for providing the samples. Thanks to the staff members of Materials Research Laboratory at UIUC.

I am deeply indebted to all Bangladeshi community members at Urbana-Champaign. A very special thank you to my friends: Silvi Apu, Ezaz Vai, Nila Apu, Shameem Vai, Sharna, Azam
Vai, Reem, Anu Vai, Sabrina Apu, Farhan Vai, Kallol, Hasib, Khurshid Vai, Reaz, Mazhar, Reza, Amreen for the support they’ve lent me over all these years. I am grateful to Dr. Taher Saif for his valuable suggestions during our difficult situations. Thanks a lot for everything.

I would also like to thank my parents, Sultan Ahmed and Noor Nahar, for their faith in me and allowing me to as ambitious as I wanted. Also, I thank my in-laws family for providing me unending encouragement. I am thankful to my siblings: Sonia, Mitu and Saju as well.

Finally, but most importantly, I would like to thank my lovely wife Shahla Chowdhury (Diana). Words cannot express my gratitude for everything you have done. Her encouragement, patience and unwavering love were undeniably the bedrock upon which the past 6 years of my life have been built. She spent so many sleepless nights while I was working and encouraged me to accomplish this adventure.
# TABLE OF CONTENTS

CHAPTER 1 ......................................................................................................................... 1

INTRODUCTION ................................................................................................................. 1

1.1 ALTERNATIVE REFRIGERANTS: ENVIRONMENTAL & TRIBOLOGICAL CHALLENGES .................................................................................................................. 4

1.1.1 Environmental and Chemical Issues ........................................................................ 5

1.1.2 Thermodynamic Compatibility .............................................................................. 7

1.1.3 Tribological Compatibility ...................................................................................... 8

1.2 SCOPE OF RESEARCH .............................................................................................. 8

1.2.1 Defining the Research Problem ........................................................................... 8

1.2.2 Novelty of Research ............................................................................................ 9

1.2.3 Impact of Study .................................................................................................. 10

1.3 RESEARCH APPROACH .......................................................................................... 11

1.4 THESIS OUTLINE ..................................................................................................... 13

CHAPTER 2 ....................................................................................................................... 14

BACKGROUND ON TRIBOLOGY OF REFRIGERANTS .................................................... 14

2.1 METALLIC RESPONSES: ROLE OF REFRIGERANTS ............................................ 17

2.2 TRIBOLOGY OF POLYMERIC COATINGS: INFLUENCE OF REFRIGERANTS .......... 24

CHAPTER 3 ....................................................................................................................... 28

SELF-LUBRICITY OF HFO-1234YF REFRIGERANT ....................................................... 28

3.1 EXPERIMENTAL PROCEDURE ............................................................................... 29

3.1.1 Controlled Tribological Experiments .................................................................... 29

3.1.2 SEM/EDS ............................................................................................................ 31

3.1.3 XPS .................................................................................................................... 31

3.2 RESULTS AND DISCUSSIONS ............................................................................... 32

3.2.1 Tribological Observations ................................................................................ 32

3.2.2 Wear Analysis .................................................................................................. 34

3.2.3 SEM Analysis ................................................................................................ 36

3.2.4 EDS Analysis ................................................................................................ 37

3.2.5 XPS Analysis ................................................................................................ 40

3.3 TRIBOCHEMISTRY DISCUSSION ......................................................................... 43

3.4 CONCLUSIONS ........................................................................................................ 45

CHAPTER 4 ....................................................................................................................... 47
## 7.1.2 Tribological Applications

### 7.2. TRIBO-EXPERIMENTAL DETAILS

- **7.2.1.** Experimental Conditions
- **7.2.2.** Experimental Samples

### 7.3. TRIBOLOGICAL RESULTS

- **7.3.1.** Frictional Behavior
- **7.3.2.** Microscopic and Topographic Measurements
- **7.3.3.** Wear Analysis

### 7.4. DURABILITY STUDY

### 7.5. MORPHOLOGICAL ANALYSIS

- **7.5.1.** Morphology of Coatings
- **7.5.2.** Role of Transfer Layer

### 7.6. SUMMARY

## CHAPTER 8

### CONCLUSIONS AND FUTURE WORK RECOMMENDATIONS

- **8.1.** CONCLUSIONS
- **8.2.** FUTURE WORK RECOMMENDATIONS

### BIBLIOGRAPHY
CHAPTER 1
INTRODUCTION

In recent years, the research fields of alternative refrigerants have been intensified due to environmental concerns. The leakage of refrigerants in the atmosphere, for example from mobile air-conditioning compressor (MAC) is a significant contributor to global warming [1]. The inevitable exposure of the refrigerants causes either depletion of the ozone layer [2], quantified by a metric called ozone depleting potential (ODP), or raising the earth’s temperature, measured as Global warming potential (GWP). The climatic adversities associated with automobile refrigerants have promoted countries throughout the world to pass legislations (according to the Montreal Protocol and Kyoto Protocol) to phase out the usage of such environmentally harmful compounds [3-4]. In response to these concerns, scientific consensus has been reached to reduce/eliminate the use of chlorine (ozone depleting agent) from the refrigerants in the late 1980s. As a result, in the early 1990s, automotive and refrigeration industries have shifted their interests to use Hydrofluorocarbon (HFC) based refrigerants (for example, HFC-134a: that has zero ODP and 1400 GWP) instead of chlorine containing Chlorofluorocarbon (CFC) based refrigerants (e.g., CFC-12: ODP ~1 and GWP ~10000). However, the transition involved significant technical difficulties related to tribological and lubricant incompatibilities and required major system modifications [5-6]. Note that, any design alteration imposes significant cost and changes the system’s performance dramatically. Despite these issues, HFC-134a refrigerant is being almost exclusively used in MAC systems since the early 1990s. Most recently, the Kyoto Protocol, pursuant to the United Nations Framework Convention on Climate
Change (UNFCC) sets binding target to reduce the use of HFC-134a refrigerant as a global warming producing gas. Moreover, in the European Union, regulations have already been enacted to substitute HFC-134a refrigerant in MAC system by a refrigerant having GWP less than 150 [7]. Due to this fact, it is expected that automotive industries will confront another unprecedented transition from HFC-134a refrigerant to alternative refrigerants. However, this time scientific and industrial attempts are coming together to develop a refrigerant without any system mitigation for a quick, cost-effective and sustainable replacement.

Several alternative refrigerants could be considered to replace the current refrigerant (HFC-134a). However, selecting an alternative refrigerant is always challenging as several interconnected parameters are involved which will require close scrutiny [8-9]. Among the candidate refrigerants, naturally occurring carbon dioxide (R-744) has attained significant research attention [10-13]. This naturally abundant refrigerant has proven to be non-toxic and non-flammable with zero ODP and GWP index of only one. In addition to desired environmental and chemical properties, a candidate refrigerant must also possess compatible thermo-physical and tribological characteristics [14-16] to ensure cost-effective and reliable substitution. This gas (R-744), however, exhibits improved tribological and thermodynamic performance at higher environmental pressures [17]. Thus, deployment of this gas as refrigerant involves system modifications with high-pressure equipment, which in turn increases the cost and reduces. These concerns limit the applicability of carbon dioxide widely in the air-conditioning system. Scientists continue their efforts to formulate a refrigerant, which meets all the desired properties. Consequently, new refrigerants have been developed (synthetics) which consist an olefin backbone (-C=C-) in their chemical structure. This is believed that, such kind of chemistry will offer low environmental impact while fulfilling almost all other desired properties. Along this
line, refrigerant 2,3,3,3 – Tetrafluoropropene or HFO-1234yf having a GWP of 4, which is about 355 times less than HFC-134a has been developed [18-23]. This environmentally friendly refrigerant is also considered as a ‘drop-in’ solution to substitute HFC-134a gas, indicating no requirement of system mitigation. However, the proposition is based on similar thermo-physical properties of HFO-1234yf and HFC-134a refrigerant, excluding tribological compatibility. Admittedly, the substitution of a refrigerant will not be viable unless examining the impact on compressor’s reliability and efficiency in the presence of the new refrigerant. Importantly, the compressor’s effective life-cycle and durability is directly or indirectly related to friction and wear characteristics in refrigerated environment.

Note that, clear understanding towards the tribological behavior of a contact pair is complicated as several uncertainties are involved. Among these parameters, environmental conditions, refrigerant in this case, play a pivotal role to determine the overall tribological performance [24]. Since a refrigerant passes through different components of a refrigeration cycle, it will interact with critical tribo-components in the compressor system. The frictional behavior and wear performance of compressor greatly depends on those interactions [25]. Furthermore, with the introduction of the compressor lubricant, these interactions will be more complicated and rely on tribochemical reactions. Based on these interactions, different surface layers can be formed which govern wear and frictional responses. Therefore, investigating the tribological performance of the new refrigerant for compressor specific conditions is essential. The lubricity effect and its interaction with system parameters, including lubricants and materials, must be addressed prior to widely use in the refrigeration system. In this work, tribological performance of HFO-1234yf will be studied for different compressor materials, including advanced polymeric coatings.
1.1 ALTERNATIVE REFRIGERANTS: ENVIRONMENTAL & TRIBOLOGICAL CHALLENGES

Identifying an alternative refrigerant is always challenging due to involvement of several factors as stated earlier. Among these factors, environmental, thermodynamic and tribological issues are of prime concerns. This is almost certain that an alternative refrigerant would be environmentally benign even with respect to decomposition products. The legislation and protocols will not allow any refrigerant having high ozone depleting potential (ODP) and GWP. Furthermore, the refrigerant would be nontoxic, nonflammable and completely stable inside a refrigeration system [26]. Thermo-physical and thermodynamic properties are other main issues that need to be evaluated to examine the compatibility. Similar thermodynamic properties will insure less modification of the refrigerant system, which is cost effective.

Most importantly, the refrigerant would be self-lubricating and compatible with compressor surface materials. In addition, its’ interaction with state-of-art lubricants would be tribologically beneficial. This tribological compatibility is directly related with compressor life-cycle, performance and durability as discussed before. In addition, the refrigerant’s fluid and thermal properties are also important for selection criteria. Issues related with alternative refrigerant are presented graphically in fig. 1.1. Environmental, thermodynamic and tribological issues will be discussed briefly as they carry special importance.
1.1.1. **Environmental and Chemical Issues**

Formulating an alternative refrigerant possessing both low atmospheric adversities and low flammability is challenging. These two intertwining issues limit few options for alternative refrigerants depending on constituent elements. Note that, early refrigerants consisted of only organo-halogen (fluorine, chlorine or bromine) based components [27]. However, these refrigerants have been proved as high ODP and high GWP producing gases and have been phased out. Environmentally harmful chlorine has been replaced by a hydrogen molecule to develop alternative refrigerants. McLinden et al. have provided a useful guideline to synthesize future alternative refrigerants [28]. They have illustrated how constituting elements are
contributing to environmental (ODP and GWP) and chemical (Flammability and Toxicity) adversities as shown in fig. 1.2. Note that, increasing the fluorine or chlorine content increases the atmospheric stability, which prolongs the atmospheric life time. Refrigerants containing no chlorine have ODPs that are almost zero. Similarly, increasing fluorine usually raises GWP. Substituting hydrogen shortens atmospheric life time, but increases flammability issues. HFO-1234yf refrigerant has an olefin bonding (-C=C-) in its structure which is reactive to atmosphere, shortening the atmospheric life time [25]. This chemical backbone for refrigerant is novel and its reaction to refrigeration system is still unknown, necessitating detail investigations. The tribological nature of the refrigerants has also been influenced by these elements and will be discussed in the next chapter. A prediction of the tribo-beneficial effects based on chemical components is marked (arrow along the side) in fig. 1.2.

![Diagram showing the dependency of refrigerant’s chemistry on environmental, chemical and tribological properties](image)

**Fig. 1.2:** Dependency of refrigerant’s chemistry on environmental, chemical and tribological properties [28]
1.1.2. Thermodynamic Compatibility

This is one of the most important issues for selecting a refrigerant. The new refrigerant should possess similar thermo-physical and thermodynamic properties to assure a cost efficient refrigerant transition. Any mismatch in thermo-physical properties will require design modification which will in turn increase system costs. For example, carbon dioxide exhibits similar thermo-physical performance at high operation pressure as stated before. Therefore, carbon dioxide refrigerant will require system mitigation. However, newly developed HFO-1234yf refrigerant possess similar thermodynamic properties to HFC-134a. Important thermo-physical characteristics are tabulated in table 1.1. Note that, based on these similar thermo-physical properties this refrigerant could be considered as direct replacement.

<table>
<thead>
<tr>
<th></th>
<th>HFO-1234yf</th>
<th>HFC-134a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>CF&lt;sub&gt;3&lt;/sub&gt;CF=CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;FCF&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>114</td>
<td>102</td>
</tr>
<tr>
<td>Ozone Depletion Potential</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Global Warming Potential</td>
<td>4</td>
<td>1430</td>
</tr>
<tr>
<td>Boiling Point, (°C)</td>
<td>-29</td>
<td>-26</td>
</tr>
<tr>
<td>Critical Point, (°C)</td>
<td>95</td>
<td>102</td>
</tr>
<tr>
<td>Vapor Pressure, (Mpa)</td>
<td>0.673</td>
<td>0.665</td>
</tr>
<tr>
<td>Liquid Density, (kg/m&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>1094</td>
<td>1207</td>
</tr>
<tr>
<td>Vapor Density, (kg/m&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>37.6</td>
<td>32.4</td>
</tr>
</tbody>
</table>
1.1.3. **Tribological Compatibility**

Tribological compatibility includes ability to form anti-wear films on compressor surface materials. Therefore, an alternative refrigerant would possess this characteristic to ensure a reliable and smooth operation. Furthermore, the frictional behavior and anti-seizure loads must be comparable or better than the existing system. Note that, refrigerants can decompose at the frictional surface and result in different tribo-chemical interactions on the surface. The interactions should be tribologically beneficial so that no system mitigation is required. Moreover, the refrigerant should not adversely interact with the state-of-art lubricants used in today’s compressors. These aforementioned tribological performances must be examined for a reliable operation. In the next chapter, the tribological performance of different materials under various refrigerants will be discussed.

1.2. **SCOPE OF RESEARCH**

1.2.1. **Defining the Research Problem**

A change in working fluid significantly influences the tribological behavior of an interface. Importantly, tribological changes are directly related to energy consumptions by a compressor in MAC system. Therefore, an alternative refrigerant should possess both environmentally and tribologically friendly properties to ensure sustainable replacement. For example, unproven sustainability of HFC-134a is attributed to degradation of tribological performance compared to CFC-12 refrigerant. Since HFC-134a refrigerant will be substituted by new olefin (-C=C-) based refrigerants, the challenging issues are how this replacement will contribute to tribological changes. Note that, this kind of chemistry, as a refrigerant, is novel and its interfacial interactions are unknown. Therefore, to guarantee a sustainable transition, the tribological
behavior of the new refrigerant must be investigated for compressor specific applications. In view of this, the ensuing research problems will address the following questions –

1. Comparison of self-lubricity between HFC-based refrigerant (HFC-134a) and hydrofluoroolefin based refrigerant (HFO-1234yf). This will provide a significant insight to understand the overall tribological performance of common compressor surface materials in the presence of HFO-1234yf refrigerant.

2. Possible tribological interactions of HFO-1234yf refrigerant with state-of-art compressor lubricants. This study will be helpful to identify appropriate lubricants for HFO-1234yf refrigerant. Additionally, this will elucidate whether there is any need for lubricants’ optimization.

3. Clear understanding towards the wear mechanisms of gray cast iron interface under varying loading conditions in HFO-1234yf environment. This study is particularly important for better design approach.

4. Identifying potential advanced polymeric based coating solutions to use with alternative refrigerant. This kind of surface modification is important to design against aggressive loading conditions, enabling high-performance and reliable operations.

### 1.2.2. Novelty of Research

Hydrofluoroolefin (HFO) based refrigerants are a unique innovation to substitute environmentally harmful refrigerants. Tribological behavior of advanced metallic and polymeric surfaces in the presence of such gases is unknown. To date, only few qualitative assessments have been found to address the interfacial issues associated with this refrigerant. However, the reported works will not be sufficed to ensure sustainable design as those are based on
oversimplified assumptions. Moreover, it is not clear how an unsaturated chemical compound will decompose on frictional surfaces and control the wear and friction mechanisms. These two parameters directly govern the compressor’s life-cycle and durability. In order to ensure a sustainable design approach, the tribological properties of this refrigerant are evaluated and future modifications are recommended. Additionally, to provide guidelines for industrial practitioners, tribological investigation is performed from different perspectives, for example identifying suitable lubricant systems.

Another domain of uniqueness is introduction of advanced polymeric based coatings, namely aromatic thermosetting polyester (ATSP) based coatings. The bulk ATSP material has excellent wear resistance and exhibits improved friction behavior when blended with Polytetrafluoroethylene (PTFE). Motivated by ATSP’s excellent performance, this material is being examined as a coating material for compressor’s tribocomponents. Furthermore, interaction of lubricants and polymeric coatings has never been investigated, although this involves significant design challenges. For the first time this will be examined to check possible synergy or adverse interactions, enabling better surface integrity associated with friction and wear.

1.2.3. Impact of Study

Implementing the new refrigerant (HFO-1234yf) will affect the energy consumption and reliability of the MAC compressor industry by altering friction and wear behavior as mentioned before. The results from this research will be served as directive for automotive and refrigerant industries. The physics of friction and wear associated with olefin chemical structure can be used as deterministic mechanisms whether the new refrigerant will be feasible to deploy.
Another potential field of application is in lubricant and additive industries. This research will show run-in behavior in friction coefficient characteristic, suggesting inclusion of optimized additives with state-of-art lubricants. The lubricant-based tribological knowledge will help to develop more advanced synthetic lubricants to use with HFO-1234yf refrigerant. Therefore, the outcomes from this research will be served as recommendations for relevant industries.

Another potential impact area is in coating industries. This thesis will experimentally show better performing polymeric based coatings in the presence of HFO-1234yf/lubricants environment. This study will provide significant insight to develop more advanced coatings for future applications. The benefits and pitfalls from some commercial basic coatings will be addressed, urging to modify coating chemistries or filler materials.

1.3. RESEARCH APPROACH

Pursuing this research, two simultaneous approaches have been taken, namely controlled tribological experiments and materials characterization. For the first approach, tribological experiments will be performed to simulate actual compressor conditions in the presence of HFO-1234yf and HFC-134a refrigerants. This approach has different domains where each area will address different perspective of tribological issues. In the first study, the self-lubricity effect of this new refrigerant will be investigated and will be compared with the existing HFC-134a refrigerant. This study will dictate overall friction and wear response of compressor materials in HFO-1234yf environment. Secondly, lubricants are introduced at the interface to understand the interactions between lubricants and refrigerants. This study will explain how current state-of-art lubricants will behave with HFO- based refrigerants in the frictional zone. Another study is carried out where tribological performance has been evaluated under various loading conditions.
Dominating wear mechanisms have been revealed from this study. Finally, tribological experiments have been carried out over advanced polymeric coating based solutions. Both dry and lubricated conditions have been considered in this case.

**Fig. 1.3:** Experimental and analytical research outline

Subsequent to tribological experiments, the amount of wear has been quantified using profilometric analysis. In addition, morphological evolution of the surface has been revealed under scanning electron microscope (SEM). Since the tribological nature of the materials in the presence of refrigerated environment is mainly dictated by tribochemical reactions, chemical analyses have been performed as well. Chemical elements of surface layer have been identified via Energy Dispersive Spectroscopic (EDS) analysis. In some cases, the chemical state of the
constituting element has been examined utilizing X-ray Photoelectron Spectroscopy (XPS). The systematic approach of the research is outlined in fig. 1.3.

1.4. THESIS OUTLINE

The main objective of this dissertation is to study the tribological behavior of different advanced compressor surface materials in the presence of HFO-1234yf refrigerant. In order to accomplish this objective each chapter will discuss different domains of tribological investigations.

Background on tribological performance of different surface materials in the presence of different refrigerants will be described in chapter two. Chapter three focuses on lubricity effect of HFO-1234yf refrigerant. Results from tribological experiments along with morphological analysis will be presented in this chapter. Understanding towards the science of different tribological behavior will also be elucidated here with the aid of EDS and XPS analyses.

Chapter four describes tribological performance of HFO-1234yf refrigerant under starved lubricated conditions with the introduction of a PAG based lubricant. In this chapter, the tribological performance of HFO-1234yf and HFC-134a will be compared. Morphological and chemical analyses will also be included to explain the underlying wear mechanisms. Interactions between current state-of-art lubricants and HFO-1234yf will be presented in chapter five.

Dominating surface damage mechanisms associated with scuffing and wear failure will be demonstrated in chapter six. A wear mechanism map will be presented, indicating prevailing wear modes, in this chapter along with morphological analyses. Chapter seven will focus on the tribological performance of polymeric coatings in the presence of HFO-1234yf refrigerant. The wear mechanisms and physics will be described with analytical measurements. Chapter eight will summarize the main findings along with ideas for future works.
CHAPTER 2

BACKGROUND ON TRIBOLOGY OF REFRIGERANTS

‘Tribology’ is a derivative word from Greek words ‘tribos’ (τρίβος) and ‘logos’, meaning rubbing and word respectively [29-30]. In practice, this includes controlling friction and wear of critical mechanical components under sliding or oscillatory motion. This term was first coined by J.P. Jost in 1960s, although it is being practiced since the time of Aristotle (384-322 BC). The key components of any mechanical system are durability and sustainability, which is directly related to frictional and wear losses. Therefore, clear understandings towards the mechanism of friction and wear are necessary to ensure a reliable life-cycle of a component. However, the knowledge of tribology was dormant until the early 18th century when the industrial revolution emerged. Unfortunately, environmental quality considerations were significantly neglected after this industrial revolution. In this era, scientists and engineers focused their concentration on the advancement of technologies and exhaust gases were neglected, without measuring future impacts. This wasteful use of such compounds caused an increment of emission of greenhouse gases, leading to an energy crisis in the mid-1970s. As a consequence, regulations have been enacted to control the use of environmentally harmful refrigerants. In response to climate concerns, the new research area of ‘green or environmental tribology’ emerged, dealing with sustainable energy, environmental protection as well as enhancement of effective lifecycle of critical tribomechanical components. Nowadays, tribology is an interdisciplinary field of research investigating efficiency and durability of manufactured systems (lubricants/refrigerants/surface materials). This is believed that, every newly manufactured product will
have impact in mechanical systems. Specifically, the new component will alter the interfacial performance, necessitating clear ideas underpinning the operation.

From a tribological viewpoint, the design and performance of a mechanical system greatly depends on contact severity and lubrication conditions. The main elements for a tribological design consist of surface materials, lubricants, the environment and loading conditions. Altering any of these system parameters will change the tribological performance, which must be investigated. The so-called ‘Streibek curve’ can be used to elucidate contact severity during operation (refer to fig. 2.1). Three different lubricating regimes can be identified in this graph, namely (a) boundary, (b) starved/mixed, and (c) elastohydrodynamic or hydrodynamic lubrication regimes. Among these regimes, boundary and starved lubrication represents the most aggressive conditions, which are encountered during startup and shutdown of a mechanical system. In addition, such conditions prevail due to insufficient replenishment of the lubricant at the contact interface. For engineering practice, this is believed that effective life-cycle of a component will be reduced by $1/10^{th}$ if this is operated under starved lubrication method. Therefore, designing a component under boundary lubrication will provide a directive idea of overall tribological performance.

Importantly, in this regime of lubrication, different surface layers can be originated from tribological interactions among surface materials, lubricants and environmental fluids (liquid or gas) [33-34]. Such kind of interactions are referred as ‘tribobchemical interactions’ and hence the developed layers are ‘tribofilms’. Tribofilms can offer beneficial effect by separating the two sliding surfaces from asperity contact.
The nature and stability of tribofilms is primarily governed by the presence of environmental agents. There are several possible routes, namely adsorption, chemisorption or kinetic chemical reactions, by which tribofilms can be evolved. Regardless of the evolving process, the morphological integrity of tribofilms is crucial. Improved tribofilms can prevent from severe wear and can reduce friction. Moreover, sustainable tribofilms can enhance effective life-cycle of a moving component, even under dry condition. In the case of compressor specific environment, refrigeration can significantly alter the nature of tribofilms. Note that, refrigerants mainly consist of Hydrogen, Halogens, Oxygen or Carbon as discussed in the first chapter. All these elements are chemically reactive and can interact with the system components. A self-lubricating refrigerant has the ability to develop tribofilms under dry condition, meaning less or no requirement of extreme pressure (EP) additive in the lubricant. On the other hand, a poor-
lubricating refrigerant will require significant amount of additives in the lubricant to prevent against premature and catastrophic failures. For instances, HFC-134a refrigerant has less lubricious effect compared to CFC-12 refrigerant. In the later section, tribological nature and tribofilms of some refrigerants will be discussed. Five commonly used refrigerants will be considered based on their chemical elements and chemical bonding. This is believed that five different chemistries which will be described will contribute to understand future refrigerants as well. However, discussions on influence of refrigerant over surface materials are divided into two sections, namely metallic response and polymer coating based response.

2.1. METALLIC RESPONSES: ROLE OF REFRIGERANTS

Chlorine Containing Refrigerants (CFC or HCFC)

Chlorine-based refrigerants are considered as second generation of compounds as classified by J. Calm [8]. This refrigerant offers self-lubricity effect by developing protective tribofilms without any aid from lubrication. The advantageous features of chlorine for tribological applications is known and well documented, making it as an antiwear additive in lubricant industries [35-36]. Its lubricious functionality remains in gaseous conditions as well. Therefore, this is expected that, chlorine-containing refrigerants would exhibit better tribological performance. Komatsuzaki et al. conducted a series of tribological experiments on CFC-12 (R12), HCFC-22 (R22) and HFC-134a (HFC-134a) refrigerants [37]. They observed superior tribological performance for CFC-12 and HCFC-22 refrigerants compared to HFC-134a refrigerant (refer to fig. 2.2). They concluded that elimination of chlorine could lead to deterioration of wear performance in the case of HFC-134a refrigerant. They also found minor influence on tribological performance of HFC-134a refrigerant compared to air. On the other
hand, CFC-12 showed better performance compared to HCFC-22 refrigerant due to the presence of higher chlorine concentration. The observed tribofilm was chloride based, which can be acted as self-lubricating EP agent. As a result, anti-wear film was developed and a reduced wear scar at a specific load.

![Self lubricity: R12 > R22 > Air](image)

**Fig. 2.2:** Self-lubricity effect of CFC-12 and HCFC-22 refrigerants compared to air [37]

**Hydrofluorocarbon Based Refrigerants (HFC-134a)**

Tribological and lubricity effect of HFC-134a based refrigerant has attained significant interest by the scientific community in early and mid-1990s after phase out of chlorine containing refrigerants. This transition was not technologically easy, partly due to the fact that, this refrigerant shows complete immiscibility with mineral oil. Another reason was the reduction of chlorine concentration, a self-lubricating agent. Tribological performance of compressor surfaces was greatly impacted due to this change as discussed before. Development of tribofilms in the case of HFC-134a refrigerant under dry conditions was not well defined. Thus, it is suggested
that, this refrigerant does not have the ability to form tribofilms. Most of the studies in this area focused on formation of tribofilms under lubricated conditions in the presence of HFC-134a refrigerant [38-40]. In addition, it is believed that the performance of HFC-134a refrigerant greatly depends on the choice of lubricants and surface materials. For example, Cong et al. demonstrated that the lubricating effect of this gas depends on the chemical nature of the surface [41-42]. They reported that HFC-134a gas is more effective in the case of covalent ceramics, including Si-C, Si-N, Al-N, and Si-O. The surface interactions resulted in metal fluoride which eventually lowered the friction coefficient as well as the wear rate. It was believed that HFC-134a decomposed on the surface, leading to form an olefin (-C=C-) via polymerization over the nascent surface. This polymerization process accelerates the decomposed products to react with active sites of the surface.

Yoon et al. conducted scuffing experiments in the presence of PAG/HFC-134a system under boundary lubricated conditions [43]. They measured scuffing resistant loads at a wide range of operating conditions including velocities, lubricant supply rate, and roughness parameters. Protective oxide layers, delaying scuffing associated failure, at the interface were identified from their observations. They reasoned that the failure originated from the formation of macroscopic adhesion causing plastic shearing of the bulk materials. On a different study, Ciantar et al. reported the influence of alloying elements on the tribological performance of POE/HFC-134a refrigerant [44]. They also compared PAG/HFC-134 and POE/HFC-134a mixture and concluded that POE/HFC-134a showed better protection against wear. Note that, these studies did not identify any tribofilms, originating from the refrigerant itself.

Note that, HFC-134a refrigerant is now under pressure of being controlled or phased out in the future due to global warming concerns as discussed before. Three refrigerants are being
considered for potential replacement, namely hydrocarbon based R600a (which is flammable), naturally available carbon dioxide R744 (which operates at very high pressures, thus costly), and hydroolefinic based (HFO-1234yf or HFO-1234ze) refrigerants (likely more expensive). The discussion will be continued on these three refrigerants.

**Hydrocarbon (HC-600a)**

Isobutane (R600a) is also considered as another possible replacement of CFC-12 and HCFC-22 refrigerants. This refrigerant is cheap, non-toxic and environmentally benign. However, its performance for compressor specific applications is worse as studied by Kemal et al. [45]. Their experimental investigations have revealed an increase in friction and wear performance for steel versus 100Cr6 alloy in R600a refrigerant. The measured values are higher compare to air. This is believed that presence of R600a blocks formation of oxide layer on the surface. Thus, R600a interacts adversely over the steel surfaces, leading higher wear rate and higher friction. However, with the application Si-rich multifunctional DLC coatings, tribological performance of R600 has improved significantly as studied by De Mello et al. [46]. They have compared R600a with carbon dioxide and air and demonstrated lower friction coefficient for R600a refrigerant. Nonetheless, this gas has limitations due to high flammability issue.

**Carbon Dioxide (CO₂)**

Of the candidate refrigerants, the most promising includes carbon dioxide which is naturally abundant and its tribological behavior is well documented. Pioneering works in this field include the studies done by Demas and Polycarpou. For example, they compared tribological performance of carbon dioxide with other gases, namely, nitrogen, oxygen, air and HFC-134a
They reported beneficial tribological behavior for CO$_2$ over other refrigerants. A lower friction coefficient and wear depth was measured from their tribological investigation as presented in fig. 2.3. They attributed such improving behavior due to formation of carbonate based tribofilms. Note that, they also identified oxide based surface layer in the case of air. However, from friction and wear behavior, this was evident that Carbonate based tribolayes outperformed oxide based tribofilms. Wu et al. also evaluated lower friction coefficient in the presence of carbon dioxide compared to vacuum and air [47]. This study also confirmed the influence of refrigerants on tribofilms in order to predict tribological performance of compressor materials.

**Fig. 2.3:** Tribological comparison of CO$_2$ with other gases [16]
Wu et al. studied the influence of environmental pressure on the tribological behavior of carbon dioxide for 52100 steel interfaces. They observed an optimum pressure for which carbon dioxide exhibits better tribological performance. On a different study, Demas et al. proved that higher environmental pressure is required to obtain improved friction behavior [17]. These studies, therefore, suggested installing of high pressure equipment in the system for utilizing carbon dioxide as a refrigerant.

![Operating pressure of CO2 refrigerant](image)

**Fig. 2.4:** Operating pressure of CO2 refrigerant [47]

Nunez et al. introduced lubricants with carbon dioxide to investigate the interactions between state-of-art lubricants and the refrigerant [48]. They concluded that, Polyalkylene glycol (PAG) based lubricant performs better than Polyolester (POE) based lubricant for the case of carbon dioxide. They obtained higher scuffing loads and lower friction coefficient for PAG/CO$_2$ system compared to POE/CO$_2$ system. Jeon et al. also observed similar findings while they were working with steel versus cast iron interface [49].
**Hydro Fluoroolefin (HFO-1234yf)**

This new refrigerant consists of an olefinic (-C=C-) backbone in its chemical formula. This kind of chemical structure is reactive and can accelerate the polymerization process at the interface. This will be further accelerated due to frictional heating. Therefore, HFO-1234yf will interact with surface materials and lubricants differently than HFC-134a refrigerant. Anti-scuffing and anti-wear properties will be altered due to this interaction. Consequently, there might be an increasing need for lubricating oils containing optimized additives when substitution of HFC-134a has taken place. The mechanism to clarify the contribution of this refrigerant towards tribological behavior is less understood and unknown. Open literature revealed only a qualitative analysis to predict wear in the presence of HFO-1234yf refrigerant as shown in fig. 2.5 [18]. However, this study is not adequate to address the behavior under aggressive operating conditions. Additionally, the self-lubricity of a refrigerant is needed to be examined as a very first approach. That’s why; we investigate the detailed tribological performance of this refrigerant to address – self-lubricity effect, lubricant-materials interactions and influence of polymeric materials.
Fig. 2.5: Qualitative measurement of wear of swash plates and bearing shaft in presence of HFO-1234yf refrigerant [18]

2.2. TRIBOLOGY OF POLYMERIC COATINGS: INFLUENCE OF REFRIGERANTS

In recent years, increasing demand for reliable and efficient operation of compressors has driven intensive research and industrial efforts towards the development of polymeric coatings based surface modification [50-52]. The critical tribo-mechanical systems are often subjected to aggressive tribological conditions associated with higher sliding velocities and loads along with inadequate replenishment of the liquid lubricant at the contact interface as stated earlier. These system parameters, therefore, limit the effectiveness and functionality of liquid lubricants, necessitating the development of protective solid polymeric coatings. However, shifting from liquid to solid lubricant requires system modifications which might be expensive. Furthermore, during this transitional phase the existence of polymeric coatings and liquid lubricants will
overlap, resulting in an interaction of polymer materials and lubricant under contact conditions. Such kind of interaction is also crucially important and plays a vital role to determine the tribological performance of coatings/lubricants systems. Nevertheless, scientific attempts to elucidate the interaction between polymers and lubricants are essentially nonexistent, especially addressing the issues related with tribocompatibility. Note that, adverse reactions may lead to an early failure of the mechanical components due to severe wear or higher friction. This negative effect can be alleviated by choosing an advanced polymer coating which offers both better tribological behavior and improved interaction with the existing system environment (working medium and lubricant). Therefore, a detailed tribological investigation is required to identify the functional polymers, demonstrating frictional and wear behavior under realistic operating conditions. Herein, we consider automotive air-conditioning compressor systems, potential application field for polymeric coatings, to investigate the tribological performance of advanced coatings and their interactions with current state-of-art synthetic lubricants.

Commercially available PTFE- and PEEK-based high bearing polymeric coatings have attracted the attention of several researchers in the field of air-conditioning compressor systems in recent years [53-56]. Among the candidate coating materials, PTFE has received significant attention due to its low shear strength, and resulting low friction coefficient [57-58]. However, continuous transfer of the polymeric materials to the counter surface is typical characteristic of PTFE material, causing a higher wear rate. That’s why; different filler materials are blended with PTFE to improve wear resistance and to control the wear rate of PTFE. For example, PEEK blended with 10-20% PTFE showed better tribological behavior, ensuing low friction coefficient and high wear resistance compared to neat PTFE [59-60]. Nunez et al. applied this coating for
MAC system in the presence of HFC-134a refrigerant [53]. They reported better tribological performance for this coating compared to PTFE/MoS$_2$ coating. However, their work cannot be transferred to modern MAC systems due to change of the working environment (refrigerant in this case). Note that, the tribological performance of polymeric materials and coatings significantly depends on working environment i.e., refrigerant and lubricant. That’s why, Yeo et al. studied the tribological performance of PEEK and PTFE based coatings for MAC systems in the presence of alternative refrigerant carbon dioxide CO$_2$ [55] Interestingly, they demonstrated better performance for PTFE/MoS$_2$ compared to PTFE/PEEK coating in CO$_2$ environment, unlike HFC-134a based refrigerant. This would further support the dependency of the working environment on the tribological performance of the polymeric coatings as shown in fig. 2.6.

**Fig. 2.6:** Tribological performance of commercial coatings: (a) in CO$_2$ environment [55], and (b) in HFC-134a refrigerant [53]

Nevertheless, to-date no relevant research addressing the tribological performance of polymeric coatings in HFO-1234yf environment is available. Akram et al. investigated the responses of metallic interface and lubricant for this refrigerant [61-63]. They demonstrated frictional instability for this refrigerant, indicating required optimization of the lubricant or polymeric
coatings. Since liquid lubricants often fail to endure aggressive conditions, polymeric based coating solution has been emerged as discussed before.

This warrants a comprehensive study in order to measure the tribological performance of polymeric coatings in the presence of HFO-1234yf refrigerant under dry and lubricated conditions. All the aforementioned coatings for MAC system produced some degree of wear, limiting the effectiveness of the coating system. Moreover, wear particles can easily get trapped into the refrigeration cycle systems and will deteriorate the overall performance of the refrigerant cycle. This would trigger to formulate new coatings with almost no wear. Along this line, we have developed ATSP blended with PTFE coating for compressor applications [64-66]. This material has good thermal and dimensional stability along with very high wear resistance. These features would be utilized to develop this material based coating. A brief description about this material will be elaborated in chapter seven.
CHAPTER 3

SELF-LUBRICITY OF HFO-1234YF REFRIGERANT

This chapter will elucidate self-lubricity effect of new alternative refrigerant (HFO-1234yf). This is believed that a tribocompatible refrigerant will offer better lubricity at the contact interface even under dry condition, meaning absence of liquid lubricating oil. The self-lubricity of a refrigerant can be better understood if this is tested under such unlubricated condition. Furthermore, the absence of liquid lubricant simulates extreme conditions, since it is well known that with the increase of load or decrease of relative speed in a compressor, the lubricating film at the interface may vanish and eventually metal-to-metal contact occurs. Such contacts are usually referred as ‘dry’ or ‘unlubricated’ contact, which can also be experienced when the compressor starts from the off-state as mentioned in the previous chapter. The severity of dry contact includes a sharp increase in friction and wear along with the degradation of structural integrity at the contact zone.

This chapter will also compare lubricity effect between the new refrigerant and existing HFC-134a refrigerant. Note that, one of the main differences between the two refrigerants is the presence of unsaturated (-C=C-) bond in the HFO refrigerant, which is not the case for the traditional refrigerant. It is anticipated that this difference could contribute in their chemical reactivity and ability to adhere onto the surfaces. Tribological results from step loading (or scuffing) experiments will be presented. Such experiments are performed to determine the maximum critical load that the interface can sustain before failure, referred to as “scuffing load.”
At this load, the interface becomes unstable and loses its functionality. This mechanism is characterized by sudden increase of the friction coefficient [67-70]. Morphological changes of the topmost surface layers of gray cast iron will be also presented employing scanning electron microscopy (SEM). Tribochemical analysis will be explained to reveal the underlying mechanisms towards different tribological behavior associated with refrigerants.

3.1. EXPERIMENTAL PROCEDURE

3.1.1. Controlled Tribological Experiments

Compressor conditions were simulated by performing experiments with a specialized High Pressure Tribometer in a pin-on-disk configuration [70, 16]. Two common material tribopairs were used, namely, gray cast iron disk versus gray cast iron pin and Aluminum alloy (Al390-T6) disk versus 52100 hardened steel shoe [15]. The constituent elements of both tribopairs are listed in Table 3.1. The geometrical configurations of the disks/pins setups are depicted in Fig. 3.1, where the stationary pin or shoe was held constant with a self-aligning holder against the upper rotating disk. To reduce the influence of surface roughness on the tribological properties, all the disks were machined and polished using similar technique, namely lapping. The experiments were performed at room temperature of 24 °C with a constant refrigerant chamber pressure of 0.2 MPa. This pressure is found at the inlet of the automotive air-conditioning compressor. The room temperature was chosen as this is the typical average temperature between inlet and outlet of the compressor. In addition to that, the effect of temperature on the lubricity of the refrigerant is precluded by selecting room temperature. Note that, the replication of the actual conditions found in the automotive air-conditioning compressor is complicated. Therefore, more aggressive operating conditions were used in this study for conservative design approach with the
consideration of dry contact. The experiments were conducted in the presence of either HFC-134a or HFO-1234yf refrigerant. The sliding velocity of the tribo-contacts was about 2.4 m/s. In general, automotive air-conditioning compressor runs at variable speed depending on the engine speed [71-72]. However, this speed is being used for experimental simulation in order to evaluate tribological performances at the compressor material interface. Normal step loading of 20 N/min was used for 20 minutes of testing duration unless scuffing failure occurred earlier. A preload of about 50N was applied to ensure the complete and smooth contact between disk and pin or shoes.

Table 3.1: Chemical composition of gray cast iron and Al390-T6 alloy [15].

<table>
<thead>
<tr>
<th></th>
<th>Gray Cast Iron</th>
<th>Al390-T6 Alloy</th>
<th>52100 Steel Alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum, Al</td>
<td>-</td>
<td>76.0</td>
<td>-</td>
</tr>
<tr>
<td>Carbon, C</td>
<td>3.0-3.4</td>
<td>-</td>
<td>0.9-1.1</td>
</tr>
<tr>
<td>Copper, Cu</td>
<td>-</td>
<td>3.0-4.0</td>
<td>-</td>
</tr>
<tr>
<td>Iron, Fe</td>
<td>Balance</td>
<td>1.0</td>
<td>Balance</td>
</tr>
<tr>
<td>Magnesium, Mg</td>
<td>-</td>
<td>0.4-1.0</td>
<td>-</td>
</tr>
<tr>
<td>Manganese, Mn</td>
<td>0.7-0.8</td>
<td>0.5</td>
<td>0.25-0.45</td>
</tr>
<tr>
<td>Silicon, Si</td>
<td>2.5-2.6</td>
<td>16-18.5</td>
<td>0.15-.35</td>
</tr>
<tr>
<td>Zinc, Zn</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Chromium, Cr</td>
<td>-</td>
<td>-</td>
<td>1.3-1.6</td>
</tr>
</tbody>
</table>

The samples were ultrasonically cleaned with acetone before each experiment and then rinsed with propanol. Each experiment was performed at least twice to ensure reproducibility. After each experiment, surface topography and wear were quantified using a Tencor P-15 contact profilometer.
Fig. 3.1: Materials used for tribological experiments: (a) gray cast iron disk versus (b) nominally flat gray cast iron pin and (c) Al390-T6 disk versus (d) 52100 crowned steel pin (or shoe). Arrows on the pins indicate the contact side.

3.1.2. SEM/EDS

Scanning electron microscopy was employed to identify the morphological changes of the surface of the gray cast iron disks and pins in the presence of both refrigerants. A JEOL 6060LV SEM operated at 20 KV was used to obtain the surface topography. After the tribological experiments, EDS was used to obtain the chemical composition of the worn surfaces. An area map of 400 μm x 400 μm was used in this purpose.

3.1.3. XPS

XPS analysis [73-74] was conducted on a Perkin Elmer PHI 5400 spectrometer equipped with a hemispherical electron analyzer and a non-monochromatic Mg Kα X-ray source (1253.6 eV). All reported photoelectron binding energies are referenced to the C 1s feature of adventitious carbon at 285 eV (internal standard) to take into account charging effects. XPS studies were performed inside and outside the wear tracks of the gray cast iron surfaces and on the gray cast iron pins (counter surface). The survey spectra were acquired at pass energy of 178.95 eV. A certain
region of the spectrum was scanned a number of times to obtain a good signal-to-noise ratio (the detailed scan was performed at a pass energy of 35.75 eV). The measurements were performed in three different areas inside the wear track for each individual sample for repeatability purposes. The peak fitting was performed using Casa XPS (version 2.3.14) software.

3.2. RESULTS AND DISCUSSIONS

3.2.1. Tribological Observations

Fig. 3.2 shows typical tribological results in the presence of both HFC-134a and HFO-1234yf refrigerants, for the gray cast iron interface and the aluminum alloy interface. From Fig. 3.2(a) it is observed that the gray cast iron interface exhibits lower friction coefficient (of about 0.2) compared to Al alloy interface (of about 0.6). More importantly, shown in Fig. 3.2(b), the gray cast iron interface didn’t fail during the whole test duration of 20 minutes, while Al390T6 failed at the very early stage of the tribological experiment. Therefore, gray cast iron interface offered superior tribological performance in the presence of HFO-1234yf, compared to Al390-T6 surface versus 52100 steel interface.

Fig. 3.2(c) presents the frictional behavior of the contact interfaces in the presence of HFC-134a refrigerant. In this case, scuffing failure of the gray cast iron interface is also observed. Fig. 3.2(d) shows the step-load experimental profiles until failure of the interfaces in the presence of HFC-134a. From these figures, gray cast iron interfaces exhibited better performance compared to Al alloy, in the presence of HFC-134a as well.
Fig. 3.2: Tribological experimental results comparing the frictional behavior Al390-T6 interface and gray cast iron interface in the presence of HFO-1234yf refrigerant: (a) friction coefficient, (b) Step-loading, and HFC-134a: (c) friction coefficient, (d) Step-loading.

From the tribological experiments presented above one can draw the conclusion that aluminum/52100 steel interfaces exhibit the same performance in the presence of both refrigerants. Therefore, for probing the impact of the two refrigerants and to compare the gray cast iron tribological performance in their presence, next we concentrate on the gray cast iron interface. Since in the presence of HFC-134a, the cast iron interface failed due to scuffing, it indicates that no tribologically protective layers on the topmost surface of either the disk or pin have been formed. On the other hand, in the case of HFO-1234yf refrigerant, the interface sustains its lubricity for the whole duration of the experiment without failure. Note that the initial
friction coefficient was about 0.30 and after running-in it decreased and stabilized at 0.20. The tribological performance demonstrates the positive lubricity effect of the new refrigerant having unsaturated olefin bond. It is hypothesized that this lubricity effect can be attributed to the formation of tribolayers. This passive layer can be formed based on a tribochemical reaction between the gray cast iron surface and fluorine species coming from the unsaturated refrigerant breakdown, which is associated with the combined effect of mechanical forces and frictional heating. A detailed investigation of this layer was performed using SEM, EDS and XPS as will be discussed in the sections below.

3.2.2. Wear Analysis

Fig. 3.3 presents optical microscopy images of gray cast iron disks after testing in the presence of HFO-1234yf (Fig. 3.3(a)) and in the presence of HFC-134a (Fig. 3.3(b)) refrigerants. For comparison purposes, Fig. 3.3(c) and Fig. 3.3(d) show the scuffed Al390-T6 alloy disk in the presence of HFO-1234yf and HFC-134a, respectively. A clear difference in surface morphology is observed in the case of Al390-T6 disk which appear rough, in contrast with the gray cast iron disks in the presence of HFO-1234yf where the worn surfaces are very smooth.

Using surface profilometric scans the wear was quantified, as shown in Fig. 3.4. Specifically, no significant surface wear was found after the experiments with HFO-1234yf refrigerant except some minor burnishing, as shown in Fig. 3.4(a). In this case, the wear depth varies from 1 µm to 2 µm which is negligible compared to the wear depth in the case of HFC-134a, which is about 15 µm, Fig. 3.4(b).
**Fig. 3.3:** Optical Microscopy images of tested gray cast iron disks in the presence of (a) HFO-1234yf, (b) HFC-134a, and Al390-T6 disks in the presence of (c) HFO-1234yf, (d) HFC-134a.

**Fig. 3.4:** Profilometric scans of the cast iron wear tracks after experiments in the presence of (a) HFO-1234yf and (b) HFC-134a.
3.2.3. SEM Analysis

Figures 3.5(a) and 3.5(b) depict the SEM images after tribotesting of gray cast iron in the presence of HFC-134a and HFO-1234yf, respectively. Referring to Fig. 3.5(a), severe abrasive wear was observed in the presence of HFC-134a. A series of grooves are seen, which indicate scratching along the sliding direction due to abrasive wear. Also, seen in the same SEM image is adhesive type of wear, where material was transferred from the disk surface to the counter pin surface, which is clearly seen under higher magnification, Fig. 3.5(c). In the presence of HFO-1234yf, after tribotesting a smoother wear track is observed. This corroborates with the retaining of the protective tribolayer, which remains intact, Fig. 3.5(b). In this case, no abrasive wear was evident and this intact tribolayer will be further discussed in the XPS section. The SEM image revealed a smoother counter pin surface as well, which is shown in Fig. 3.5(d). The SEM analysis of the aluminum interfaces is not discussed here as this interface didn’t show significant difference in the cases of the two refrigerants. However, the EDS analysis was performed for both contact pairs, namely gray cast iron/gray cast iron and aluminum/52100steel to investigate the chemical composition of the worn surfaces.
**Fig. 3.5:** Scanning Electron Microscopy images after tribotesting of gray cast iron: (a) disk, HFC-134a, (b) disk, HFO-1234yf, (c) pin, HFC-134a, (d) pin, HFO-1234yf.

### 3.2.4. EDS Analysis

EDS results are presented in Fig. 3.6 where the spectra of both contact pairs and in the presence of both refrigerants are provided. Spectrum 1 portrays the elemental chemical composition of the virgin (no refrigerant exposure) gray cast sample for comparison purposes. Spectrum 2 shows the chemical composition of the worn surface (inside the wear track) in the presence of HFC-134a. Spectrum 3 presents the EDS spectrum obtained inside the wear track (HFO-1234yf), while spectrum 4 is from the periphery of the contact region in the presence of HFO-1234yf. In both cases, inside and at the periphery of the wear track (Fig. 3.6, Spectra 3 and 4), fluorine was clearly present. However, there is no detectable fluorine in the case of gray cast iron in the
presence of HFC-134a refrigerant (Fig. 3.6, spectrum 2). The qualitative chemical composition presented in spectrum 2 is similar with that of the virgin sample (spectrum 1) indicating no chemical changes (minimum reactivity) during the tribo-experiments in HFC-134a environment. These findings, along with the SEM results presented above, support the development of a fluorine-enriched tribolayer in the presence of HFO-1234yf with cast iron interface. These findings are in agreement with the XPS analysis (next section). It is suggested that the fluorine-based adsorbed layer provides anti-scuffing properties to the gray cast iron surface. Fluorine-containing species onto the surface, originated from the refrigerant fragmentation, are likely linked with the improved tribological performance of gray cast iron in the presence of HFO-1234yf refrigerant.

Spectrum 5 depicts the bulk chemical composition of the virgin Al390-T6 alloy. A strong peak for Al and Si were detected which are the main components of the Al390-T6 alloy along with a minor peak for Cu. Spectrum 6 illustrates the chemical analysis realized in the worn Aluminum surface in the presence of HFO-1234yf refrigerant. No chemical change was detected after the tribo-experiments in HFO-1234yf environment. Also no fluorine peak was identified either due to the very early scuffing of the interface (not enough time for the fluorine layer to be formed or due to an insufficiently adhered fluorine layer, which was expelled from the contact zone due to the severity of the contact conditions). Based on the above results, it can be stated that no protective layer was developed at the aluminum interface, a condition that results to a higher friction coefficient and scuffing failure.
**Fig. 3.6:** EDS spectra of different material interfaces. Spectrum 1: Gray cast iron (virgin sample), Spectrum 2: inside the wear track, HFC-134a. Spectrum 3: Gray cast iron, inside the wear track, HFO-1234yf. Spectrum 4: Gray cast iron, at the periphery of the wear track, HFO-1234yf. Spectrum 5: Al390-T6, virgin sample and Spectrum 6: Al390-T6, inside the wear track, HFO-1234yf.
3.2.5. XPS Analysis

As it was shown above, in the case of HFO-1234yf refrigerant, the friction coefficient remained low for the duration of the test, but this was not the case when HFC-134a refrigerant was used. X-ray photoelectron spectroscopy (XPS) was used to study the chemical environment inside and outside the wear tracks in the cases of HFO-1234yf (not scuffed, test duration, t=20 min), HFC-134a (scuffed, t=6 min) and HFC-134a (not scuffed, at t=4 min). The shorter experiment for HFC-134a was performed to be able to analyze the tribolayer and not the substrate (as in the scuffed case).

Figs. 3.7(a-c) present the C1s, Fe2p and F1s core level spectra obtained on the gray cast iron sample (in the presence of HFO-1234yf) tested after 20 min of tribo-experiment (equivalent to 450N of normal load) along with the Fe2p spectrum of the virgin (no refrigerant exposure) gray cast iron sample, and Fig. 3.7(d) presents the F1s spectra obtained on gray cast iron in the presence of HFC-134a refrigerant under non scuffed conditions (control experiment, t=4 min). No Fluorine was detected in the case of HFC-134a scuffed conditions. In the case of C1s spectrum, the peaks at 287 and 289 eV correspond to C-CF and C-C-F_{n} bonding environment, two different carbon atoms in terms of chemical surroundings [73-75], whereas the peak at 285 eV corresponds to -CH_{2}- impurity, that is always present. Fig. 3.7(b) presents the Fe2p core level spectra which demonstrate the presence of Fe in FeF_{3} (~713 eV) and Fe_{2}O_{3} (~710 eV) environments. Comparing the Fe2p spectrum of the virgin gray cast iron with the rest of the spectra it is observed that as the analysis is moved from the virgin surface to OWT (outside the wear track)→bordeline→IWT (inside the wear track) the contribution of the FeF_{3} component is progressively increasing. In particular, the FeF_{3} component contribution is turning from zero (virgin) to low (OWT) and high (borderline, IWT), talking always in a comparative manner.
**Fig. 3.7:** (a, b, c) C1s, Fe2p and F1s core level spectra obtained on gray cast iron in the presence of HFO-1234yf refrigerant along with the Fe2p spectrum of the virgin (no refrigerant exposure) gray cast iron sample (b) and (d) F1s obtained on gray cast iron in the presence of HFC-134a refrigerant under non scuffed conditions (control experiment, t=4 min). IWT: inside the wear track; OWT: outside the wear track.

In the regions of Fe 2p3/2 and Fe 2p1/2 the components corresponding to iron fluoride (~713 and ~727 eV) appeared as tails at the higher binding energy side of the peak (lowering part of the spectrum) in the case of spectrum corresponding to the OWT region. These peak components
appeared as "true" part of the peak in the case of inside and borderline of the wear track which would imply a higher contribution of iron fluoride component. Fe$_2$O$_3$ is due to surface oxidation that took place due to air exposure of the sample. Peak fitting in the iron peak Fe2p3/2 region would not be accurate due to the Fe satellite peak.

The sample tested in the presence of HFO-1234yf refrigerant has been analyzed inside, outside and in the borderline of the wear track. Based on Fig. 3.7(c), it can be seen that two clear peaks of fluorine-containing species are observed, based on the binding energies, inside and at the borderline of the wear track. In particular, the peaks at 688.6 and 684.8 eV correspond to the organic (C-F) and inorganic (e.g., Fe-F) species with a 24% and 76% surface atomic concentration, respectively, i.e., 1:3.2 ratio (based on peak fitting). The inorganic species (Fe-F) are originating from the tribochemical reaction between gray cast iron of the disk and fragmented C-F species coming from the refrigerant breakdown under the application of mechanical forces during tribotesting. It is important to notice that outside the wear track only traces of fluorine-based species could be identified (signal intensity which is slightly above the noise). This result further supports that the combine effect of mechanical forces and heat along with the chemical nature of the new refrigerant (carbon-carbon double bonds) makes the difference inside the wear track and sustains a low friction through the formation of a fluorine-rich protective layer. In the case of gray cast iron in the presence of HFC-134a refrigerant (scuffed, t=6min) no fluorine was detected by the XPS (tested under identical loading conditions). Based on the fact that the experimental conditions applied were the same and the main difference is the presence of unsaturated (HFO-1234yf) or not (HFC-134a) carbon-carbon bonds, it can be stated that in the case of the unsaturated C=C (double bond) containing refrigerant, the protective tribofilm is more strongly adsorbed and adhered to the disk surface than in the case of the saturated bonds.
containing refrigerant (C-C, single bond). It cannot be excluded that a tribolayer was formed in the case of the HFC-134a (saturated) refrigerant but under the heat and mechanical forces along with the loose adsorption its removal from the contact zone took place.

A control experiment in the presence of HFC-134a was performed with total experiment duration of 4 min in order to avoid scuffing (observed at 6 min) and be able to analyze the formed tribolayer, if any. The XPS results are presented in Fig. 3.7(d), where the F1s core level spectra inside and outside the wear track are presented. A peak at 685 eV is clearly seen which corresponds to the inorganic metal fluoride species, most likely FeF$_3$, due to the predominant presence of Fe in the disk surface. Though, it can be seen that the peak is more pronounced inside the wear track. A minor peak at 688 eV corresponds to the fluorine-containing organic species (e.g., C-F-), and is only seen in the case of the analysis inside the wear track.

In the case of gray cast iron pins investigated following tribotesting in the presence of either HFC-134a or HFO-1234yf refrigerants, no fluorine-containing species were identified. This corroborates for the disk well-adhered tribologically protective layer in the case of HFO-1234yf refrigerant. In the case of HFC-134a, the pin analysis depicts an insufficiently low amount of fluorine-containing species, which were expelled out of the contact zone (low adhesion) and not even transferred to the counter surface contributing ultimately to high coefficient of friction.

3.3. TRIBOCHEMISTRY DISCUSSION

Fluorine-enriched layers have been reported to provide scuffing resistance and offer better tribological properties [76-78]. At this point some simple chemical considerations should be taken into account in order to understand the formation of the fluorine-containing tribolayer. First it is known that the -C=C- double chemical bonds are more reactive than the single bonds
since the electrons of the double bond are unstable [79]. During the gray cast iron tribotesting, material removal is taking place and bonds are breaking. The newly exposed bonds on the surface, i.e., dangling bonds, are prone to react and this is enhanced in the case of the new refrigerant (HFO-1234yf). The freshly exposed bonds react with the surrounding atmosphere. In our case, the surrounding atmosphere is the refrigerant used. This is more obvious in the case of the new refrigerant which is more prone to get adsorbed onto the surface. This happens due to the fact that the new refrigerant has C=C double bonds which means a more delocalized and labile electronic cloud. This is favourable cause lead the surface to a more energetically stable state (reduction of surface energy). The increased reactivity in the case of unsaturated refrigerant likely leads to an increased coverage of adsorbed refrigerant (likely refrigerant fragments) which forms a more homogeneous protective layer (confirmed by the morphological SEM findings). The layer is also well adhered onto the surface (since it is still present when XPS and EDS studies were carried out, which was after cleaning the samples with acetone prior the analysis).

The normal load and the mechanical motion that is experienced under tribological testing facilitate the tribochemical reaction which leads to metal fluoride species formation. In the case of the saturated HFC-134a refrigerant, we have less extended adsorption.

In terms of the C-F bonds present in both refrigerants (different chemical environments), C-F bonds are highly polar bonds ((C\(\delta^+\)-F\(\delta^-\)), which are one of the strongest bonds. This is why fluoroalkanes exhibit very low reactivity since C-F bond is shorter than the C-H bond [34]. These considerations are supported by the XPS results presented in Figs. 3.7(c) and 3.7(d), where in the case of HFC-134a the lack of reactivity leads to a no adhesive organic C-F layer outside the wear track. During testing the dangling bonds are exposed, and the cast iron surface is more prone to organic fluoride formation, which however is still limited due to the short duration of
this test (growth process of the organic C-F layer is likely controlled kinetically). At the same time the metal fluoride component is increased inside the wear track (Fig. 3.7(d)) due to the formed dangling bonds which exhibit an intrinsic enhanced reactivity. In the case of HFO-1234yf, where the reactive unsaturated bonds (C=C) are present, both fluoride components, metallic and organic, are well formed. The mechanical forces and heat causes fragmentation of the refrigerant and a subsequent formation of active C-F species takes place. These species are suffice to develop the fluorine-enriched components (e.g. metal fluorides, F-containing organic layer) through adsorption onto or reaction with gray cast iron surface. In the case of cast iron in HFC-134a environment where scuffing took place (t=6min), no fluorine species were identified.

3.4. CONCLUSIONS

A comparative study of the tribological performance of two refrigerants namely HFO-1234yf and HFC-134a was carried out. The tribological experiments were performed under unlubricated conditions for better understanding of the lubricity of the refrigerants (decoupling lubricant-refrigerant effects). Two commonly used material pairs (gray cast iron/gray cast iron and aluminum alloy/52100 steel) were investigated, with gray cast iron performing better in the presence of both refrigerants, compared to the aluminum alloy interface. The tribological experimental results demonstrated a better frictional behavior in the presence of the new environmentally friendly refrigerant HFO-1234yf with the gray cast iron pairs. This better performance was due to the formation of a protective layer on the disk surfaces. SEM microphotographs revealed the smoothness of this passive layer in the gray cast iron disks in the presence of HFO-1234yf refrigerant. This layer also resists further wear, which was seen from optical microscopy and wear profiles. There was no such tribolayer found in the presence of HFC-134a refrigerant. EDS analysis showed the presence of fluorine in the presence of HFO-
1234yf environment for gray cast iron. This fluorine-based species in the tribolayers are responsible for sustaining a low coefficient of friction at the interface and a smooth pin surface, as revealed using SEM analysis.

From the XPS analysis, the chemical environment of the fluorine-containing layer was obtained. It was found that fluorine-containing species composed the protective layer. This fluorine-based species were coming from the unsaturated HFO-1234yf breakdown. These species are highly reactive and subsequently strongly adhered to the surface. However, there was no fluorine substance in the presence of HFC-134a and can be inferred, based on the early scuffing of this case, that no protective layer was observed. The feature of forming a protective layer on the cast iron surface is very important. Therefore, HFO-1234yf offers excellent lubricity in comparison to HFC-134a for gray cast iron material interfaces.
In this chapter, a comparative tribological investigation between HFO-1234yf and HFC-134a refrigerants, under boundary lubrication method, will be discussed. In current compressor systems, lubricants are used and could play an important role in determining the tribological properties, especially under starved/boundary lubricated conditions, which was excluded in the previous chapter. Under such starved lubricated conditions, the maximum critical load at the interface, termed as scuffing load/resistance, along with the frictional resistance, wear, and subsurface contact temperature are very important and could lead to sudden catastrophic failure of lubricated sliding contacts as mentioned in the previous chapters. This severe phenomenon of wear is accompanied by abrupt rise in friction, and sometimes associated with noise and vibration.Delaying or eliminating scuffing failures in the presence of lubricant/refrigerant mixture means better performance, i.e., the interface can withstand higher load in that particular refrigerant/ lubricant mixture. In addition to scuffing performance, this chapter will explain the wear and friction performance using constant load experiments.

During the lifetime of a compressor, different stages of wear may occur including running-in and steady-state wear as discussed in chapter 2. The initial stages of running-in wear, especially under boundary/mixed or starved lubricated conditions are critical and strongly influence the overall tribological performance [80]. Starved lubricated conditions in a compressor (i.e., in the absence of full film conditions) represent aggressive operating conditions, which are either encountered by tribopairs away from flooded areas, or during transient operation. In this work, a
small predetermined amount of lubricant is directly applied at the interface, which is also flooded with vapor refrigerant. Polyalkylene Glycol (PAG) lubricant, linear polymer of ethylene and propylene oxides having the general formula \( RO-[CH_2CHOCH_3]_n[CH_2CH_2O]_m-H \), will be used for this purpose. Note that, PAG is commonly used in automotive air-conditioning compressors and has good miscibility with the refrigerant and good compatibility with compressor materials, including elastomers [81].

### 4.1. EXPERIMENTAL PROCEDURE

The experimental procedures are almost identical as described in chapter 3. However, the experimental and operating conditions are different in this case. Three different sets of experiments have been performed to understand the interfacial behavior under boundary lubricated condition. Since morphological investigations will be extensively use in this work, microstructure of virgin cast iron surface has been shown here for better comparison. Additionally, all the experiments will be carried out under starved lubrication method. The lubricant will be applied directly at the interface before initiating the experiments as shown in fig. 4.1b. This is believed that this method of lubrication can simulated boundary lubrication regime. The tribo-contancts are cast iron disk versus cast iron pin, simulating pin-on-disk configuration.

The first set of experiments was scuffing type experiments under step loading at room temperature of 23°C. Two different refrigerants were used namely, HFO-1234yf and HFC-134a. Details of the refrigerants can be found in the manufacturer’s data sheet [chapter 1]. The chamber pressure was kept constant at 0.2 MPa, which was found at the inlet of automotive air conditioning compressor system. A small amount (about 23 mg) of PAG lubricant (Idemitsu
Kosan Co., Ltd, Grade: PZ68S) was applied directly at the interface as shown in fig. 4.1b, before the initiation of the test. This lubrication method precluded the influence of lubricant supply rate and variability of pressure/miscibility effect on the tribological performance. A rotational speed of 1000 rev/min which corresponds to a linear speed of 2.4 m/s was used. The interfacial normal load was increased in steps of 89 N every one minute until scuffing occurred (as characterized by an abrupt change in friction).

**Fig. 4.1:** (a) Microstructure of cast iron in SEM mode, (b) Method of applying lubricant

Experiments in Set 2 and Set 3 were carried out by keeping the normal load constant to measure the wear under starved lubrication. Set 2 experiments were performed at 222 N for 30 minutes in the presence of both refrigerants, while Set 3 experiments were conducted at 445 N. Besides the loading schemes, the remaining experimental parameters were identical in all three Sets of experiments, as detailed in Table 4.1. Note that, wear experiments were also conducted at 222 N under dry condition in the presence of HFO-1234yf only, to understand the influence of lubricant in the tribological performance.
Table 4.1: Summary of experimental conditions

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Set 1</th>
<th>Set 2</th>
<th>Set 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of experiment</td>
<td>Scuffing</td>
<td>Wear</td>
<td>Wear</td>
</tr>
<tr>
<td>Direction</td>
<td>Unidirectional</td>
<td>Unidirectional</td>
<td>Unidirectional</td>
</tr>
<tr>
<td>Loading</td>
<td>89 N/min</td>
<td>222 N</td>
<td>445 N</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>23</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>Chamber Pressure, MPa</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Lubricant</td>
<td>PAG</td>
<td>PAG</td>
<td>PAG</td>
</tr>
<tr>
<td>Amount of Lubricant, mg</td>
<td>23</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>Linear Speed, m/s</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
</tr>
</tbody>
</table>

4.2. RESULTS AND DISCUSSION

4.2.1. Friction and Scuffing Performance

Fig. 4.2 depicts typical experimental results for Set 1 scuffing experiments, comparing the performance of HFO-1234yf with HFC-134a under identical conditions. Fig. 4.3 illustrates the tribological results obtained from wear experiments. Fig. 4.2a shows the maximum scuffing load and Fig. 3b presents the frictional behavior in the presence of the two refrigerants. As seen in Fig. 3a, the scuffing resistance of the cast iron-cast iron interface in the presence of HFC-134a environment was approximately 600 N, whereas for HFO-1234yf was twice as much at about 1250 N.

The steady-state friction coefficient (before scuffing occurred) in the presence of HFC-134a was slightly higher (0.09) compared to HFO-1234yf (0.075). These tests indicated the maximum interfacial load that a tribo-pair can withstand, and their lubricity (measured via their steady-state friction coefficient). Clearly, the interface could sustain a significantly higher load in the
presence of HFO-1234yf refrigerant, compared to HFC-134a under starved lubrication. Note that these observations, which were under starved lubrication, were in accord with our previous study under dry conditions [chapter 3].

**Fig. 4.2:** Comparison of (a) scuffing load, and (b) friction coefficient in the presence of HFO-1234yf and HFC-134a refrigerants (Set 1, Table 4.1).

**Fig. 4.3:** Experimental results under constant load wear experiments in the presence of HFO-1234yf and HFC-134a: (a) friction coefficient, Set 2 (222 N), Set 3 (445 N), (b) near-contact temperature Set 2 (222 N).
In-situ friction coefficient and near-contact temperature under constant load wear experiments (Sets 2 and 3, Table 1) are presented in Fig. 4.3. The friction behavior under the two different loadings is shown in Fig. 4.3a, comparing the tribological performance of the two refrigerants. The friction characteristic of HFO-1234yf refrigerant under dry condition is also presented.

In all cases the initial transient friction coefficient behavior was somewhat erratic, showing fluctuating values around 0.1 due the starved lubricated conditions and until the surfaces were run-in. Interestingly steady-state behavior was delayed until about 2,800 m sliding distance, even though the near contact temperature reached steady-state after 1,400 m. The steady-state values were almost the same for both refrigerants. At the low load (Set 2, 222 N), the average friction coefficient for HFO-1234yf was 0.06 compared to 0.065 for HFC-134a. At the higher load (Set 3, 445 N), the interface failed in the presence of HFC-134a, before the completion of the experiment. In contrast to the HFC-134a environment, the tribo-samples were able to operate successfully without failure for the entire duration of 4,320 m sliding distance in the presence of HFO-1234yf refrigerant. Thus, it was envisaged that as the test progressed, tribo-beneficial layers developed at the interface in the presence of HFO-1234yf refrigerant, which protect the substrate from adhesive wear. It is worthy to note that, even under dry condition the experiment did not fail and the average friction coefficient was about 0.16.

In HFO-1234yf environment, an interesting trend in the frictional behavior is observed after the initial run-in period for both dry and starved lubricated conditions. As indicated above, the initial friction coefficient was low and then increasing and fluctuating, and subsequently becomes stable. This characteristic was believed to be due to the chemical reactions at the interface which eventually lead to the formation of the beneficial tribo-layers. Thus it was hypothesized that after this stage which can also be termed as “transitional phase” preventive tribo-layers were
formed on the surface. This conjecture will be verified with the aid of SEM and XPS analysis. No such behavior was observed in HFC-134a environment, and thus the tribo-layers formed should be different.

Comparing the overall tribological behavior under unlubricated [chapter 3] and starved lubricated conditions, clearly starved lubricated conditions, under both HFO-1234yf and HFC-134a refrigerants, offer significant tribological benefits, as far as maximum load carrying capacity, and low friction are concerned. Having said this, under both unlubricated and starved lubricated conditions HFO-1234yf outperforms HFC-134a refrigerant.

Fig. 4.3b shows the near contact temperature from the Set 2 wear experiments (222 N) under starved lubrication. Even though the miniature thermocouple was positioned 2 mm underneath the contacting interface and could not measure the exact interfacial temperature, it provided useful information of the near-contact temperature and frictional heating that the interface experienced. Fig. 4.3b shows that in the case of the 222 N load, the near contact temperature increases during the running-in period for both refrigerants and reached a steady value after about 10 minutes or 1,400 m sliding distance. The initial rate of temperature increase is higher in HFO-1234yf environment. The steady-state temperature values were 65°C and 40°C for HFO-1234yf and HFC-134a, respectively. The rise in temperature in the presence of HFO-1234yf could be partly corroborated to the aggressive chemical reactivity of this refrigerant which is expected on the basis of fluro-olefins. Thus, higher frictional heating is evident in the presence of HFO-1234yf. The elevated sub-surface temperature indicates that different events could be taking place on the surface such as bond breaking and concomitant reactivity in the case of HFO-1234yf refrigerant. Therefore, sufficient amount of elemental components of HFO-1234yf would be available at the interface for the formation of different surface species allowing
different chemistry to happen. Components of the surface chemistry will be presented and discussed in the XPS section. The tribological properties obtained from the experiments are summarized in Table 4.2, clearly showing that HFO-1234yf exhibits better performance compared to HFC-134a.

**Table 4.2: Comparative tribological performance of HFO-1234yf and HFC-134a**

<table>
<thead>
<tr>
<th>Properties</th>
<th>HFO-1234yf</th>
<th>HFC-134a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set 1: Scuffing load, N</td>
<td>1200</td>
<td>600</td>
</tr>
<tr>
<td>Set 1: Average friction coefficient (before scuffing)</td>
<td>0.09</td>
<td>0.085</td>
</tr>
<tr>
<td>Set 2: Average friction coefficient (222 N)</td>
<td>0.06</td>
<td>0.065</td>
</tr>
<tr>
<td>Set 2: Near-contact temperature (222 N), °C</td>
<td>65.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Set 2: Maximum wear depth (222 N), µm</td>
<td>&lt; 1.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

**4.2.2. Wear Analysis**

Wear analysis was first carried out qualitatively using low magnification optical microscopy. The images were taken inside and near the wear tracks of the disk surfaces as shown in Fig. 4.4. The sliding direction is indicated by the solid yellow arrow. Initial machining marks, especially outside the wear tracks (shown with red arrows) are also visible. Fig. 4.4a and Fig. 4.4b show the wear tracks in the presence of HFO-1234yf and HFC-134a refrigerants (Set 2), and Fig. 4.4c and Fig. 4.4d for Set 3.
Fig. 4.4: Low magnification optical microscopy images after wear experiments in the presence of HFO-1234yf (a) Set 2, (c) Set 3 and in the presence of HFC-134a (b) Set 2 and, (d) Set 3.

In the case of Set 2 (222 N), there was no measurable wear on the disk surface under HFO-1234yf environment, just some minor burnishing. On the other hand, significant wear was seen in the HFC-134a environment as shown in Fig. 4.4b. At 445 N (Set 3), in the presence of HFO-1234yf, burnishing is seen, Fig. 4.4c. Since the interface failed at 445 N in HFC-134a environment, severe wear and scuffing is seen in Fig. 4.4d. Clearly, the presence of HFO-1234yf refrigerant was beneficial leading to improved tribological performance.

To quantify the amount of wear, long profilometric line scans across the disk wear tracks were performed, as shown in Fig. 4.5. Fig. 4.5a and 4.5c show the profilometric analysis of the worn
disks in the presence of HFO-1234yf at 222 N and at 445N, respectively. As seen in the optical microscopy images, with 222 N and HFO-1234yf environment, no wear was seen, whereas a moderate amount of wear (about 4 µm deep) was found in HFC-134a environment, Fig. 4.5b. At 445 N, burnishing and very light wear of 1 µm depth is seen in Fig. 4.5c, in the presence of HFO-1234yf. In contrast to the HFO-1234yf environment, severe wear of about 12 µm along with deep wear scratches (about 16 µm) were seen in the presence of HFC-134a which is depicted in Fig. 4.5d.

The influence of starved lubrication on the wear behavior of gray cast iron in HFO-1234yf environment appeared to be negligible, as it is similar to the un lubricated case. Fig. 4.6 depicts a low magnification image and a profilometric scan of the worn disk tested under dry condition in HFO-1234yf environment. Referring to Fig. 4.6, no significant wear is seen on the disk surface. Thus, in the presence of HFO-1234yf under a constant load of 222 N, mild burnishing is observed of the order of 1-2 µm, irrespective of using either starved lubrication or dry condition. Therefore, it is believed that protective layers are formed during the wear experiments irrespective of using the lubricant or not in HFO-1234yf environment. These protective layers were believed to form during the friction transitional phase as discussed in the previous section. This was in contrast with HFC-134a refrigerant, where wear behavior was significantly improved with the application of lubricant. Details on the mode of wear are analyzed via SEM in the following section.
Fig. 4.5: Wear profiles after Set 2 (222 N) experiments: (a) HFO-1234yf; (b) HFC-134a, after Set 3 (440 N) experiments: (c) HFO-1234yf, and (d) HFC-134a.

Fig. 4.6: (a) Optical microscopy image and (b) wear profile of the worn disk tested at 222 N under unlubricated conditions in HFO-1234yf environment.
4.2.3. SEM Analysis

Fig. 4.7a and Fig. 4.7b show SEM images inside the wear tracks of the disk and the pin in the presence of HFC-134a (Set 2). Abrasive wear was visible on both samples resulting in deep grooves, Fig. 4.7b. These findings inferred the absence of any significant protective tribo-protecting layer in the presence of HFC-134a or if any was formed it was prematurely expelled out from the contact zone, providing no surface protection. The material removed from the interfaces in the form of wear debris amalgamated inside the contact region and eventually caused cold junction, namely adhesive wear, which is clearly seen at higher loads, Fig. 4.7c (disk) and Fig. 4.7d (pin) (Set 3).

![SEM images](image)

**Fig. 4.7**: SEM images in the presence of HFC-134a: (a) disk, Set 2, (b) pin, Set 2, (c) disk, Set 3, and (d) pin, Set 3.
In contrast to the effect of HFC-134a, under HFO-1234yf, smoother wear is observed, as shown in Fig. 4.8 for both Set 2 and Set 3 experiments. In both cases, no dominant wear mode is observed except some minor burnishing. There was also less evidence of abrasive wear over any of the samples. This implied the presence of some sort of protective layers on the surface. Remarkably, some perforated like surface was visible over the pin surface. The formation of such kind of surface layer might be originated from the chemical reaction of the refrigerant at the interface.

![SEM images](image.png)

**Fig. 4.8:** SEM images in the presence of HFO-1234yf: (a) disk, Set 2, (b) pin, Set 2, (c) disk, Set 3, and (d) pin, Set 3.

As discussed above, in the presence of HFO-1234yf some sort of transitional friction behavior is observed. To investigate this behavior a separate experiment in the presence of this refrigerant...
and under Set 3 (445 N) load conditions was conducted and stopped after 5 mins or 700 m of sliding distance. Fig. 10a depicts SEM images of the evolutionary changes of the pin surface in the presence of HFO-1234yf refrigerant at this transitional stage. A lower exciting voltage of 5 kV was used in order to avoid charging effects coming from the nonconductive "patch-like" film on the surface and hence for achieving a better capturing of the surface changes. Observing Fig. 4.9a, there were some particles, aligned with the sliding direction. These bundles of material were believed to be the initiation of the tribo-layers originating from the chemical reaction involving HFO-1234yf refrigerant and surface iron. Since these particles could act as “bumps” or obstacles at the interface, the friction behavior was not steady, as discussed in the preceding section. However, as the test progresses, the particles grew continuously over the surface and eventually developed a fluorine-enriched layer. This layer had a tribo-beneficial effect which reduced the friction coefficient and wear. Note that, no such particles were seen on the disk surface as shown in Fig. 4.9b. This could be explained from the contact point of view. Since the pin is engaged constantly, tribo-layer can be formed easily over the pin surface compared to the disk surface. In addition, during the experiments, some fluorine-enriched material might transfer to the pin surface from the disk surface which will be verified later via EDS and XPS. There is no evidence of fluorine-based layer when scuffing occurred. In other words, interfacial failure occurred when the last protective layer, which might be consisting of fluorine-containing species, is completely expelled from the contact interface. Therefore, it might be envisaged that the presence of fluorine layer prolongs the scuffing behavior, which is the case in HFO-1234yf environment. This is in accordance with our previous findings, where we demonstrated the existence of fluorine under dry condition for non-scuffed samples [61].
Fig. 4.9: SEM images in the presence of HFO-1234f during the transitional stage (700 m sliding distance): (a) pin, 445 N, and (b) disk, 445 N

4.2.4. EDS Analysis

The chemical composition of the pin surface is shown in Fig. 4.10 with the spectra extracted from EDS analysis after the wear experiments at 222 N (Set 2). An area map of 200 µm x 200 µm was used for this purpose. No EDS analysis was performed for the wear experiments at 445 N and for the scuffing experiments (Set 1). Only successful (no catastrophic failure) wear experiments were analyzed for a fair comparison. Through this analysis the influence of the two different refrigerants on the bulk chemistry of the cast iron was investigated. Fig. 4.10a presents the spectrum in the presence of HFC-134a, while Fig. 4.10b presents the spectrum in the presence of HFO-1234yf. Part of oxygen that was detected, might be originated from the PAG lubricant, since in the chemical structure of PAG there is terminal –OH group. Similar oxygen peak was detectable in the HFO-1234yf spectrum. One of the significant differences between the two spectra was the existence of fluorine element on the substrate. The enrichment of the surface in fluorine was only found in the HFO-1234yf spectrum. Since the experiment was performed in a closed/controlled chamber, the appearance of the fluorine peak in EDS originated from the
refrigerant. However, no such peak was identified in the case of HFC-134a refrigerant. This result suggested fluorine-containing adsorbed layers in HFO-1234yf atmosphere, which provided anti-wear protective properties to the gray cast iron surface.

![EDS Analysis](image)

**Fig. 4.10:** EDS analysis after Set 2 wear experiments: (a) HFC-134a, (b) HFO-1234yf.

### 4.2.5. XPS Analysis

**Disk Surface Analysis**

XPS analysis was performed in the cases of wear tracks formed under scuffing and wear experiments conditions as described in Table 4.1. Fig. 4.11 presents the F1s core level spectra obtained over the wear tracks in the presence of PAG/HFC-134a (Fig.12a) and PAG/HFO-1234yf (Fig. 4.11b) under Set 3 conditions (445 N). The main peak was observed at 684.3 eV corresponded to the inorganic metal fluoride species, most likely FeF$_3$, due to the predominant presence of Fe in the gray cast iron disk surface. No fluorine species were found in the case of scuffing experiments either in the case of PAG/HFO1234yf or in the case of PAG/HFC-134a. This could be understood based on the severity of the contact leading to collapsing and expelling of any formed tribo-protective layer.
**Fig. 4.11:** F1s core level spectra obtained over the gray cast iron disks following the PAG starved lubricated experiments (Set 3) in the presence of (a) HFC-134a and (b) PAG/HFO-1234yf.

Among the starved lubricated wear experiments with HFO1234yf Set 2 (222 N), HFO1234yf Set 3 (445 N) and HFC-134a Set 2, fluorine species were found only in the case of HFO1234yf Set 3. Note that the gray cast iron disk did not survive under the HFC-134a Set 3 conditions and scuffed. The fluorine species in the case of HFO1234yf demonstrate the superiority of HFO1234yf refrigerant compared to HFC-134a. The fact that fluorine-containing species were found only in the case of Set 3 (445 N) and not in the case of Set 2 (222 N) is indicative that under higher load (and contact pressure) conditions, the tribo-protective layer that is formed in the contact zone is more well adhered. It appears that in the case of Set 2, the tribo-layer which is adhered due to chemical affinity between the surfaces and mechanical pressure is loosely bonded to the gray cast iron surface.
Pin surface analysis

The pins surface was also characterized using XPS following the scuffing and wear experiments in the presence of HFO-1234yf and HFC-134a refrigerants. Fig. 4.12 presents the F1s XPS spectra for the scuffing Set 1 and wear Set 2 (222 N) experiments. As mentioned above, no fluorine species on the gray cast iron disk surface were found in the case of scuffing experiments either in the case of HFO1234yf or in the case of HFC-134a. This was not the case for the pins, where in both the HFO-1234yf and HFC-134a cases, fluorine species were found. Though, a major difference was noticed; in the case of HFO-1234yf refrigerant, the F1s XPS spectrum was dominated by two peaks, (~685 and ~688.7 eV), while in the case of HFC-134a only one F1s peak was observed (689.2 eV).

The same trend as above, regarding the fluorine species was noticed in the case of pins after Set 2 (222 N) wear experiments. In the case of HFC-134a only one peak (~685 eV) was observed, whereas in the case of HFO-1234yf two distinct peaks (~684.4 and ~688.4 eV) were identified. As mentioned before, on the disk surface, fluorine-containing species were found only in the case of Set 3 (445 N) and not in the case of Set 2 (222 N) experiments. This happened since, as the pin analysis herein proves, the fluorine tribolayer in the particular cases has migrated onto the pin surface.

The peak at ~685 eV corresponds to metallic fluorine-containing species, whereas the peak at ~688 eV corresponds to organic fluorine-containing species as has been reported in the previous chapter. The metallic component (~685 eV) is mainly coming from a reaction between the refrigerant and the gray cast iron surface (tribo-chemical reaction), whereas the organic fluorine species (~688 eV) are formed due to refrigerant fragmentation. From this perspective it is

64
important to notice that in the case where HFO-1234yf refrigerant is present at the interface, the formation of metallic F-containing species was facilitated. Ultimately, due to the mechanical forces applied, these species were found on the pin surface (Fig. 4.12a and Fig. 4.12d). This was true in both the scuffing and wear experiments. The organic fluorine-containing species play the role of the third body ensuring the sustainability of the interface in terms of friction and wear; whereas the metallic component provides better adhesion due to its nature (refrigerant/lubricant fragment reacted with elements/species coming from gray cast iron surface).

**Fig. 4.12:** F1s core level spectra obtained over the gray cast iron pins following the PAG starved lubricated experiments in the presence of (a) HFO-1234yf, Set 1, (b) HFC-134a, Set 1, (c) HFC-134a, Set 2, (d) HFO-1234yf, Set 2.
Another interesting point of the current findings is that the peak corresponding to the organic fluorine-containing species appeared at different binding energies (eV). In particular, for the cases of HFO-1234yf (Set 1), HFC-134a (Set 1) and HFO-1234yf (Set 3) the binding energies are 688.8 eV, 689.5 eV, and 688.3 eV, respectively. It is observed that the binding energies in the case of HFC-134a is far away (689.5 eV) from the other two values (688.8 eV and 688.3 eV for HFO-1234yf). This can be due to the different chemical identity of the organic patch formed (e.g., different hydrogen (H-) or oxygen (O-) content in the fragments) [82]. This can be caused due to different interaction between PAG and HFC-134a or HFO-1234yf under the surrounding mechanical forces.

4.3. TRIBOCHEMISTRY CONSIDERATIONS

As stated above, the organic fluorine-containing species (~688 eV) are coming from the unsaturated refrigerant (HFO-1234yf) fragmentation and were not identified in the case of the saturated refrigerant (HFC-134a). In last chapter, where aggressive unlubricated conditions were applied, thus allowing for direct comparison of how the chemical nature of refrigerants affects their ultimate performance, it was reported that the unsaturated refrigerant facilitates the formation of a well-adhered tribologically protective layer. Beyond this, some chemical considerations should be taken into account in order to explain the observed behavior. In principle, the C=C double chemical bonds are more reactive than the single bonds. During the tribological performance evaluation, material removal off the surface of gray cast iron takes place, leading to the exposure of new “fresh” bonds on the surface (dangling bonds). These new bonds function as active sites and react with the surroundings, which in this case is the PAG/HFC-134a and PAG/HFO1234yf systems. Since PAG lubricant is a common component in both cases, the main difference is coming from the interaction of PAG with the saturated and
unsaturated refrigerant (miscibility factor) and from the refrigerants itself (chemical nature factor). It is anticipated that C=C double bond in the HFO-1234yf, due to their more delocalized and labile electronic cloud, lead the surface to a more energetically stable state (reduction of surface energy due to the dangling bonds) through increased interaction with the surface. Ultimately, it is believed that the increased reactivity in the case of unsaturated refrigerant likely leads to an increased coverage of adsorbed refrigerant (most likely refrigerant fragments which were seen only in this case, peak at 688 eV) which give rise to a more homogeneous protective layer (confirmed by the morphological SEM findings). In the case of the saturated HFC-134a refrigerant the metallic component of fluorine species (FeF3 observed at 685 eV) is originated from the reaction between the Fe (gray cast iron as source) and fluorine (F) likely coming from the rapture of the highly polarized Cδ+-Fδ- bond (pool of F-species).

4.4. CONCLUSIONS

An experimental investigation simulating realistic air-conditioning and refrigeration compressors was carried out to compare the tribological performance under PAG starved lubricated conditions and two different refrigerants, HFO-1234yf and HFC-134a. Three different sets of tribological experiments were conducted: Time-to-failure via step loading known as scuffing experiments, and wear experiments under two different loading conditions. The findings, based on the scuffing experiments, show that under HFO-1234yf atmosphere, the gray cast iron interface can sustain as much as twice the loads before failure compared to HFC-134a. The wear experiments also confirmed the superiority of the HFO-1234yf refrigerant, with less wear. These findings are in accord with earlier studies under unlubricated conditions.
SEM images revealed the initiation and formation of tribo-protective layers on the gray cast iron surface in the presence HFO-1234yf. During the formation of this tribo-layer, the friction coefficient exhibited some instability due to formation and nucleation of bump like particles. Once the tribo-layers were formed, the friction coefficient was stable and low. Also from SEM images, abrasive wear was evident in HFC-134a environment. The abrasive particles amalgamated perpendicular to the sliding direction and eventually caused failure (adhesive mode). This mode of wear was not seen in the case of HFO-1234yf. This can be corroborated to the formation of preventive layers which impede abrasive wear. However, eventual failure was occurred when the tribo-layers completely removed from the contact interface. That’s why no fluorine enriched substance is identified after scuffing experiments. Note that, fluorine based substance was found for the non-scuffed samples which is in agreement our previous findings. In the presence of HFO-1234yf, fluorine based elements were detected from EDS analysis which was further verified using XPS analysis. The mechano-chemical environment (applied load, refrigerant/lubricant mixture) seems to have an impact on the formation and migration of the F-tribo-protective layers from the disk surface to the pin.
In the previous chapters, we have seen that fluorine enriched tribofilms are formed over gray cast iron surfaces in the case of hydrofluoroolefin based refrigerant (HFO-1234yf), unlike HFC-based refrigerant (HFC-134a). The development and growth of such films are strongly influenced by the mutual solubility of lubricants and refrigerants inside the compressor systems which have not been addressed so far. Excessive dissolution of lubricant in the refrigerant usually deteriorates the tribological performance due to degradation of the lubricant’s viscosity and thus functionality. Therefore, a compatible lubricant is necessary prior to implement an alternative refrigerant to ensure reliable operation. A compatible lubricant can be identified by examining two factors, namely miscibility and solubility. Miscibility is of prime concern to evaluate the thermodynamic performance in a lubricant/refrigerant mixture [83]. This is important to avoid accumulation of lubricant in the evaporator, condenser or expansion device. This miscibility issue has triggered the development of synthetic lubricants, such as PAG (Polyalkylene glycol) and POE (Polyol Ester) in early 1990s to use with HFC-134a refrigerant. It is worth to note that mineral oil is not miscible with current HFC-based refrigerants [84].

While miscibility studies are important, tribological studies along with mutual miscibility are critical in order to select an appropriate lubricant for a specific refrigerant. For example, carbon dioxide exhibits better tribological performance with PAG-based lubricants, compared to POE lubricants [48-49]. These studies demonstrated that in the case of lower mutual solubility of PAG lubricants and refrigerant gas, better performance was achieved. Note that, tribological
experiments could be used as a predictive tool for understanding the solubility limit of any lubricant at the interface. Thus, high solubility results in reduction in viscosity, implying a weaker interface, which in turn leads to higher wear rate. To date, there is no significant scientific work available in the literature, focusing on how the tribological properties of certain lubricants are influenced by their solubility in the presence of HFO-1234yf refrigerant. That’s why; this chapter will address the tribological performance of gray cast iron with different lubricants for a clear understanding of the lubricant-compatibility with the environmental friendly refrigerant HFO-1234yf.

5.1. EXPERIMENTAL SIMULATION

5.1.1. Controlled Tribological Experiments

Scroll type compressor conditions (where the main tribological interface can be simulated with a nominally flat pin-on-disk unidirectional motion as discussed in chapter 4) are experimentally simulated using a specialized high-pressure tribometer (HPT). The question of compressor lubrication conditions (in the field) and laboratory conditions to simulate aggressive compressor conditions is an important one. It is well understood that even though most air-conditioning/refrigeration compressors have an abundant amount of oil in a sump, critical tribocontacts do not experience fully flooded conditions and typically experience boundary/mixed lubrication conditions as mentioned earlier. It has been shown that under fully flooded conditions, scuffing is usually not experienced and thus our laboratory experiments (using a small predetermined amount of lubricant at the contact) simulate aggressive compressor conditions. These aggressive experiments would determine the overall lifecycle and reliability of a critical tribo-component as discussed in chapter 2.
A series of experiments under different sliding velocities [Fig. 5.1] has been conducted, confirming mixed/ boundary lubrication conditions. Note that, these experiments have been performed in the presence of PAG/HFO-1234yf system at room temperature. Earlier studies have reported an average coefficient of friction (COF) value of 0.2 for the same interface under no-lubrication (chapter 3 and 4), keeping the remaining conditions identical. This further verifies a mixed or boundary lubrication regime of operation.

Fig. 5.1: Photographs of Strubeck graph with method of lubrication

In all cases, three different lubricants, namely PAG, POE and mineral oil are used to investigate the mutual solubility (lubricant and refrigerant) on the tribological performance. To date, some data of qualitative assessments of lubricant miscibility with HFO-1234yf are available [18]. These studies reported better miscibility of POE and PAG lubricants with HFO-1234yf refrigerant, compared to mineral oil, which is characterized by a complete immiscibility. Thus, it is anticipated that mineral oil may not be as highly performing due to its immiscibility.
Nevertheless, the aforementioned studies excluded the influence of miscibility on friction and wear behavior. Therefore, a detailed investigation is needed in order to determine the most appropriate lubricant for this relatively new refrigerant. The properties of the lubricants are given in table-1 which are measured at 40 °C (as per manufacturer’s data). In this study, the influence of HFO-1234yf on lubricant’s properties was not considered. Note that, in refrigerated environment the viscosity value, as measured in the above temperature conditions, could be altered and also under the effect of the sliding motion, a further change in the viscosity can be caused.

Table 5.1: Properties of state-of-art lubricants

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Manufacturer</th>
<th>Grade</th>
<th>Viscosity</th>
<th>Mass of 1 drop</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAG</td>
<td>Idemitsu Kosan Co., Ltd</td>
<td>PZ68S</td>
<td>300 SUS</td>
<td>23 mg</td>
</tr>
<tr>
<td>POE</td>
<td>Nu-Calgon Wholesaler, Inc.</td>
<td>RL68H</td>
<td>300 SUS</td>
<td>24 mg</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>Calumet Lubricants</td>
<td>C-4S</td>
<td>300 SUS</td>
<td>26 mg</td>
</tr>
</tbody>
</table>

Two Sets of experiments were performed: Set 1 tribological experiments were conducted under scuffing conditions with a step load of 89 N/min. The load was increased up to the onset of scuffing which was associated with a sudden increase in the friction coefficient. The chamber pressure was kept constant at 0.2 MPa. The pressure was chosen so that, there will be no influence of pressure on the viscosity of the lubricant. Therefore, any change in viscosity will be affected by mutual solubility of the refrigerant and lubricant. This will facilitate better understanding of the performance of the lubricant/refrigerant at the interface. Room temperature (24°C) was selected for the first set. The chosen temperature is an average temperature of inlet and outlet refrigerant conditions. Moreover, these environmental conditions (temperature and pressure specified in set 1) could be directly used for a comparison between dry [61] and
lubricated cases. **Set 2** experiments were also scuffing type experiments at an elevated temperature of 110 °C. The chosen temperature is a typical outlet temperature of the compressor under aggressive conditions. At high temperatures lubricant viscosity is anticipated to be reduced, thus resulting in a better solubility with the counter-component, the refrigerant. Therefore, it is important to examine the tribological performance at this high temperature.

**Table 5.2:** Experimental conditions for Set 1 and Set 2 tribological experiments

<table>
<thead>
<tr>
<th></th>
<th>Set 1</th>
<th>Set 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal load</td>
<td>89 N/min</td>
<td>89 N/min</td>
</tr>
<tr>
<td>Sliding Speed</td>
<td>2.4 m/s</td>
<td>2.4 m/s</td>
</tr>
<tr>
<td>Sliding Direction</td>
<td>Unidirectional</td>
<td>Unidirectional</td>
</tr>
<tr>
<td>Lubricant</td>
<td>PAG, POE, Mineral oil</td>
<td>PAG, POE, Mineral oil</td>
</tr>
<tr>
<td>Amount of lubricant</td>
<td>1 drop</td>
<td>1 drop</td>
</tr>
<tr>
<td>Method of lubrication</td>
<td>Starved</td>
<td>Starved</td>
</tr>
<tr>
<td>Chamber Pressure</td>
<td>0.2 MPa</td>
<td>0.2 MPa</td>
</tr>
<tr>
<td>Temperature</td>
<td>24 °C (Room)</td>
<td>110 °C</td>
</tr>
<tr>
<td>Refrigerant</td>
<td>HFO-1234yf</td>
<td>HFO-1234yf</td>
</tr>
</tbody>
</table>

Note that, replication of actual compressor conditions in lab-scale testing is complicated, as stated before. Thus aggressive conditions were chosen for a conservative design approach by considering a high temperature. Note that, a temperature higher than 110°C could cause severe carburization along with breakdown of the lubricant at the interface. As in the Set 1 case, the scuffing point was characterized by a sudden increase in the friction coefficient, leading to catastrophic failure of the interface as discussed in the previous chapters. At the scuffing point, the interface loses its functionality and thus indicates maximum critical load. Unidirectional
experiments with a sliding velocity of 2.4 m/s were used for both Sets 1 and 2. The experimental conditions are summarized in Table 5.2.

5.2. RESULTS AND DISCUSSION

5.2.1. Controlled Tribological Experiments

Fig. 5.2 illustrates typical results of scuffing experiments from Set 1. The frictional behavior is depicted in Fig 5.2(a) and the corresponding maximum normal interfacial loads are shown in Fig. 5.2(b). Three different lubricants were considered as mentioned earlier, namely PAG, POE and mineral oil. Among the three lubricants, PAG/HFO-1234yf system exhibited better performance, with a maximum scuffing load of 1100 N. On the other hand, about 750 N of scuffing load was measured for the POE/HFO-1234yf system. Scuffing loads for mineral oil/HFO-1234yf mixture were found to be in between the PAG and POE systems at 900 N.

![Graphs showing friction behavior and scuffing loads for different lubricants.](image)

**Fig. 5.2:** Scuffing experiments at Set 1 conditions: (a) Friction behavior for PAG, POE and Mineral oil lubricants and (b) corresponding scuffing loads.

The friction coefficient was also lower for PAG/HFO-1234yf lubricant, which is 0.11. An interesting run-in behavior was observed for PAG/HFO-1234yf system. The friction coefficient
was gradually increasing, which was later healed during the progress of the experiment. This behavior could be explained with the findings from previous work [62]. In that study, a fluorine enriched layer was reported at this stage. Thus, with PAG/HFO-1234yf system, the new refrigerant exhibited the tendency of fluorine based surface layers. During the evolution of this layer, some friction coefficient instability was observed which became steady once the protective layer was completely formed. This was in contrast for POE/HFO-1234yf system. The friction coefficient was steady until the catastrophic failure, suggesting a rather brittle mode of wear unlike PAG/HFO-1234yf system. Therefore, it is believed that, the surface failed due to no or very thin protective boundary layer between the contacting surfaces. The friction coefficient was about 0.13, which was comparable to PAG/HFO-1234yf system. The friction coefficient for the mineral oil was unsteady, fluctuating between 0.15 and 0.1 before catastrophic failure. This could be attributed to severe plastic flow. The plastic flow was further intensified with high frictional heat at the interface originating from the mechanical load. The friction coefficient (approximately 0.16) was also higher compare to PAG/HFO-1234yf and POE/HFO-1234yf system cases. Therefore, it could be inferred that, mineral oil is not appropriate with this refrigerant. Note also that there is an issue with mineral oil miscibility with the HFO-1234yf refrigerant.

The onset of scuffing failure greatly depends on the nature and thickness of the boundary films, developed through tribo-chemical interactions at the interface [85]. A thicker boundary film could sustain higher contact loads, delaying scuffing failure. On the other hand, a thinner film would increase the probability of more asperities in contact, leading to an early occurrence of scuffing. A correlation between the thickness of the boundary film and lubricant viscosity was also demonstrated [86]. It reported formation of thicker boundary films in the presence of
viscous lubricant and vice versa. Since POE dissolved excessively in HFO-1234yf refrigerant, its viscosity would degrade during tribo-experiments, resulting a thinner or no protective boundary films. Thus, for POE/HFO-1234yf system, scuffing occurred earlier compared to PAG/HFO-1234yf system. On the other hand, for PAG/HFO-1234yf system boundary film integrity and thickness was maintained by less degradation of the lubricant’s viscosity, ensuing a delay in scuffing. The miscibility of different lubricant/HFO-1234yf systems is confirmed via XPS studies in a later section. Furthermore, a fluorinated tribo-film was a special characteristic for this refrigerant, which could also be observed from frictional behavior, as mentioned before. The mechanisms and development of these layers were elucidated in previous work [chapter 3 and 4]. Based on the current experiments and previous findings, it could be inferred that tribo-film development of the POE lubricant was limited in HFO-1234yf environment. This is in contrast with PAG/HFO-1234yf system, where a thick tribo-film was developed.

Experimental results for Set 2 scuffing tests at higher temperature are shown in Fig. 5.3. As can be seen from Fig. 5.3(b), a scuffing resistance of about 200 N was measured in the case of POE/HFO-1234yf. The resistance was significantly lower compared to the interface lubricated with PAG/HFO-1234yf system, for which the scuffing load was 800 N, as also shown in Fig. 5.3(b). Similar to room temperature, mineral oil/HFO-1234yf system performed in between the other two cases of PAG and POE lubricants.

The friction coefficient was not steady in all three cases. However, PAG/HFO-1234yf system performed better as it scuffed at a higher load, suggesting reduced deterioration of the viscosity. This was indicative of a lower solubility of PAG lubricant with HFO-1234yf refrigerant even at high temperature. On the contrary, with the POE/HFO-1234yf system, the friction coefficient was unsteady and failed immediately (within the first two minutes of the experiment).
Fig. 5.3: Scuffing experiments at Set 2 conditions: (a) Friction behavior for PAG, POE and Mineral oil lubricants and (b) corresponding scuffing loads.

The variation of scuffing loads with temperature is presented in Fig. 5.4. It is evident that in the case of PAG/HFO-1234yf system a better lubricity is achieved compared to the case of POE/HFO-1234yf system. Even at the high temperature of 110°C, the reduction in scuffing load was not as significant for PAG/HFO-1234yf system compared to POE/HFO-1234yf. The error bars for the PAG/HFO-1234yf system were smaller compared to POE/HFO-1234yf system, suggesting more uniform interface for PAG/HFO-1234yf system. The experiments for this case were reproducible, generating no significant variation on the scuffing loads. For instances where scuffing occurred at the transition from one load to the next, the error bars show the value of the step load (±89 N). On the contrary, the error bars were calculated from three or four experiments for the cases of POE/HFO-1234yf and Mineral oil/HFO-1234yf systems. Note that, the lubricant viscosity usually degrades with increasing temperature [87]. Therefore, the deterioration of the scuffing loads with POE/HFO-1234yf could be attributed to viscosity degradation due to excessive dissolution of the lubricant in the refrigerant. However, this will be
further degraded with the over dilution of the lubricant in the refrigerant. These experiments clearly demonstrated that the better solubility of POE with refrigerant corresponds to higher friction and lower scuffing loads. On the other hand, with the PAG/HFO-1234yf system, protective lubricant films were formed at the interface, which prevent the surface from wear and thus prolong the interface from sudden failure. This will be verified later with the aid of surface morphological analysis in conjunction with XPS analysis.

**Fig. 5.4:** Scuffing load comparison for different lubricants (tested under Set 1 and Set 2 conditions).

### 5.2.2 Wear Analysis

Optical microscopy images of the pin surfaces were captured after the experiments as shown in Fig. 5.5. The pin surface, viewed from top, and the pin holder are shown in Fig. 5.5(a). Noticeable amount of wear debris was found around the pins for POE/HFO-1234yf as shown in
Fig. 5.5(c) and 5.5(f). This could suggest a very thin film or no protective film layer at the surface and thus could indicate that abrasive wear governs the interfacial behavior. On the other hand, in the presence of PAG/HFO-1234yf system, less amount of wear debris was observed, as seen in Figs. 5.5(b) and 5.5(e). Thus, it is postulated that in the presence of PAG/HFO-1234yf the lubricating film is adhered to the counter-surfaces, thus prolonging the scuffing behavior. A thick viscous layer of lubricant residue was obtained in the presence of mineral oil/HFO-1234yf system, as can be seen in Figs. 5.5(d) and 5.5(g).

Fig. 5.5: Optical images of (a) Untested pin with holder viewed from top; the wear residue after tribological experiments (before any cleaning) at Set 2 (110 °C): (b) PAG, (c) POE, (d) Mineral
oil; and at Set 1 (24 °C): (e) PAG, (f) POE (g) Mineral oil [single arrow inside the pin area indicates sliding direction].

5.2.3. SEM Analysis

Fig. 5.6 illustrates SEM images of the worn surfaces tested under PAG/HFO-1234yf system environment. Fig. 5.6(a) and 5.6(b) show the surfaces following the tribological testing performed under Set 1 conditions at different magnification-scales. From these micrographs, remnant of tribo-films were observed. Plasticity induced material flow was observed in the vicinity of the tribo-films. This flow of material was likely developed from delamination of protective films under high scuffing loads, as can be seen in Fig. 5.6(b). Moreover, plastic flow could originate from the asperities exceeding the local yield due to higher loads for PAG/HFO-1234yf system. Nevertheless, no significant scratches or grooves were seen on the surface indicating negligible amount of abrasive wear. Therefore, it was believed that with the progression of the experiment, different surface layers were developed at the sliding zone, thus preventing abrasive wear between the two contacting surfaces. Thus, surface films were produced during sliding, and the interface ultimately failed due to adhesive wear. The chemical composition of the protective film will be discussed in a later section.
Fig. 5.6: SEM micrographs at two different magnifications of the worn disk samples tested under PAG/HFO-1234yf at (a), (b) Set 1 (room temperature), and (c), (d) Set 2 (110 °C) conditions. The sliding direction is indicated by the single arrow pointing north.

Fig. 5.7(c) and Fig. 5.7(d) show the interface morphology after having been subjected to the 110°C tribological test (Set 2). Plastic flow associated with adhesive type wear can be seen in Fig. 5.7(c). This plastic flow caused an unstable fluctuation in the friction coefficient profile, and the surface became rougher with the softening of the materials and pile up in the contact zone. The piled up materials therefore created the friction coefficient instability. Note that, micro-pitting was also observed at higher magnification as can be seen in Fig. 5.7(d). The micro-pitting was likely due to the absence of a protective layer on the surface. Similar surface morphology was demonstrated by Ciantar et al. [44] while working with POE/HFC-134a system. They reported degradation of the lubricant’s (POE) viscosity with HFC-134a for worse tribological
performance. Therefore, it could be envisaged that reduction of PAG’s viscosity at high
temperature in HFO-1234yf refrigerant would cause metal-to-metal contact at some locations,
resulting in micro-pitting.

SEM micrographs of the worn disk samples tested under POE lubricant are depicted in Fig. 5.7.
Severe roughening is observed in Fig. 5.7(a), implying materials removal from the top surface
and piled up at the contact zone due to high contact pressure.

![SEM micrographs of the worn samples tested under POE/HFO-1234yf at (a), (b) Set 1
(24 °C ), (c), (d) Set 2 (110 °C) conditions at two different magnifications. The sliding direction
is indicated by the single arrow pointing north.]

The process was further accelerated due to thermal softening of the asperities originating from
high frictional heat. Material roughening or “bulges” were oriented either along the sliding
direction or near the edges. There was no trace of protective tribo-films unlike the case for PAG/HFO-1234yf system. Note that, some removed material was expelled from the interface resulting in wear debris formation.

At high temperatures (Set 2 conditions), both surface delamination (adhesive type) and abrasive wear are dominant as can been seen in Fig. 5.7(c). A deep groove-like scratch was revealed from the SEM analysis, and the material removed from the groove resulted in wear debris formation. Surface cracks were seen at higher magnification SEM, as shown in Fig. 5.7(d). The crack was initiated at the site of graphite flakes. Note that, in cast iron material, graphite flakes were encompassed by a matrix consisting of free ferrite and pearlite [88]. Graphite is peeled off from the surface due to mechanical rubbing and making voids in the matrix. The void then acted as a crack nucleation site and eventually failed along the entire wear track. This could likely be the reason for not facilitating the formation of an anti-wear film during the tribological experiments. Therefore, nascent surfaces were easily exposed during the sliding action and facilitating the removal of graphite flakes, as will be further verified using XPS.

SEM analysis was also conducted on the samples tested under mineral oil/HFO-1234yf mixture for comparison purpose, as shown in Fig 5.8. Severe roughening caused from the tribological experiments was observed under both Set 1 and Set 2 conditions. With adhesive wear being more dominant at the high temperature (Set 2) tribo-testing case. The adhesive wear might be associated with plastic flow over the surface. This is in accordance with tribological experiments where friction coefficient gradually increased up to failure. Some layers could be expected to develop as this oil has less affinity to mix with the refrigerant. The surface interaction will be examined later with the aid of XPS analysis.
Fig. 5.8: SEM micrographs of the worn samples tested under Mineral oil/HFO-1234yf mixture at (a) Set 1 (24 °C), (b) Set 2 (110 °C) conditions. The sliding direction is indicated by the single arrow pointing north.

5.3. TRIBOCHEMICAL ANALYSIS

Fig. 5.9 presents the F1s core level spectra obtained after the Set 2 conditions tribo-testing over the gray cast iron disks that had been exposed under different environments, namely PAG/HFO1234yf, POE/HFO1234yf and mineral oil/HFO1234yf systems. In the case of PAG/HFO1234yf system, the main F1s peak was observed at 685 eV corresponding to inorganic metal fluoride species, most likely FeF$_3$, due to the predominant presence of Fe in the gray cast iron disk surface. In the case of POE/HFO1234yf system, only traces of F-containing species at 685 eV were found, indicating that the extent of the tribo-chemical reaction was limited in this case and no protective layer was formed. In the case of Mineral oil/HFO1234yf system two clear peaks were observed, one corresponding to the metal fluoride (~685 eV) and one corresponding to -CF$_2$- species (~690 eV). It is likely that the -CF$_2$- species are emerged in this particular case due to the immiscibility of fluoro-refrigerant with the lubricant (mineral oil). This has left the –CF$_2$- groups originating from the refrigerant fragmentation intact (no interaction with the oil) and thus available to attach to the interface.
In the case of PAG/HFO1234yf system when the tribological tests were conducted under Set 1 conditions, XPS analysis revealed F-species with F1s peak maximum at 684.3 eV, only under wear-type experiments. Under scuffing conditions (similar to the ones reported in Table 2 in this work) at 24 °C and PAG/HFO1234yf, no fluorine species were found. The presence (at 110°C) or not (24 °C) of F-entities supports a temperature-induced difference in refrigerant/lubricant miscibility and viscosity change, which ultimately changes the PAG/HFO-1234yf (or species coming from its fragmentation) adhesion on the surface and its overall performance under mechanical load.

In the case of the Mineral oil, poor tribological performance at Set 2 conditions (110°C) was observed mainly due to the lack of miscibility between HFO1234yf and Mineral Oil. The presence of HFO1234yf refrigerant still gave rise to F-containing fragments that adhered to the surface in the case of Set 2 conditions (see Fig. 5.10b). Though, the lack of synergy between the refrigerant and lubricant led to poor performance. When the tribo-testing was performed at Set 1 conditions, no fluorine species were found in the case of mineral oil/HFO1234yf with the exception that some traces of F-species were identified on the borderline of the wear track. This finding supports the pile up of F-species that failed to stay adhered on the surface, and thus, they are gathered on the borderline of the wear track at the end of the experiment. In the case of POE/HFO1234yf, likely due to the higher miscibility of the components, a change in the population (availability) and properties of the F-containing species onto the interface is likely. In the case of PAG/HFO1234yf system, due to the lower miscibility of the components, the F-species that emerged on the interface following the test are of different chemical nature.

The effect of miscibility on the different chemical nature of F-species can also be observed based on the C1s core level spectra obtained over the different cases investigated herein (Fig. 5.10).
**Fig. 5.9:** F1s core level spectra obtained over gray cast iron disks following tribo-testing at Set 2 conditions (110°C) in the presence of (a) PAG/HFO1234yf system, (b) POE/HFO1234yf system, and (c) mineral oil/HFO1234yf system.

Different F-species corresponding to different peaks (α, β, γ) were observed. These species can arise from the different extend of carbon atom fluorination (CFₓ, x>1). As more fluorine atoms are coordinated with carbon, the latter’s binding energy is shifted to higher values due to the formation of a more electronegative environment. It seems that the higher degree of carbon fluorination is facilitated only in the case of a threshold value of miscibility between the two components of the system (PAG/HFO1234yf). The extent of carbon fluorination is believed to
be affected by the degree of miscibility, which can be considered as interaction between the two components of the system. The above coincides with the fact that F-species (Fig. 5.10) appeared at different binding energies (e.g., 685.22 eV for PAG/HFO1234yf and 685.80 eV for POE/HFO/1234yf system).

![Graphs showing C1s core level spectra](image)

**Fig. 5.10.** C1s core level spectra obtained over gray cast iron disks following tribo-testing at Set 2 conditions (110°C) in the presence of (a) PAG/HFO1234yf system, (b) POE/HFO1234yf system, and (c) mineral oil/HFO1234yf system.

It is worthwhile to mention that representative XPS data showed that the distribution of F-species was changing across the wear track. Based on the F1s core level spectra obtained at different...
locations of the wear track (moving from the center towards the borderline) for the case of the PAG/HFO1234yf system, it was obvious that the F-containing species are present in the whole area of the wear track investigated. This demonstrates the protective role of the F-containing layer and that the latter is kept well-adhered during the test with no important degree of wear.

5.4. CONCLUSIONS

The tribological performance of gray cast iron in the presence of environmental friendly refrigerant HFO-1234yf was evaluated in the presence of commonly used air-conditioning lubricants. Starved lubrication conditions were adopted to simulate aggressive air-conditioning compressor systems. Two different temperatures (24 °C-Set 1 and 110°C-Set 2) were used to investigate the influence of mutual solubility on the tribological performance. PAG/HFO-1234yf system exhibited superior tribological performance compared to POE/HFO-1234yf and Mineral oil/HFO-1234yf systems at both temperatures. Higher anti-scuffing loads along with lower friction coefficient were measured for PAG/HFO-1234yf system compared to POE/HFO-1234yf and Mineral oil/HFO-1234yf at room temperature. The difference in tribological performance is attributed to lubricant/refrigerant miscibility, which in the case of PAG is such that allows the PAG constituents to preserve their lubrication properties. In the case of POE, the higher miscibility with HFO1234yf is likely to lead to deterioration of its lubrication functionality. Note that, mineral oil is not miscible with HFO-1234yf and it was used in this study only for comparison purpose.

Based on SEM, adhesive type wear associated with plastic flow was revealed for PAG/HFO-1234yf, and no significant wear particles were found. Remnants of the surface indicated tribo-beneficial layers that developed during the tribological experiments. Abrasive wear was observed
for POE/HFO-1234yf, with micro-pitting, deep scratches and breakdown of the surface, generating wear debris. This corroborates with the fact that either a very thin or no protective layer was formed in the case of POE/HFO-1234yf. XPS studies performed at both 24 °C and 110°C demonstrated that temperature increase changes the profile of F-species on the surface. This was proved for the cases of PAG/HFO1234yf and mineral oil/HFO1234yf systems, since F-species were found only in the case of the 110°C and not in the case of the room temperature. The temperature is most likely to have contributed in the increase of miscibility between the constituents of the different systems changing the nature (and the adhesion) of the F-species found on the surface, as they appeared in different binding energy (eV) values in the XPS spectra. Also, the different degree of solubility is likely to have affected the degree of carbon fluorination for the different systems studied herein.
In the previous chapters, friction and wear behavior of different metallic interfaces were discussed in the presence of HFO-1234yf refrigerant. However, relations between loading conditions and wear behavior were not clarified although it has significant influence to ensure better design approach. Note that, automotive compressors are usually operated under varying loading conditions throughout their life-cycle. Wear prediction, therefore, needs to be investigated for a wide range of operating conditions for practical and scientific considerations. Furthermore, HFO-1234yf has an unsaturated olefinic backbone (-C=C-) in its chemical structure making it more reactive, compared to HFC-134a. Besides the chemically induced different wear mechanisms, the interfacial behavior may also change with operating conditions. This necessitates a comprehensive study of wear mechanisms under different conditions in the presence of HFO-1234yf.

Different tribolayers are developed throughout complex tribochemical reactions at interfaces as explained in preceding chapters. However, the tribological nature of these films depends on the kinetics of constituent chemical elements along with operating conditions, such as sliding velocity and normal load (Biswa[89]; Cutiongo, et al.[90]). The evolution and properties of such tribofilms were studied by Cong, et al. [91] for aluminum surfaces in the presence of HFC-134a refrigerant, and reported tribologically beneficial aluminum fluoride-based tribofilms. Several authors studied wear maps for gray cast iron interfaces under dry conditions (Lim [92]; Leach, et al. [93]; Riahi, et al. [94]; Wei, et al. [95]). These studies were based on simplified
assumptions, limiting their effectiveness in practical applications, especially under harsh conditions associated with HFO-1234yf refrigerant. Limited earlier studies reported that this new refrigerant has the tendency to form fluorine-enriched tribolayers on gray cast iron surfaces (Akram, et al. [61-63]). These studies also reported a frictional instability during the formation of this fluorine-enriched film (FeF$_3$), which was later self-healed. Herein, this chapter will identify dominating wear mechanisms at different sliding velocities and loads under aggressive boundary lubricated conditions in HFO-1234yf environment, and specifically the effect of tribofilms.

6.1. EXPERIMENTAL PROCEDURE

6.1.1. Materials and Lubricants

Scroll type air-conditioning compressor geometry and conditions were experimentally simulated in this study. The contact interface was gray cast iron, grade: Dura-Bar G2, flat pins versus gray cast iron disks, which are common for this compressor. This type of gray has iron consisted of 95% Iron (Fe), 2.7-4.0% Carbon (C) and traces of Silicon (Si), Manganese (Mn), Tin (Sn), Sulfur (S), Copper (Cu), and Phosphorous (P). Photographs of the pin and disk are shown in Fig. 6.1, identical to the previous studies as described in chapter 3-5.

Fig. 6.1: Tribological samples: (a) gray cast iron disk, (b) gray cast iron flat pin, (c) schematic of pin-on-disk configuration.
Before initiating an experiment, the samples were prescreened both optically and using a contact profilometer to ensure they have minimal surface damage from machining. The samples had an initial surface roughness (root-mean-square value) in the range of 0.4-0.7 μm. All the samples were cleaned ultrasonically before and after the experiments by immersing in a pool of acetone. The samples were then rinsed with Propanol-2 and subsequently dried with warm air.

Polyalkylene Glycol (PAG) based synthetic lubricant was used in the experiments. This double end-capped PAG lubricant (Manufacturer: Idemitsu Kosan Co. Ltd, Grade number PZ68S) was specifically synthesized for automotive air-conditioning compressor systems. The viscosity of this lubricant is 300 SUS at 40°C. The viscosity changes with the interaction of the refrigerant were not specifically investigated in this study. The lubricant supply rate was controlled in the range of 25-35 mg/min, for consistency.

6.1.2. Controlled Tribological Experiments

A specialized high-pressure tribometer (HPT) was used to simulate the scroll type compressor system as discussed in preceding sections. Two different sets of experiments were conducted, namely scuffing or step load experiments and constant load, wear experiments. For the first set of experiments, normal contact loads were incrementally changed at 89 N/min until failure of the interface, indicated by a sharp rise in the friction coefficient, namely scuffing (Ludema (28)). For these experiments, the sliding velocities were varied from 0.6 m/s to 4.8 m/s to investigate the dominant wear modes at different sliding velocities. The experiments were carried out at a constant chamber pressure of 0.2 MPa (using HFO-1234yf refrigerant). Maximum interfacial
loads were determined from the first set of step-loading experiments in a similar fashion as explained in chapter 3 and 5.

Based on the first set of experiments, a second set of experiments at a constant load was conducted at sliding velocities varying from 0.6 m/s to 3.6 m/s. The different values of the constant loads were taken at 25% of the scuffing/failure loads determined from the first set of scuffing experiments, at a specific velocity. In addition, wear experiments (maintaining constant velocity but different loads) were carried out to confirm the consistency of surface morphology. Note that, all experiments were conducted at room temperature in order to preclude the effect of viscosity change at different temperatures. At the initiation of each experiment, a preload of 50 N was applied to ensure smooth run-in, and all the experiments were performed at least twice to ensure repeatability. The experimental details for both Set 1 and Set 2 experiments are summarized in Table 6.1, and the loading conditions for Set 2 wear experiments are tabulated in Table 6.2.

**Table 6.1: Operating and environmental conditions for tribological experiments**

<table>
<thead>
<tr>
<th></th>
<th>Set 1-Scuffing</th>
<th>Set 2-Wear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direction</td>
<td>Unidirectional</td>
<td>Unidirectional</td>
</tr>
<tr>
<td>Normal applied load, N</td>
<td>89 N/min</td>
<td>See Table 2</td>
</tr>
<tr>
<td>Sliding velocity, m/s</td>
<td>0.6-4.8</td>
<td>See Table 2</td>
</tr>
<tr>
<td>Chamber pressure, MPa</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Chamber temperature, °C</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>Lubricant</td>
<td>PAG (300 SUS)</td>
<td>PAG (300 SUS)</td>
</tr>
<tr>
<td>Refrigerant</td>
<td>HFO-1234yf</td>
<td>HFO-1234yf</td>
</tr>
<tr>
<td>Amount of lubricant, mg/min</td>
<td>25-35</td>
<td>25-35</td>
</tr>
<tr>
<td>Lubrication condition</td>
<td>Boundary/mixed</td>
<td>Boundary/mixed</td>
</tr>
</tbody>
</table>
Table 6.2: Velocity/Loading Conditions for Set 2 Wear Experiments

<table>
<thead>
<tr>
<th>Sliding velocity, m/s</th>
<th>0.6</th>
<th>1.8</th>
<th>2.4</th>
<th>3.0</th>
<th>3.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Applied normal load, N</td>
<td>650</td>
<td>333</td>
<td>222</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Specific nominal pressure, MPa</td>
<td>20.90</td>
<td>10.70</td>
<td>7.13</td>
<td>2.40</td>
<td>2.40</td>
</tr>
</tbody>
</table>

6.1.3. Wear Rate and Near Contact (Interface) Temperature

Each specimen was weighted before and after each wear experiment (with an accuracy of 1 mg). The mass loss was then converted to wear rate (by dividing mass loss by the sliding distance and normal load). The near contact temperature was measured using a commercial K-type thermocouple probe with a stainless steel sheath of 1 mm outer diameter. The thermocouple was placed about 2 mm beneath the interface.

6.1.4. SEM/EDS Analysis

The worn samples were analyzed using a Scanning Electron Microscope to observe the morphological changes of the gray cast iron surfaces. A JEOL 6060LV SEM coupled with an Energy Dispersive Spectroscopic (EDS) gun operated at 20 KV was used to obtain the surface topography. EDS was used to quantify the changes in chemical composition of the surfaces tested at different sliding velocities. This would indicate the influence of chemical changes on the different wear mechanisms. An area map of 500 x 500 μm² was used for this qualitative compositional analysis.
6.2. RESULTS AND DISCUSSION

6.2.1. Set 1 - Scuffing Experiments

Tribological Experiments

Figure 6.2 depicts typical in-situ coefficient of friction (COF) and sub-surfaces or near contact temperature (NCT) measurements as a function of time for different sliding velocities under scuffing (step loading) conditions (Set 1). An interesting ‘run-in’ behavior was observed in both the COF and NCT results. The COF became unsteady, and increased, followed by a self-healing steady period at an intermediate phase of the sliding experiments. The frictional instability depended on the sliding velocity:

Fig. 6.2: Set 1 scuffing experiments versus time: (a) Coefficient of friction (COF), (b) Near Contact (sub-surface) Temperature (2 mm below the contact interface).

Lower sliding velocities delayed the initiation of the ‘run-in’ behavior, needing higher normal loads to cause the instability. For instance, at 0.6 m/s the instability started at about 15 minutes i.e., at about 1400 N. For 2.4 m/s sliding velocity, the unstable behavior began at 350 N (at 4 minutes, which coincidentally corresponds to an almost linear ratio). The COF fluctuation was
associated with the formation of fluorine-enriched tribofilms as documented by Akram, et al. [61, 62].

Based on these results, higher sliding velocities initiated fluoride-layer formation faster (i.e., at lower normal loads) compared to lower sliding velocities. This observation was valid up to a velocity of 3.0 m/s, as at higher velocities the interface failed within a short period after initiating the experiment, characterized by an abrupt rise in the COF. This catastrophic failure could be attributed to the absence of a protective layer in the contact zone. Such protective layers are shown to originate through tribochemical interactions at the contacting surfaces in the presence of HFO-1234yf refrigerant, as mentioned before. At 3.0 m/s or higher velocities, the removal rate of the protective layer likely exceeded the formation rate of the protective layer. This phenomenon was in agreement with the experimental observations by Cutiongco et al. [90]. Therefore, the transitional velocity from 2.4 m/s to 3.0 m/s could be considered as a ‘critical velocity’ for tribofilm formation. Interestingly, all experiments failed in a similar fashion for velocities above this critical limit suggesting a mechanical/rubbing dominated wear mechanism. This hypothesis will be further verified using morphological SEM and EDS analyses.

The NCT exhibited similar run-in behavior as the COF, as shown in Fig. 6.2(b). During the instability in the COF, the NCT was also unsteady and later self-repaired. Interesting to note that, the unsteady behavior started when the NCT temperature reached about 70°C. It is postulated that at this temperature the refrigerant interacted with the nascent gray cast iron surface and lubricant, resulting in fluorine-passivated tribofilms. The COF and NCT became steady once the passivation of the surface was completed through the complex triboreactions. Ultimately, failure of the interface occurred when the tribofilms were penetrated or broken under high normal loads associated with either adhesive or abrasive type of wear.
The above results were presented as a function of time, whereas Fig. 6.3 depicts the same COF experiments as in Fig. 6.2, plotted versus sliding distance. Specifically, Fig. 6.3(a) shows the cases where the sliding velocities were below the critical value of 3.0 m/s, and Fig. 6.3(b) shows the cases where the velocities were higher than the critical limit. Referring to Fig 6.3(a), all three cases withstood more than 1100 m sliding distance. Also, all three experiments scuffed at about the same sliding distance (between 1100 m and 1400 m). Referring to Fig. 6.3(b), all the experiments failed below 800 m sliding distance. The longer sliding distance-to-failure, for low velocities, was attributed to the formation of protective tribolayers.

Fig. 6.3: Set 1 scuffing experiments versus sliding distance: (a) below critical velocity; (b) above critical velocity.

Figure 6.4(a) shows the in-situ normal load versus testing time for the same experiments shown in Fig. 6.2. The maximum interfacial loads to cause scuffing decreased with increasing sliding velocity, as can be clearly seen in Fig. 6.4(b). A transition in scuffing load behavior is seen when the sliding velocity reached 3.0 m/s, as below this value, the decrement in scuffing load with sliding velocity was almost linear. At velocities higher than 3.0 m/s no significant change in
the scuffing load was observed, as at higher velocities tribochemical reactions were limited, resulting in predictable mechanical rubbing.

SEM Analysis

Figure 6.5 illustrates SEM micrographs of the worn gray cast iron disk samples tested under different sliding velocities. In the case of the lowest velocity of 0.6 m/s, the SEM revealed a smooth tribolayer in conjunction with ‘peeling’ of material from the interface, which could be attributed to an adhesive wear mechanism. Material was removed from the disk surface and transferred to the counter surface resulting in scuffing failure. Severe plastic flow was observed on the worn sample tested at 2.4 m/s, as can be seen in Fig. 6.5(b). The plastic flow could be attributed to the high frictional heating originating from the higher sliding velocity. Traces of the smoother surface were still present, suggesting the development of protective tribolayers before failure. The eventual failure occurred due to plasticity dominated adhesive flow.

**Fig. 6.4:** Set 1 scuffing experiments: (a) Scuffing load versus time, (b) Scuffing load versus sliding velocity.
Figures 6.5(c) and 6.5(d) depict the SEM micrographs of the gray cast iron samples tested above the critical velocity. The bare substrate (without any protective tribolayer) was exposed during these experiments. Specifically, severe roughening associated with mechanical rubbing between the contacting surfaces was observed for the 3.0 m/s case, with no evidence of smooth tribofilms on the surface (validating the absence of protective layers originating from tribochemical reactions, and thus imminent interfacial failure).

![Fig. 6.5: SEM images of disk samples after Set 1-scuffing experiments: (a) 0.6 m/s, (b) 2.4 m/s, (c) 3.0 m/s, (d) 4.8 m/s [thick white arrows pointing north indicate sliding direction]. Similar morphology was seen for the 4.8 m/s case shown in Fig. 6.5(d). However at this velocity, patchy gross material removal from the surface was also seen, resulting in severe surface damage. This was in accord with the tribological results discussed in the previous section, and validating the fact that at higher sliding velocities, the destruction rate of the protective films is greater, compared to the tribofilms formation rate.](image-url)
EDS Analysis

Figure 6.6 shows the qualitative chemical composition of the worn gray cast iron surfaces utilizing EDS (examining three chemical elements of Carbon, Oxygen and Fluorine). For comparison purposes, the chemical elements of the untested samples (unexposed to refrigerant and lubricant environment) are also presented in the same plot. The amount of carbon, in graphite form, did not change significantly with tribotesting, except for the case of the highest 4.8 m/s velocity. It was noted, however, that in general the amount of carbon was decreased slightly with higher sliding velocities, indicating removal of the graphite from the pearlite matrix. No boundary film was developed at higher velocities to prevent the attached graphite loss from the cast iron interface, which is in agreement with the SEM findings, where gross failure was seen with no protective films.

Beneficial effects of oxide layers on gray cast iron were also reported in Gomes, et al. [96], and Ghaderi, et al. [97]. Oxide films developed under the exposure of air or in the presence of oxygen-enriched environment. Since PAG lubricant (possessing -O- bond) was used in this study, oxide film could be formed due to interaction of lubricant and surface material. The amount of oxygen was increased significantly on the surface during tribotesting for the lower velocities (compared to the untested/virgin samples), whereas it dropped significantly at velocities higher than the critical velocity (to reach similar levels as the untested samples). This correlated with earlier observations that at higher velocities, oxide-rich protective layers are unable to form in a stable manner. Note that even though oxygen could also originate from the surface when exposed to air during the EDS analysis, the data in Fig. 6.6 clearly show that the dominant oxide layers were formed during tribotesting.
Examining the fluorine element present on the surface, as expected the untested surface has no trace of fluorine, there is a significant amount of fluoride for the lower velocities and minimal amounts on the surfaces tested above the critical velocity. It should be noted that fluorine is one of the most crucial chemical elements of halogenated refrigerants, specifically for HFO-1234yf, which influences its tribological performance. The significant presence of fluorine at 0.6 m/s and 2.4 m/s, indicating the development of fluorine-passivated boundary tribofilms, was in agreement with the tribological and SEM findings.

6.2.2. Set 2 - Wear Experiments

Tribological Experiments

Figure 6.7(a) shows typical COF values versus sliding distance, under different velocity and normal load conditions. These experiments were conducted at 25% of the maximum scuffing load for each of the velocities, as shown in Table 6.2. At a lower velocity of 0.6 m/s and load of...
650 N (which is 25% of the scuffing load at 0.6 m/s), the friction coefficient was steady at about 0.08, with no run-in behavior or instability during the entire experiment. It is postulated that at such relatively mild condition of low load and low velocity, the interface formed well-adhered oxide layers separating the two contacting surfaces. Moreover, the operating conditions were not favorable to initiate fluorinated interaction at the interface. Therefore, under these sliding conditions oxygen-enriched tribochemical reactions prevailed, which was also confirmed in the preceding sections.

**Fig. 6.7:** Typical Set 2 wear experiments: (a) COF versus sliding distance, (b) Wear rate versus sliding velocity.

For intermediate velocities (between 1.2 m/s and 3.0 m/s), a run-in behavior was observed suggesting fluorine-dominating surface interactions at the contact interface. The COF became unstable followed by self-healing, as discussed in the previous section. Interesting to note that in these cases, under steady-state conditions, the friction coefficient was lower in the range of 0.045-0.07, compared to 0.08 in the case of 0.6 m/s. It is suggested that fluorine-passivated tribofilms have a lower shear strength, compared to the oxide-layer for the 0.6 m/s case, resulting in lower friction. Above the critical velocity, the interface failed before completing the
experiments, which is attributed to the rate of tribolayer removal being higher than the rate of formation, thus exposing the bare material. Interestingly, at higher sliding velocities (3.6 m/s or above) the COF was very low at 0.03. This could be attributed to “melt lubrication,” originating from melting of surface material at high sliding velocities. The melted metal forms a liquid film of lubrication at the interface and results in very low friction coefficient. However, subsequent cooling would solidify this melt metals and a non-functional rougher surface would evolve, namely galling. This observation was in accord with the findings by Lim et al. [98].

Figure 6.7(b) shows the calculated wear rate as a function of sliding velocity, obtained from the Set 2 - constant load wear experiments that were present in Fig. 6.7(a). At 0.6 m/s and low load of 650 N, the wear rate was the lowest ~10^{-5} mg/m-N, compared to higher sliding velocities, attributed to the beneficial tribolayer formation. No significant change in the wear rate was observed until the critical velocity. The wear rate increased sharply by an order of magnitude to 10^{-4} mg/m-N for 2.4 and 3.0 m/s, due to mechanical rubbing.

SEM Analysis

Figure 6.8 shows the SEM micrographs of the worn disk surfaces tested under Set 2 – wear experiments. Figure 6.8(a) shows an untested/virgin sample, which was not subjected to refrigerant/lubricant environment. Graphite flakes in the pearlite matrix were seen, which is typical microstructure of gray cast iron. No graphite flakes were visible on the surface after the tribological experiments at 0.6 m/s, Fig. 6.8(b). It appears that the graphite flakes were completely covered by the oxygen-rich tribofilms with no surface irregularities. Furthermore, the intact and uniform nature of the oxygen-based layer led to stable friction behavior. Conversely, a rough or ‘porous’ typed structure was seen after tribotesting at 1.8 m/s, Fig. 6.8(c), 2.4 m/s,
Fig. 6.8(d), and 3.0 m/s, Fig. 6.8(e). This change in morphological evolution could be attributed to different tribochemical reactions under these velocities and loads. Moreover, a self-healing ‘run-in’ behavior was observed under these velocities, as discussed earlier, due to the refrigerant/lubricant fluorine-enriched tribofilm formation.

Initiation of plastic-flow induced adhesive wear was seen for the sliding velocity of 3.0 m/s. This was an early symptom of tribofilm breakdown, which eventually led to catastrophic failure due to adhesive wear. On the other hand, severe roughening of the surface associated with mechanical rubbing was seen for the higher sliding velocity of 3.6 m/s (above critical velocity). Formation of tribofilms was limited under this velocity, resulting in gross damage of the surface, Fig. 6.8(f). Significant amount of material loss from the surface was evident, leading to high wear rate, which is in agreement with the tribological results.

**EDS Analysis**

Figure 6.9 shows the EDS results of the tested samples under Set 2 – wear experiments. The variation of carbon, oxygen and fluorine elements was similar with the results of the Set 1 - scuffing experiments. The amount of carbon on the surface changed at high sliding velocities, indicating no protective tribolayers. The amount of oxygen at 0.6 m/s is higher compared to the other sliding velocities and no fluorine was detected at this velocity. From the tribological experiments, a steady COF was measured, implying no intermediate action due to fluorination. Thus, at low sliding velocities and loads, fluorinated reactions did not take place at the interface, and the wear was dominated by the presence of oxide layers.
Fig. 6.8: SEM micrographs of the worn samples tested under Set 2 wear experiments: (a) Untested/Virgin sample; (b) 0.6 m/s and 650 N; (c) 1.8 m/s and 250 N; (d) 2.4 m/s and 200 N; (e) 3.0 m/s and 75 N; (f) 3.6 m/s and 75 N [thick white arrows show sliding direction].

For velocities of 1.8 m/s and 2.4 m/s, the amount of oxygen was slightly reduced, whereas the amount of fluorine dramatically increased. Thus, we conclude that fluorinated reactions took place over the oxide layer, and such reactions were governed by a temperature of 70 °C. At very
high sliding velocities, both oxide and fluoride films were destroyed resulting in severe mechanical surface damage.

![Bar chart showing EDS analysis of worn samples (disks) tested under Set 2 - wear experiments.](image)

**Fig. 6.9:** EDS analysis of the worn samples (disks) tested under Set 2 - wear experiments.

### 6.3. WEAR REGIMES AND WEAR MAP

Figure 6.10 summarizes the influence of operating conditions on the prevailing wear mechanisms, using both Set 1 –scuffing, and Set 2 –wear experiments. Four distinct wear regions were identified based on the operating conditions (and also shown by representative SEM micrographs). These regions, which are designated as regimes I, II, III, and IV are separated by three different lines (AB, CD and DE), and are described below. Note that, Lim et al. [98] devised several wear maps for different steels and introduced different terminologies to describe dominating wear mechanisms. We also observed two similar wear mechanisms based on the operating conditions, namely melt wear and oxidative wear. However, other mechanisms
differ significantly due to the presence of refrigerant and lubricant. The study by Lim et al. was under dry sliding condition and in the presence of atmospheric air, limiting its usefulness for compressor systems that operate under refrigerant/lubricant environments. For this reason, in this study we introduced two different wear mechanisms associated with refrigerant and lubricant, namely delamination/breakdown of protective films and fluorinated dominating wear.

**Regime I—Severe Adhesive Wear or Delamination of Protective Film.** Encountered at low to moderate sliding velocities and high normal applied loads. Surface damage was due to scuffing failure associated with breakdown of the protective tribolayers. The tribolayers were composed of oxygen and fluorine-based species that were developed during the triboexperiments. Plasticity-induced adhesive failure accompanied by spalling was observed, along with traces of tribofilms, Fig. 6.10(a).

**Regime II—Mechanical Rubbing or Melting Wear.** Encountered at high sliding velocities and low to moderate loads. It is predominantly a high wear regime, where gray cast iron interface failed due to mechanical rubbing resulting in ‘galling’ type damage, Fig. 6.10(b). The influence of normal load was less significant in this regime, suggesting failure due to higher sliding velocities (above a critical value), where tribofilm destruction rate is higher that tribofilm formation rate.

**Regime III—Moderate Wear or Fluorine Dominated Wear.** Encountered under moderate loads and moderate velocities. The wear in this regime was dominated by fluorine-enriched tribofilms. Porous surface morphology was developed, Fig. 6.10(e), due to tribochemical interactions in the contact zone, and a self-healing run-in behavior in the COF was observed.
**Region IV—Minimal Oxidative Wear.** Encountered at low loads and low sliding velocities. No significant damage was observed in this region, suggesting intact tribofilm development, Fig.
6.10(d). The main chemical composition of the protective tribofilm is oxygen, which is protecting the surface from wear.

6.4. CONCLUSIONS

Tribological experiments were performed using gray cast iron under a broad range of loading and sliding conditions in the presence of environmentally friendly HFO-1234yf refrigerant. Two types of experiments were conducted to measure the maximum scuffing loads and associated wear mechanisms. From the scuffing experiments, it was found that scuffing loads decreased with increasing sliding velocity, following a linear trend up to a critical velocity. Beyond the critical velocity, scuffing loads remained unchanged with sliding velocity, suggesting a mechanical-dominant wear mode. Below the critical velocity, the wear mechanisms were predominantly influenced by the formation of tribofilms. The formation of tribofilms (fluorine enriched) was initiated when the bulk temperature reached about 70 °C due to either reaction kinetics or frictional heating. Moreover, sliding duration also played a major role in initiating such protective films. SEM morphological analysis revealed scuffing type wear mechanisms below the critical velocity at high loads. In contrast, at high sliding velocities above a critical velocity, galling behavior was predominant, regardless of the normal load.

Two different tribofilms were detected, namely oxygen-enriched and fluorine-based tribofilms, which determined the wear mechanisms at different velocity/loading conditions. In the oxygen-dominating wear regime, a compact nature of oxide layer was seen, resulting in stable and steady friction behavior. On the contrary, in the fluorine-dominating wear regime, a porous-textured surface morphology was seen via SEM. The formation of tribofilms at this region involved a self-healed instability in the COF behavior. These conditions prevailed either at low sliding velocities and high normal loads or at intermediate velocities (velocities between 1.2 m/s to 3.0
m/s) and moderate loads. Based on experimental and morphological finding, four different wear regimes were constructed, identifying competitive influence of oxygen or fluorine enriched tribofilms along with mechanical rubbing.
CHAPTER 7
ADVANCED POLYMER COATINGS IN HFO-1234YF ENVIRONMENT

This chapter describes tribological performance of state-of-art polymeric based coatings in the presence of new environmentally friendly refrigerant (HFO-1234yf). Earlier studies on the tribological performance of some polymeric coatings in refrigerated environments have been discussed in chapter two. This chapter will emphasize the synthesis and performance of an advanced coating system, namely aromatic thermosetting polyester (ATSP) blended with PTFE, referred to as PTFE/ATSP. Furthermore, how the topmost surface of a polymer governs the tribological performance is also addressed in this chapter. Additionally, interactions between polymer materials and a PAG-based lubricant will be discussed from a tribological perspective.

7.1. AROMATIC THERMOSETTING POLYESTER (ATSP)

The ATSP material was invented/synthesized by Dr. Economy in the mid-1990s [99-100]. Since then further development of this material, as far as its tribological performance, has been undertaken by several researchers [64-66]. This material possesses the backbone structure of polyester, which has the tendency to exhibit liquid crystallinity as invented by Reinitzer [101]. Note that, the tribological performance can be improved with the introduction of liquid crystallinity as addressed by numerous studies [102-103]. Thus, the beneficial effect of liquid crystallinity in ATSP has made this material a potential candidate for tribological applications.
Furthermore, ATSP exhibits good dimensional and thermal stability (up to 350°C in air and 425°C in nitrogen), good resistance to flame and ablation, good chemical resistance, and good adhesion and repair capabilities. Additionally, ATSP shows the characteristic of Interchain Transesterification Reactions (ITR), which facilitates the synthetic process and recovers micro-crack and voids in the material system. The synthesis process of the ATSP blend with PTFE materials is been discussed below.

7.1.1. Synthesis Process

Two end groups, namely carboxylic acid (oligomer C2) and acetoxy (oligomer A1), are used as the precursors of ATSP materials as shown in fig. 7.1. These oligomers were made from a mixture of hydroquinone diacetate (HQDA), p-acetoxybenzoic acid (ABA), isophthalic acid (IPA), and trimesic acid (TMA). Oligomer C2 and A1 was produced by mixing TMA, ABA, IPA and HQDA as a moral ratio of 1:6:4:4 and 2:5:2:7, respectively. The oligomers were mixed in a ratio 1.44:1.00 by weight (C2/A1) and then dissolved in N-Methyl-2-Pyrrolidone solution. The oligomers were then processed through several synthesizing and curing steps until obtaining the final solidified products. The solidified products were then grounded to fine powder in order to facilitate the mixing with PTFE. The powders were dissolved into N-Methyl-2-Pyrrolidone solution and sprayed over gray cast iron samples to apply it as a coating. Coating uniformity was maintained through controlled spray rate per pass. Further details of the synthesis process can be found elsewhere [104].
Fig. 7.1: Oligomers: C2 and A1 for ATSP based polymeric coatings

7.1.2 Tribological Applications

Understanding the tribological performance of ATSP materials has seen interests in recent years. However, these studies mostly focus on evaluating the friction and wear behavior for bulk composites. For example, Demas et al. investigated a wide range of compositions using blends of ATSP with polytetrafluoroethylene (PTFE) [65]. PTFE has been widely used because of its unique characteristics of chemical inerterness, high and low-temperature stability, and above all...
excellent lubricity effect. However, PTFE shows poor wear resistance due to continuous transfer of material to the counter surface as explained in chapter 2. Such kind of issues can be mitigated with inclusion fillers including PEEK [59-60], MoS$_2$ [105-106], Graphite, Polyimide, and so on. Nevertheless, no matter which filler is used, any improvements towards the wear resistant generally occur at the expense of lubricity. On the other hand, neat ATSP material shows comparatively higher friction. Therefore, this is believed that blend of ATSP and PTFE will offer better interfacial integrity, meaning low wear and low friction.

ATSP is considered as a potential candidate for advanced tribological interfaces for possessing good thermal and dimensional stability along with strong adhesive nature to the surface, as mentioned before. Yongqing et al. demonstrated an improved surface integrity and tribological performance for ATSP blended with ultrahigh molecular weight polyethylene (UHMWPE) and polyethylene-co-acrylic (PEA) acid as compatibilizer [64]. They reported almost zero wear and self-healing nature of ATSP/UHMWPE (with PEA) to counter surface voids and micro-cracks. Such study could be used for bio-tribological applications, for example in the field of hip-joint assemblies. Demas et al. studied the tribological performance of different blends of ATSP and PTFE for air-conditioning compressor applications [65]. In this study, they compared ATSP/PTFE bulk materials with high bearing state-of-the-art commercially available polymers in order to investigate friction and wear behavior. They also reported an excellent wear resistance for ATSP materials when an optimum PTFE-based blending composition was used. On a different study, Zhang et al. also showed superior performance of ATSP materials with fluoro-additives, applied as solid lubricant, compared with high-grade PTFE coatings [66]. Nonetheless, these studies were conducted for bulk composite and under dry conditions only.
Note that, the tribological behavior of a material as a coating will likely be different from the bulk system due to imposed boundary conditions. The boundary of a coating is confined by air-coating interface and coating-substrate interface. Besides the geometrical constrain issues, the tribological performance of polymeric systems strongly depends on working environments, for examples the presence of lubricants or refrigerants. In this study, therefore, the tribological investigation has been performed for state-of-the-art coatings and advanced ATSP/PTFE coatings.

7.2. **TRIBO-EXPERIMENTAL DETAILS**

7.2.1. **Experimental Conditions**

Herein, we have researched the possible applications of advanced polymeric materials in mobile air-conditioning systems, as discussed in the preceding sections. In order to investigate this feasibility, swash-plate type automotive air-conditioning compressors were experimentally simulated using a specialized high pressure tribometer (HPT). The pins used in this work were from actual components of automotive air-conditioning compressors, referred to as “shoes.” The shoe surface is crowned to retain the lubricant during sliding contact, as shown in fig. 7.2. A self-aligned holder is used for the shoe to ensure evenly distributed normal contact load. Note that, most of the experimental details have already been discussed in the preceding chapters.
Fig. 7.2. (a) Experimental simulation of swash plate compressor using pin-on-disk configuration, (b) 52100 steel shoe with crowned shape, and (c) cross section of polymeric coating [55]

Two sets of experiments were performed, namely under dry/unlubricated conditions (set 1) and boundary lubricated conditions (set 2). All the experiments were carried out under a normal load of about 445 N and sliding velocity of 3.6 m/s (1500 rpm). Note that, such experimental conditions have been used in previous studies for CO₂ [55] and HFC-134a refrigerants [53]. Therefore, a comparative analysis will be possible to understand the influence of specific refrigerants on polymeric coatings.

A separate set of experiments was performed on ATSP/PTFE and PTFE/MoS₂ coatings. These two coatings have been chosen due to the fact that they represent two extreme performance characteristics (best and worst). For this set of experiments, tribological tests have been carried out for 60 min at a sliding velocity of 3.6 m/s to produce 1200 m of sliding distance. A small amount of lubricant (46 mg) is directly applied at the interface to develop boundary lubrication conditions. A commonly used Polyalkylene Glycol (PAG) based lubricant is used for
this study. This lubricant is synthetic and suitable for HFO-1234yf refrigerant as discussed in chapter 5.

The tribology chamber pressure was kept constant at 0.3 MPa of HFO-1234yf refrigerant. The operating temperature was 90°C, which is typically found at the outlet of automotive air-conditioning compressor systems. The experimental conditions are summarized in table -7.1.

Table 7.1: Experimental and operating conditions for polymer coatings

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Dry (Set 1)</th>
<th>Boundary (Set 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Unidirectional</td>
<td>Unidirectional</td>
</tr>
<tr>
<td>Normal Load, N</td>
<td>445</td>
<td>445</td>
</tr>
<tr>
<td>Sliding Velocity, m/s</td>
<td>3.6</td>
<td>3.6</td>
</tr>
<tr>
<td>Chamber Pressure, MPa</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Operating Temperature, °C</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Lubricant</td>
<td>Dry</td>
<td>PAG (300 SUS)</td>
</tr>
<tr>
<td>Duration, min</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>

7.2.2. Experimental Samples

Five different coatings, namely PTFE/PEEK, PTFE/Pyrrolidone, PTFE/MoS$_2$, Fluorocarbon and ATSP/PTFE, were used in this study. These coatings were deposited on gray cast iron substrates. Note that, gray cast iron is commonly used material for air conditioning compressor systems (chapter 3 and 6). The coatings were obtained from different suppliers. Therefore, the actual compositions of the coatings were somewhat unknown as they are propriety of the coating suppliers. However, some information regarding these coatings can be found elsewhere [55].
Noteworthy, ATSP/PTFE is consisted of ATSP and 5% weight of PTFE only. No other substances or fillers have been used in this polymeric composite, unlike traditional commercial coatings. The glass transition temperature for ATSP is about 240 °C -285 °C and its hardness is about 83 (Shore E) on Rockwell standard. Other thermo-physical and mechanical properties can be found in supplier’s catalog. For direct comparison, all the coatings have similar thickness and surface roughness. Coating materials and thickness values are tabulated in table-7.2.

### Table 7.2: Roughness and thickness of the tested polymeric coatings

<table>
<thead>
<tr>
<th>Samples</th>
<th>Roughness (µm)</th>
<th>Thickness (µm)</th>
<th>Commercial Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE/ATSP</td>
<td>1.48</td>
<td>20-25</td>
<td>ATSP</td>
</tr>
<tr>
<td>PTFE/Pyrrolidone</td>
<td>1.25</td>
<td>20-25</td>
<td>DuPont® Teflon® 958-303</td>
</tr>
<tr>
<td>PTFE/MoS₂</td>
<td>1.14</td>
<td>20-25</td>
<td>Fluorolon® 325</td>
</tr>
<tr>
<td>PTFE/PEEK</td>
<td>1.05</td>
<td>20-25</td>
<td>1704 PEEK/PTFE</td>
</tr>
<tr>
<td>Fluorocarbon</td>
<td>1.53</td>
<td>30-35</td>
<td>Impreglon® 218</td>
</tr>
</tbody>
</table>

All the samples were cleaned ultrasonically under submerged solution of isopropyl alcohol followed by drying using warm air.

### 7.3. TRIBOLOGICAL RESULTS

#### 7.3.1. Frictional Behavior

Fig. 7.3 depicts frictional behavior of five polymeric coatings, measured from controlled tribological experiments. Fig. 7.2(a) represents the variation of coefficient of friction (COF) along with sliding distance under dry conditions. Among the tested samples, ATSP/PTFE
exhibited superior performance, resulting in stable and steady friction coefficient. The friction coefficient was about 0.018 which was the lowest compared to the other coatings.

PTFE/Pyrrolidone and PTFE/MoS$_2$ showed almost similar frictional behavior in the presence of HFO-1234yf refrigerant. The friction coefficient was about 0.020-0.023 in these cases, which was comparable to the ATSP/PTFE based coatings. On the contrary, an intermediate transitional behavior was observed for PTFE/PEEK based coating, suggesting a reactive interface like the metallic contacts associated with HFO-1234yf refrigerant. Note that, such kind of ‘run-in’ behavior is a typical tribological characteristic of HFO-1234yf refrigerant [62]. In the case of Fluorocarbon-based coatings, the tribological performance was poor under this refrigerant condition, causing a COF fluctuation between 0.020 and 0.050. However, no sharp rise in friction coefficient was observed in this case.

Friction characteristics of the polymeric coatings under boundary lubrication are shown in fig. 7.3(b). Similar to dry conditions, ATSP/PTFE showed excellent performance under boundary lubrication. The COF was very low at about 0.012, which is about 33% less than the dry condition. No fluctuation in the COF was observed, meaning a steady and stable interface. Interestingly, for the case of PTFE/MoS$_2$ the friction coefficient was higher (about 0.04) compared to dry condition (COF ~ 0.022). This could be due to the impediment of the transfer film, resulting from adverse interaction between PTFE/MoS$_2$ and PAG lubricant. This phenomenon will be discussed later with the aid of SEM analysis. On the other hand, Fluorocarbon-based coatings failed before completing the experiments under boundary lubricated conditions. Remarkably, the COF increased abruptly at the onset of the catastrophic failure. This also suggested negative interactions between fluorocarbon particles and PAG lubricant.
Fig. 7.3: Frictional behavior of different polymeric coatings: (a) under dry conditions, and (b) under boundary lubricated conditions (PAG lubricant)

7.3.2. Microscopic and Topographic Measurements

Fig. 7.4 shows optical microscopic images for tested (worn) disk samples under boundary lubricated conditions. PTFE/ATSP or PTFE/C2A1 showed no wear scars on the surface, meaning better topographical integrity. This shows that the ATSP/PTFE coating system did not undergo severe contact conditions under lubricated environment, meaning a synergistic combination. The underlying mechanism will be elucidated later with the aid of morphological analysis. In the case of PTFE/Pyrrolidone, no significant surface damage was seen for lubricated conditions. On the contrary, for the PTFE/PEEK coating system, some deep wear scratch was observed. Interestingly, a rough topography associated with deep wear scratch was seen for PTFE/MoS$_2$ coating. Therefore, it is conjectured that PTFE/MoS$_2$ experienced a continuous loss of material from the top surface under boundary lubrication, meaning adverse interactions between PTFE/MoS$_2$ and PAG lubricant, as mentioned in the previous section. Note that the
Fluorocarbon based coating showed complete removal of the coating, exposing the substrate of cast iron material. In addition, the substrate materials also experienced scuffing type failure which is in accord with frictional behavior (sharp rise in friction behavior). This implied that fluorocarbon particles acted adversely with PAG lubricant system, resulting in severe scuffing type failure.

![Microscopic images of five different polymeric coatings](image)

**Fig. 7.4:** Optical microscopic images of five different polymeric coatings (tested under boundary lubrication conditions). Arrows show the direction of sliding.

### 7.3.3. Wear Analysis

Fig. 7.5 shows the quantitative wear profiles of worn polymeric disk samples tested under both dry and lubricated conditions. Almost zero wear was measured for ATSP/PTFE based coating under both dry and lubricated conditions as can be seen in fig. 7.5(a). On the other hand, PTFE/MoS\(_2\) (fig. 7.5 (b)) showed low wear under dry conditions only. The measured wear depth in this case was about 3 \(\mu\)m. However, this was increased to about 6-7 \(\mu\)m for the lubricated conditions.
condition along with about 15 μm of a deep wear scratch. This implied that PTFE/MoS$_2$ interacts negatively with PAG/HFO-1234yf system, producing significant surface cracks and micro pits. Fluorocarbon based coating exhibited almost complete removal of the coatings from the surface regardless of sliding conditions as can be seen in fig. 7.5 (c). In both of the cases (unlubricated and boundary lubricated), the average wear depth is about 30 μm, which is equal to coating thickness. Note that, the lubricated condition is more severe compared to the dry condition as identified by abrupt increases in the COF measurements. Under dry conditions, the wear debris acts as third body lubricant to protect the substrate from further wear. However, under lubricated conditions, the interface scuffed and caused scuffing failure to the substrate as well (wear scratch exceeded above 40 μm) as discussed before.

![Wear profiles of the polymeric coatings tested under both dry and lubricated conditions](image)

**Fig. 7.5:** Wear profiles of the polymeric coatings tested under both dry and lubricated conditions: (a) PTFE/ATSP, (b) PTFE/MoS$_2$, (c) Fluorocarbon, (d) PTFE/Pyrrolidone, and (e) PTFE/PEEK
PTFE/Pyrrolidone (fig. 7.5 (d)) showed better performance for lubricated condition like ATSP/PTFE-based coatings. However, the wear depth was higher for dry the condition, compared to ATSP/PTFE coating.

7.4. DURABILITY STUDY

Based on results from the comparative study of the five polymeric coatings (discussed in the previous section), two of the coatings have been further investigated for clear understanding underpinning synergistic or antagonistic performance. Fig. 7.6 depicts the tribological results, obtained from long duration experiments of 12km of sliding distance. Fig. 7.6(a) and 7.6 (b) show the COF behavior under unlubricated and boundary lubricated conditions, respectively. Under dry conditions, the COFs were almost similar for both PTFE/ATSP and PTFE/MoS$_2$ coating systems (0.019 versus 0.021), as can be seen in fig. 7.5(a). However, under boundary lubrication conditions, a distinct behavior is observed. The COF for PTFE/ATSP still remained stable and lower compared to dry condition. Interestingly, the COF for PTFE/MoS$_2$ became unstable with the inclusion of PAG based lubricant at the interface. Near contact temperature (NCT) was higher (about 180 °C) for ATSP/PTFE system compared to PTFE/MoS$_2$ (fig. 7.6 (c) and 7.6 (d)). Under such temperature, ITR mechanism is activated for ATSP material and provides better surface integrity by self-healing of voids and micro-cracks [64,104]. This mechanism prevails when the contact condition results sliding ATSP against ATSP materials. This would be possible if ATSP materials are transferred to the counter surface. In the later sections, it will be discussed how ATSP versus ATSP sliding occurs in the case of sliding contacts.
Fig. 7.6: Tribological results for durability study: (a) COF results under dry conditions, (b) COF results at boundary lubricated conditions, (c) Near contact temperature (NCT) under dry conditions, and (d) NCT under boundary lubricated conditions.

Typical profilometric wear analyses of the two coatings, namely PTFE/ATSP and PTFE/MoS$_2$, tested under both unlubricated and boundary lubricated conditions are shown in fig. 7.7. Under dry conditions, higher wear depth was measured for PTFE/MoS$_2$ compared to PTFE/ATSP (average wear depth 5 μm versus 2.5 μm, respectively). Note that, in the case of short duration experiments (about 6000 m of sliding), the measured wear depths were 1.0 μm and 2.5 μm for PTFE/ATSP and PTFE/MoS$_2$, respectively. This implies that PTFE/ATSP offers better wear
resistance compared to PTFE/MoS$_2$. Interestingly, the wear behavior decreased significantly in the case of PTFE/MoS$_2$ for boundary lubricated conditions. This observation is in accord with the previous short duration experiments. About 8 μm of average wear depth was measured in this case. This was significantly high compared to PTFE/ATSP (average wear depth was about 1μm). These observations inferred a synergistic effect for PTFE/ATSP and PAG lubricant, while antagonistic effect for PTFE/MoS$_2$ and PAG lubricant system.

![Wear profilometric analysis](image)

**Fig 7.7:** Wear profilometric analysis: (a) under unlubricated condition, (b) under boundary lubricated condition.

7.5. **Morphological Analysis**

7.5.1 **Morphology of Coatings**

SEM analysis has been performed via JEOL6060LV instrument. An exciting voltage of 10kV was used to obtain these micrographs. All the samples were sputtered with Au-Pd for 35 seconds at a rate of 4 nm/sec prior to measuring the SEM images to reduce conductivity issues. Fig. 7.8 portrays scanning electron micrographs of the virgin and tested samples of ATSP/PTFE coating. Surface segregation was revealed from this analysis, ensuing a textured pattern as can be seen in
fig. 7.8 (a). This surface segregation could be developed through crosslinking procedure [107-108]. In addition, polymeric crystallinity also caused surface segregation due to microphase-separation at the air-polymer interface [109-111], which will be discussed below.

Note that, Kun et al. observed surface segregation on ATSP blended polyimide surface for the first time [112]. They utilized different analytical instruments in order to find the mechanisms underlying this phenomenon. They reasoned that surface segregation is originated due to crosslinking of ATSP in conjunction with differences in molecular weights between ATSP and polyimide. This surface segregation can govern the tribological performance. Fig. 7.8(b) represents the worn disk sample after a tribological experiment under boundary lubrication. Material enrichment associated with surface segregation still remains intact in this case. This could be attributed to the improved tribological performance associated with patterned morphology. Note that, such kind of mechanism is analogous to surface texturing on polymer surface [113]. In the case of surface texturing, friction behavior for boundary lubricated conditions show stable nature. It is believed that, surface textures serve as micro-container for lubricating oil under sliding condition. As a result, continuous supply of lubricating oil at the interface is possible, resulting in an improvement in the friction behavior. This observation is in accord with tribological experiments of ATSP/PTFE. In the case of dry condition, segregated components are sheared off and amalgamated on the surface. Some components are also transferred to the counter surface which will be shown in the next section.
Fig.7.8: Morphology of ATSP/PTFE: (a) virgin, (b) worn sample after triboexperiment under lubricated condition, (c) worn sample under dry condition

Note that, in the case of coatings, the upper surface is bounded by air or working environment while the lower surface is confined by the substrate or base material. Due to the presence of air or refrigerant/lubricant, the upper surface undergoes different chemical and physical induced interactions, including chemisorption, diffusion, and adsorption. In addition to these chemical mechanisms, the physical state and nature of polymeric chains could also develop different properties for the upper surface. Collectively, the properties, e.g., wettability, adhesion, friction and wear, of the upper surface of a polymeric coatings differs significantly compare to bulk polymers due to these chemical and physical reasons. The morphology of the top surface usually changes due to these reasons, resulting in surface segregation and multiphase behavior. Note that, material enrichment on the surface associated with surface segregation could alter the tribological behavior. This is inherent nature of polymer materials with filler additives. However, surface segregation is related to the crosslinking process. Ming et al. showed that crosslinking procedures will result in material enrichment, depending on crosslinking agent [114].

Fig. 7.9 illustrates the surface morphology of PTFE/MoS$_2$ coated disk sample via SEM analysis. Fig 7.9(a) and 7.9(b) represents the wear mode of this coating under dry conditions and under
lubricated conditions, respectively. Surface cracks associated with micro-pitting were observed all over the surface under lubricated compared to dry conditions. Under compressive loads and sliding, these pores can be filled with lubricant and resulted in an increased hydrostatic pressure beneath the surface. This would reduce the mechanical strength of the surface and will accelerate the material removal process. Furthermore, these surface cracks could act as the local sites of oil seepage into the coating materials. This would further enhance the wear process.

**Fig. 7.9:** Micrographs of PTFE/MoS$_2$ based polymeric coating: (a) dry condition, (b) lubricated condition

### 7.5.2 Role of Transfer Layer

In the case of contacting/sliding polymers, material transfer from the polymeric surface to the counter surface is a typical phenomenon [115-116]. Such kind of material transfer governs the overall tribological performance for polymeric-based interfaces. This is believed that, transfer films on the counter surface would act as a shielding for polymer surface against contact from hard metallic asperities. Note that, the transfer film can act as a third body lubricant for the interface, reducing the wear while maintaining low COF. However, it is not clear why transfer films are selectively developed and the mechanisms underpinning this transfer. It is widely
accepted that material transfer occurs from the topmost surface of the polymer. Therefore, understanding the morphology and chemical composition of the topmost surface is critical to understand this material transfer process. Most importantly, the morphological integrity associated with better adhesion between the transfer film and the counter surface is also important to ensure a sustainable interface.

In the case of ATSP/PTFE, material enrichment towards the air-polymer interface will come in contact with the counter surface first. Segmented particles will be sheared off and will transfer to the counter surface at a subsequent stage. Since ATSP has good adhesion with most metallic surfaces, the transferred ATSP particles would firmly attach to the 52100 steel surface. Transfer of material can be hindered in the presence of liquid lubricant. Note that, a uniform transfer layer could result in a sustainable interface. On the other hand, the tribological performance can deteriorate if the migration of the polymers to the counter surface is restricted. The presence of lubricant is one kind of blockage for a successful transfer. In addition, the adhesion and chemical nature of the transfer films influence the friction and wear behavior. For example, PTFE has excellent transfer capability, resulting a low friction coefficient due to PTFE versus PTFE sliding.

Figure 7.10 shows the transfer film on the 52100 steel surface obtained via electron microscopic analysis. Fig. 7.10(a) represents the morphology of the transfer film under SEM mode, where fig. 7.10(b) depicts the same topography under backscattered electron mode (BES). From the BES mode, it is evident that material transfers from ATSP/PTFE composite and attached on the steel surface. Fig. 7.10(c) identifies intensities of chemical elements in the transfer film. The spectra for three elements have been extracted namely, Fluorine, Oxygen and Carbon. Interestingly, fluorine has been identified almost in the entire scan length. This is due to the presence of HFO-
1234yf refrigerant during the tribological experiments. Note that, refrigerant decomposes at the steel surface in the presence of HFO-1234yf refrigerant [61-63]. However, with the migration of material from the polymer surface, the steel surface was covered with a transfer film. As a result, drop in fluorine intensity has been found on the transfer film region. This would further support that, the transfer film is consisted of ATSP material. Therefore, a transfer film of ATSP is more adhesive, facilitating ATSP versus ATSP sliding in the presence of HFO-1234yf refrigerant. On the other hand, the near contact temperature is about 180 °C in the case of ATSP/PTFE. This accelerates the ITR interactions on the surface. Therefore, micro-voids and micro-cracks would be self-healed, producing better morphological integrity as observed in the previous section.

![Image of transfer layer on the counter 52100 steel shoe](image_url)

**Fig 7.10:** Transfer layer on the counter 52100 steel shoe (a) SEM micrograph, (b) Backscattered electron micrograph, (c) line scan of EDS analysis [red arrow on fig. a indicates direction of scan]
Fig. 7.11 shows the transfer film developed on the 52100 steel surface slid against PTFE/MoS$_2$ coating. EDS analysis identified the existence of fluorine on the transfer film. Thus, in the case of PTFE/MoS$_2$, it is believed that PTFE particles transferred to the counter surface. Therefore, sliding occurred between PTFE/MoS$_2$ versus PTFE, producing a low COF trend.

Figure 7.12 depicts BES micrographs of 52100 steel surface tested under boundary lubrication. Specifically, fig. 7.12(a) represents the morphology of 52100 steel surface slid against PTFE/MoS$_2$ surface, while fig. 7.12(b) shows 52100 steel surface tested against PTFE/ATSP coating. In both cases, no transfer film is observed, neither continuous or patchy forms, unlike the dry condition case. This could be attributed to the presence of liquid (lubricant) film at the interface, limiting the ability to transfer material. In the case of PTFE/MoS$_2$, the counter surface did not undergo any changes. This implies that, there was less interactions from lubricant and coating with the counter surface. As a result, continuous removal of the material occurred due to the lack of transfer film on the counter surface. On the contrary, for PTFE/ATSP system, ATSP particles attached to the counter surface as can been seen by the black spots in fig. 7.12 (b). It is
believed that the ATSP particles came off from segregated components. However, the low friction coefficient could be attributed to the presence of valleys on the surface. These micro-reservoirs could provide continuous replenishment of lubricant film during sliding operation. Therefore, PTFE/ATSP showed a synergistic effect with liquid lubricant system, which is very important, since its introduction in machinery will involve both lubricant and refrigerant.

![BES image of the 52100 steel slid against (a) PTFE/MoS\textsubscript{2} and (b) PTFE/ATSP under boundary lubricated conditions](image)

**Fig. 7.12:** BES image of the 52100 steel slid against (a) PTFE/MoS\textsubscript{2} and (b) PTFE/ATSP under boundary lubricated conditions

### 7.6. SUMMARY

The tribological performance of different coatings was measured experimentally in the presence of HFO-1234yf refrigerant and summarized in fig. 7.13. The frictional characteristics and wear behavior were evaluated by controlled tribological experiments. ATSP/PTFE based coatings exhibited superior tribological performance under specified testing conditions. A very low friction coefficient along with low wear rate was found for these cases. These coatings also
offered better performance under boundary lubricated conditions.

**Fig 7.13:** Summary of the tribological performance of five different polymer coating systems

When one considers the introduction of advanced polymeric coatings in machinery, such as air-conditioning and refrigeration compressors, it is unlikely that the lubricant will be eliminated altogether, especially until confidence in such advanced coating systems is established.

Moreover, in some cases the presence of liquid lubricant is necessary. Therefore, it is obvious that polymeric coating and liquid lubricants will be present at the same time. For the case of PTFE/ATSP, a synergistic effect has been obtained by reduction of COF by about 69%. The wear behavior was also improved with the inclusion of PAG lubricant under boundary lubrication regime. About 20% of the wear has been improved with lubricated conditions.

Material enrichment would provide the benefit of surface texturing, enhancing oil retention capabilities. PTFE/Pyrrolidone also exhibits synergistic effects in the presence of PAG/HFO-1234yf environment. Improvement towards COF and wear resistance is 63% and 15%, respectively. However, PTFE/MoS\textsubscript{2} shows a negative interaction with the PAG lubricant. Both
COF and wear resistance dropped significantly. This characteristic is attributed to the restriction of transfer film due to the presence of liquid lubricant at the interface. Interestingly, fluorocarbon fails in both the dry and lubricated conditions. Therefore, no improvement towards the wear resistance was measured. However, dry fluorocarbon particles can act as third body lubricants, keeping the COF low. Conversely, lubricated fluorocarbon particles could lead to scuffing type failure of the interface as indicated by sharp increase in COF. In the case of PTFE/PEEK, the wear behavior was improved by 43%, while the friction behavior was degraded by 9%. Comparative synergistic or antagonistic effects are showed graphically in fig. 7.14.

**Fig. 7.14:** Synergistic performance between polymer coatings and PAG lubricant in the presence HFO-1234yf refrigerant
8.1. CONCLUSIONS

In this work, the performance of a newly developed environmentally friendly refrigerant HFO-1234yf was evaluated from a wide range of tribological perspectives. Each chapter addressed different tribological issues related to sustainable solutions. Key findings and conclusions are given below:

(a) The tribological performance of advanced compressor materials in the presence of refrigerants is greatly influenced by the type of bare materials. For example, aluminum based alloy (Al390-T6) exhibits less or no significant interactions with the working refrigerants for compressor specific applications. Al390-T6 versus 52100 steel interfaces fails at the early stage of the experiments under unlubricated conditions, regardless of the type of refrigerants (HFO-1234yf or HFC-134a). On the contrary, cast iron versus cast iron based interfaces showed superior tribological performance in HFO-1234yf environment, compared to HFC-134a refrigerant. The experimental results evidenced better scuffing and friction behavior for HFO-1234yf refrigerant even under unlubricated conditions.

(b) Superior performance of HFO-1234yf refrigerant over cast iron was attributed to the formation of protective tribofilms on the surface. The new refrigerant consists of an olefin (-C=C-) bonding in its structure, being more reactive at the interface, compared
to existing single bonded (-C-C-) HFC refrigerants. Therefore, the refrigerant can easily decompose at the contact zone due to frictional heating. The decomposed products (mainly Fluorine) interact with dangling bonds of the cast iron surface, resulting in FeF$_3$ based tribofilms. Such tribofilms have been revealed via SEM analysis. EDS and XPS analysis confirmed the presence of F and FeF$_3$ based tribofilms.

(c) The tribological performance of HFO-1234yf refrigerant has also been investigated under state-of-the-art synthetic lubricants. Interestingly, a transitional behavior, followed by self-healing, has been observed with inclusion of PAG-based lubricant at the interface, under boundary lubrication (limited lubricant present at the interface). This suggests that interactions between PAG and HFO-1234yf result in fluorination at the intermediate phase of the experiment. The fluorination process is associated with transitional behavior as substantiated by tribological and morphological analysis. This has been further corroborated by tribochemical analysis utilizing XPS.

(d) Identifying a compatible lubricant to use with the newly developed refrigerant is challenging due to solubility and miscibility issues. This work has reported better performance for PAG-based lubricant over POE and mineral lubricants in the presence of HFO-1234yf refrigerant. Higher anti-scuffing loads have been measured under both high (110 °C) and room temperature for PAG, compared to POE and mineral lubricants, suggesting less solubility or low degradability of PAG’s viscosity in the presence of HFO-1234yf refrigerant. However, an intermediate transitional behavior associated with PAG-based lubricant was observed, which could potentially be optimized with additives in the lubricant.
The influence of loading conditions on tribofilms has revealed four different wear mechanisms, namely oxygen-influenced wear, fluorine-enriched wear, scuffing and mechanical rubbing. A critical sliding velocity has been measure beyond which tribofilm formation is limited. This could be attributed to higher removal rates of the refrigerant’s decomposed products compared to the formation rate. At very low loads and velocities, oxygen-enriched tribofilms are more dominant and friction coefficient is steady and stable at this region. On the other hand, at intermediate loads and velocities, the prevailing morphology includes fluorine-enriched species. An intermediate transition in the coefficient of friction (COF), followed by self-healing, is a typical characteristic for this domain of experiments. At very high sliding velocities (higher than an identified critical velocity), mechanical rubbing or galling is dominant due to limitation of tribofilms. Lastly, for velocities lower than the critical velocities and higher loads, produce scuffing type failures.

The fluorination reaction at the contact interface activates when the near contact temperature reaches 70°C. It is believed that polymerization and decomposition of the refrigerant occurs at this temperature. The fluorination reactions are also associated with transitional friction behavior. However, such interactions promote fluorine-enriched surface morphology.

Polymeric coatings interact with the working refrigerant and results in different tribological performance. Advanced ATSP/PTFE-based coatings outperform the commercial state-of-the-art coatings under both dry and boundary lubricated conditions. A synergistic effect (33% lower COF and 20% wear) is found for
ATSP/PTFE coating and PAG lubricant. Conversely, PTFE/MoS$_2$ has showed adverse interactions with lubricant, resulting in higher COF and higher wear rate.

(h) Surface segregation associated with material enrichment, via crosslinking process or coexistence of multiphase systems, offers tribo-beneficial effects. The valleys of segregated components can act as micro-reservoirs to enhance for oil retention capabilities under starved lubrication. As a result, continuous replenishment of lubricant supply is possible, which is the case for ATSP/PTFE. Remarkably, this phenomenon does not rely on formation of transfer film on the counter surface. Note that, the presence of lubricant film at the interface delays or limits the ability of transfer materials from the polymer surface to the counter surface. Therefore, under starved lubrication conditions, chemical nature and morphology of the topmost polymeric surface is critical in order to evaluate the tribological characteristics.

8.2. FUTURE WORK RECOMMENDATIONS

The novelty of this research involves the investigation of the tribological interactions between an olefin bonded gas (refrigerant) and advanced surface materials. The influence of an olefin-structured refrigerant has not been studied before (as far as the open literature is concerned). However, such kind of refrigerant possesses environmentally benign properties and several other alternatives will be developed. Below are recommendations for future works.

**Other Alternative Refrigerants**

Several other alternative refrigerants, having similar olefin-based chemical structure, are at different development stages. It is widely believed that such kind of refrigerants will have low atmospheric lifetime, that is being environmentally friendly. Future investigations could include
other candidate options, for example HFO-1234ze, HCFO-1233zd. Understanding these phenomena will clarify the impact for including chlorine molecule in the olefin-based structure. Furthermore, these studies will explain how the tribological performance will be varied with the change of olefin bonding’s orientation in a chemical structure.

**Analytical Measurements**

We have identified tribofilms in the presence of HFO-1234yf refrigerant via morphological and chemical analyses. It would also be interesting to see the chemical composition of wear debris at different phases of the tribological experiments. This will provide useful information about the evolution of surface films and will answer how the refrigerant’s chemistry is changed at the interface.

This is also recommended for future works, namely to characterize the micro- and nano-mechanical properties of the tribofilms. The measured properties can be used to develop analytical model using numerical computations. Some experimental works can be reduced if a reliable model is developed.

**Computational Modeling**

In this work, this has been experimentally evident that tribological performance of any component is greatly influenced by development of tribofilms on the surface. The tribofilms can act as a protective layer at the interface. Additionally, scuffing failure initiates when such films are broken down at the interface. Therefore, it would be an interesting future work to incorporate bulk materials, tribo-thin film, and loading conditions under a single computational scheme to predict the scuffing failure. Furthermore, we have proved that scuffing failure is associated with
change in near contact temperature. Therefore, a coupled thermal-contact simulation model can be developed, using finite element software, to predict the onset of scuffing. Friction coefficients and other parameters can be directly used from the experimental results.

**Lubricants/Additives and Materials**

This study has provided a significant insight, directive for developing future lubricants or additives. Lubricant and compressor industries are continuing their efforts to formulate an optimized lubricant for this kind of refrigerants. Therefore, it is recommended to investigate the tribological performance of newly synthesized additives or lubricants in the presence of HFO-1234yf refrigerant.

In this work, we have studied Al-alloy and Cast Iron. In future, some other tribo-pairs, for example Mn-Si brass, 4310 steel, Sn-Bi coated brass, can also be investigated to understand the interactions of alternative refrigerant and other material systems.

**Polymeric coatings**

In this work, interactions between HFO-1234yf refrigerant and advanced polymeric coating systems, including newly synthesized ATSP/PTFE coating, have been investigated. Influence of material enrichment towards the polymer-air interface on the tribological performance has been introduced in this research. This would be an interesting future work to study the distribution of segregated components on the surface and how they would govern tribological performance. In order to do this, thermosetting-based coatings with different crosslinking densities can be synthesized.
BIBLIOGRAPHY


16. Demas NG, Polycarpou AA, Conry TF. Tribological studies on scuffing due to the influence of carbon dioxide used as a refrigerant in compressors. STLE Tribology Transactions 2005; 48; 336-342.
17. Demas NG, Polycarpou AA. Ultra high pressure tribometer for testing CO2 refrigerant at chamber pressures up to 2000 psi to simulate compressor conditions. STLE Tribology Transactions 2006; 49; 291-296.


25. Demas NG, Polycarpou AA. Tribological investigation of cast iron air-conditioning compressor surfaces in CO2 refrigerant, Tribology Letters 2006; 22(3): 271-278)
26. Ayres RU, Ayres LW, Pokrovsky V. On the efficiency of US electricity usage since
1900, Energy 2005; 30: 1092-1145

27. Nagengast BA. A history of refrigerants, CFCS: Time of Transition, ASHRAE, Atlanta


31. Woydt M, Wasche R. The history of the Striebeck curve and ball bearing steels: The role

32. http://www.stle.org/resources/lubelearn/lubrication/#regimes [last accessed on
November 1, 2014]

Tribology International 1997; 30; 881-888.

34. Hsu SM, Gates RS. Effect of materials on tribochemical reactions between hydrocarbons

35. Forbes ES. Antiwear and Extreme Pressure additives for lubricants, Tribology 1970;
3(3): 145-152.

36. Papay AG. Antiwear and Extreme Pressure additives in lubricants, Lubrication Science


46. Dr Mello JDB, Binder R, Demas NG, Polycarpou AA. Effect of the actual environment present in hermetic compressors on the tribological behaviour of a Si-rich multifunctional DLC coating, Wear 2009; 267(5-8): 907-915.


48. Nunez EE, Demas NG, Polychronopoulou K, Polycarpou A A. Tribological study comparing PAG and POE lubricants used in air-conditioning compressors under the presence of CO2. STLE Tribology Transactions 2008; 51; 790-797.


70. Suh AY, Patel JJ, Polycarpou AA, Conry TF., Scuffing of cast iron and Al390-T6 materials used in compressor applications, Wear 2006; 260;735-44.


83. Yokozeki A. Solubility correlation and phase behaviors of carbon dioxide and lubricant oil mixtures. Applied Energy 2007; 84; 159-175.


86. Mizuno T, Okamoto M. Effects of lubricant viscosity at pressure and sliding velocity on lubricating conditions in the compression-friction test on sheet metals, Journal of Tribology 1982; 104(1); 53-59.


105. Winer WO. Molybdenum disulfide as a lubricant: a review of the fundamental knowledge, Wear 1967; 10: 422-452

106. Chen JH, Gage PE. Tribological characteristics of MoS2 and PTFE filled polymeric bearings, Proc. 3rd Int. ASLE Conf. on Solid Lubrication, Denver, CO 1984; 320-327.


