Tribological Performance of Polymer Based Self-lubricating Coatings

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Mechanical Engineering, master's level (120 credits)
2019

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Department of Engineering Sciences and Mathematics
Tribological Performance of Polymer Based Self-lubricating Coatings

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August 2019
Declaration

I hereby declare that this thesis has been composed solely by myself and it has not been submitted, in whole or in part, in any previous application for a degree or any other University. Except where specific reference is made to the work of others, the contents of this thesis are original.

Amit Roy
August 2019
Acknowledgments

This master thesis has been carried out at Tribolab in the division of Machine Elements at Lulea University of Technology (LTU), Sweden as part of the Joint European Master in Tribology of Surfaces and Interfaces-TRIBOS program. Therefore, I am indebted to Education, Audiovisual and Culture Executive Agency (EACEA) for funding this Erasmus Mundus TRIBOS program.

I would like to express my deep gratitude to Associate Professor Yijun Shi my project supervisor, for his patient guidance, enthusiastic encouragement and useful critiques of this research work. I would also like to thank my co-supervisor of this thesis Dr. Liwen Mu for his enormous help in doing project preparations, materials selection and training of Micro-macro Tribometer as well as result interpretation.

My grateful thanks are also extended to Professor Nazanin Emami, program coordinator of TRIBOS at LTU for her advice and assistance in keeping my progress on schedule.

Also, I wish to thank my wife Mousumi Paul Sampa who always inspire me for doing something new.

Finally, my thanks go to my parents, in-laws, and friends for their support and encouragement throughout my study.

Amit Roy
Luleå, August 2019
Abstract

The thesis comprises the two parts in each chapter: the first part focuses on the development and characterization of polyimide (PI) based composite coatings on a steel substrate. In order to improve the tribological performance of polyimide coatings, the fillers i.e. multi-walled carbon nanotubes (MWCNTs) and Graphene (GP) were added into PI and conducted friction test at elevated temperatures ranging from room temperature (RT) to 200°C. Also, the influence of fillers (MWCNTs and GP) materials into PI coatings surface, mechanical and tribological properties of polyimide composites coatings are measured. The addition of MWCNTs and GP reduces the friction coefficient as well as wear volume at elevated temperatures 50°C, 100°C and sometimes at 150°C. These temperatures play a vital role to form a lubrication layer in the contact interfaces at certain load and operating conditions. In these cases, three weight percentage (3wt%) of MWCNTs and GP into polyimide composites showed low friction and high wear-resistant as compared to other PI composites. Besides, by adding these two fillers into pure PI improved the mechanical properties such as micro-hardness and nanoindentation. The scanning electron microscope (SEM) was used to observe the wear mechanism of the composite coatings worn surfaces. The consequences expose that the fatigue wear mechanisms were predominant in the worn surfaces. Moreover, the thermal study of the polyimide composite coatings was conducted using thermal gravimetric (TG) to analyze the behavior of composite coatings at high temperatures. The results showed that the PI coatings with MWCNTs and GP have high thermal stability at 60% sample residue.

In the second part-an epoxy coatings with filler materials e.g. hexagonal boron nitride (h-BN) and expanded graphite (EG) were made and conducted their tribological i.e. friction coefficient and wear performance. Also the perfect mixing ratio 4:1 (80 wt% base epoxy matrix and 20 wt% curing agent) was determined on the basis of stoichiometric ratio to cure the epoxy accurately. Therefore, seven samples with a various weight percentage (wt%) were prepared i.e. pure epoxy, epoxy with 5wt%, 10wt%, 15wt% of h-BN and EG. All the prepared samples ran at two different loading 2 N and 4 N conditions with 5 Hz frequency, 300 rpm and 30 minutes duration. The epoxy with h-BN showed low friction as compared to EG where EG has better wear-resistant behavior than h-BN.
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Chapter 1: Introduction

This chapter extensively describes the background of polyimide coatings and epoxy coatings as well as provides the meaning and mechanism of the self-lubricating coatings. Also contains the properties and applications of polyimide, filler materials (MWCNTs; GP). Besides, this chapter includes the research gap of this study with previous work related to this performed by the researcher and the objectives of the thesis.

1.1 Tribology

Tribology is the study of science and engineering of interacting surfaces in relative motion and this study incorporates the working principles of friction, wear and lubrication. It has a vast impact on economic and industrial production since the continuously moving parts wear out and the friction resulted in a waste of energy. The proper tribological application can save around 1.3%-1.6% of a nation's GDP—which is a huge amount of money in larger countries [1]. Therefore, the self-lubricating coatings become one of the best alternative ways to reduce the friction coefficient and wear resistance of an interface.

1.2 Background of Polymer coatings

Nowadays, one of the main focal point or research area among researcher is to improve the tribological performance in moving or sliding parts like gear, bearing, bushing, etc. in automobile or spacecraft. It is estimated that the proper application of tribology study can save a huge amount of money in developed countries and contribute to boosting gross domestic product (GDP) [1]. In addition, the general trend and global demand are to reduce the friction and wear in various machine parts as well as increase the mechanical efficiency with reduced or no maintenance cost at all [2]. As a result, in order to reduce this friction produced by contacting or sliding parts, the liquid lubricants with additives are widely used nowadays. But this additives releases toxic gases, harmful metallic dust particle and eventually contaminate the environment. The governments and international organizations are much more concerned about this and putting a lot of restriction on lubricants use [3]. Hence, the researcher’s currently focusing on finding environmentally adapted additives or liquid lubricants that can reduce the existing problems of natural lubricants. But still, there are a lot of problems and limitations associated with environmentally adapted lubricants such as they can be easily evaporated at high temperature and high vacuum conditions. Besides, it can fridge at very low temperatures. These limitations restricted the use of
lubricants to reduce friction and wear in space applications. Also dissipating the frictional heat from the contact interface and maintaining the liquid lubricants in space is a challenging task. Formation of the oxide layer in the contact interface is also tough at this environment [4]. Therefore, in order to overcome all of these problems especially making possible to use in high temperature and vacuum condition, the consideration of polyimide coatings as well as epoxy coatings are emergency.

Because polyimides are well known for their excellent chemical resistant, high thermal stability, electrical characteristics, and mechanical properties. Despite this, the polyimide have high glass transition temperatures ($T_g$) ranging from 310°C - 315°C and high melting point which is not found in differential scanning calorimetry (DSC) curve [5, 6]. As such, polyimide composites coatings are often used in solar cell, spaceship antenna, light emitting diode (LED) display and in mechanical moving parts like gear, bearing and bushing etc. [7]. The major limitations of this pure polyimide coatings are high friction coefficient and high wear volume. Such poor tribological properties of polyimide coatings can be improved by the addition of various nano and micro fillers into the polyimide matrix. The summary and the purpose of the study is illustrated in figure 1.1.

**Figure 1.1:** Summary of the background of polyimide coatings

There are a lot of nano and micro fillers used by researchers into polyimide to improve tribological performance. Zhu, Mu et al. [8] used PI and carbon nanofibers (CNF) composites and tested tribological performance. Due to the addition of CNFs, the friction coefficient decreases with increasing load and sliding velocity. The heat generation and accumulation in the contact surface as a result of load and sliding velocity, soften the polymer chains and micro-melting causing lower friction. Polyimide (PI)/MWCNTs-COOH nanocomposite films were synthesized on the basis of polymerization method by Nie. Pi, et al. [9] and observed good wear resistance under seawater lubrication. The strong interfacial adhesion between PI matrix and MWCNTs-COOH nanofillers is the reason for the high wear-resistant and 0.7 wt% MWCNTs-COOH was the optimum amount for the best
tribological behavior under ocean environment. This nanofibers also increases the tensile stress and tensile modulus of the nanocomposite films. Fluorinated graphene (FG) is also used as a nanofillers in the polyimide matrix to improve the tribological performance i.e. friction coefficient by Ye, X., et al. [10]. This nanofillers also improved the mechanical and thermal performance of the PI matrix because of good dispersibility of FG sheets in PI matrix and effective transfer of stress between them [11]. Carbon fibers (CFs), having high specific strength and stiffness, excellent thermal stability and conductivity, self-lubrication and corrosion resistance [12] reinforced with polyimide increase the wear resistance due to its loading capacity. PI/CFs composites showed high friction at low temperatures but at high-temperature, COF was low [13]. To increase the tensile strength and lubricity of the PI-based coating, [14] made the homogeneous filler by inserting the MoS$_2$ nanoflowers into the hollow carbon nanofibers (HCNF). The MoS$_2$@HCNF/PI composite coatings has anti-wear and friction reduction characteristics in lubricating conditions. Satyanarayana, N., et al. [15] added single-walled carbon nanotubes (SWCNTs) into polyimide, hardness and elastic modulus increased by 60-70% of pure PI. Though the friction coefficient increased slightly the wear-resistant properties of composite coatings increased by two-fold. The coatings made on the surface of the silicon substrate. Zoo, Yeong-Seok, et al. [16] has synthesized the CNTs by catalytic decomposition and employed in ultra-high-molecular-weight polyethylene (UHMWPE) as a filler and observed that the CNTs reduced the wear significantly up to 5wt%. Cai, Hui, et al. [17], Rong, Rui Ya, et al. [18], Nie, Peng, et al. [9], Yijun, Shi, et al. [19], Ning, Wen, et al. [20], Qu, Liangwei, et al. [21], Thuau, D. et al. [22], all these researchers incorporated CNTs into pure polyimide to progress the mechanical, electrical, optical properties and also improve tribological properties. Apart from CNT, graphene is also using widely by scientists. Liu, Xiaoxu, et al. [23] incorporated graphene into the PI and tested for tensile strength. PI/GP composites increased the strength of the polymer as well as the dielectric properties. Zhang, Yanchao, et al.[4] reinforced the tribological properties of epoxy coating at higher temperature by adding graphene into it. Thermal properties, microhardness and thermal conductivity of the epoxy composite coatings were enhanced. Various studies proved that this carbon base materials i.e. MWCNT and graphene had excellent lubrication and anti-wear performance [24]. Overall, the enhancement of wear of the polymer composites was due to the formation of the lubrication layer in the contact interfaces between ball and polymer coating surfaces. The improvement of mechanical and thermal properties of the composite coatings was mainly because of proper dispersion of fillers into the polymer matrix and also the cross-linking of nanofiller in polymer structure or chains.

On the other hand, epoxies are a kind of high-performance thermosetting resin with one or more active epoxide group. This polymer have excellent chemical resistance, adhesion, durability at high and low temperatures, good electrical resistance, mechanical properties (high strength and toughness), and low shrinkage. As a result the epoxies are widely using in various fields such as protective coatings for appliances, automotive primers, pipes, encapsulation of electrical and electronic instrument, adhesives, bonding
Introduction

materials for dental usages, replacement of welding and riveting in aircraft and automobile, matrix material for composites in aerospace industry, printed circuitry, pressure vessel and pipes, and construction usages such as flooring, paving and airport runway repair [25, 26]. Proper ratio and dispersion of appropriate filler materials like hexagonal boron nitride (h-BN) and expanded graphite (EG) with epoxy gives a low wear and friction coefficient which ensures a good protective layer against wear.

1.3 Self-lubricating polymer coatings

The term of self-lubrication sometimes misleads with oil-impregnated seals and wipers along with long-term lubrication reservoirs. But actually, self-lubrication is characterized by the components ability to transfer microscopic amounts of material to the mating surface. This transfer process creates a film that provides lubrication and reduces friction over the length of the contact surfaces [27]. Furthermore, Lv, J. and J. Shang [28] defined self-lubricating as “an adjective, means- not requiring the external application of lubrication to parts that experience friction because the lubricant is self-contained.” Also, the self-lubricating coating is the coatings which usually exhibit a low coefficient of friction and low wear with relatively good hardness. These self-lubricating metal composite coatings are classified into following two ways [29]-

- Dry based lubrication via solid lubricant and
- Wet-based lubrication via liquid lubricant encapsulated in a capsule.

In the solid lubricating coating, a tribofilm is produced in the contact interfaces of two opposing surfaces which provides a dry lubricity environment.

![Figure 1.2: Mechanism for self-lubricating coatings [30]](image)

Under a certain load and speed, the shaft having microscopic roughness rotates over the felon liner and removing a layer of it and depositing on the surface of the shaft. This materials cover the valleys of the shaft and provide a solid, smooth layer on the contact
interfaces as shown in figure 1.2 which actually acts as a tribofilm and helps to reduce friction & ultimately increases wear-resistant [30]. This is the mechanism of self-lubricating polymer coatings which actually contributes to low friction and high wear-resistant behavior in different applications. However, the amount of materials transfer on the mating surface depends on several factors, including load, speed, length of stroke and environment.

1.4 Polyimide (PI)

PI is the abbreviation form of Polyimide, a monomer of imide, well known for its outstanding mechanical, thermal, optical and chemical properties than any other polymer. This is due to the strong intermolecular forces between the polymer chains and the stiffness of the aromatic parts in the repeating units in the heterocyclic structure. The intermolecular forces include the interactions of polar, stacking of aromatic and transfer of charge as shown in figure 1.3 [31]. Because of its excellent characteristics, sometimes PI is considered as the replacement of metal in some particular applications. Commercially polyimide is known as Kapton which is formed from pyromellitic dianhydride and oxydianiline precursor by the two-step method.

**Figure 1.3:** Basic structure of polyimide (PI) [31]

In the first step producing poly (amic acid) PAA by reacting dipolar aprotic solvents such as N, N-dimethylacetamide (DMAc) and polyimide precursor. In the second and final step, the PAA is heated which is known as thermal imidization [32]. Figure 1.4 depicts the chemical reaction of the polyimide polymer.

**Figure 1.4:** Reaction for the preparation of polyimide polymer
1.5 Epoxy and Curing Agent

Epoxy resins are low molecular weight pre-polymers or high molecular weight polymers containing more than one epoxide functional group as shown in figure 1.5. The epoxide group is also sometimes referred to as a glycidyl or oxirane group. The epoxide group is planar, with a three-membered ring consisting of oxygen atoms attached to two adjacent carbon atoms. Due to the high ring strain, similar to that in cyclopropane, the group is very reactive [33, 34].

![Figure 1.5: The Epoxide functional group, where R represents the functionalized molecule](image)

Bisphenol-A, bisphenol-F, novolac are common types of epoxies depending on the reactants used for their formulation. All three are produced by reactions between epichlorohydrin and phenolic compounds. While bisphenol A is produced by the reaction between phenol and acetone. Bisphenol A is a monomer for the production of epoxy resins. This difunctional epoxy resin is known as diglycidyl ether of bisphenol-A (DGEBA) shown in figure 1.6, where $n$ denotes the number of polymerized subunits and is typically in the range from 0 to 25 [35, 36]. Diglycidyl ether of bisphenol A (DGEBA), which is produced from bisphenol A and epichlorohydrin by condensation. The DGEBA is primarily cured by aliphatic amines at room temperature, but is slowly cured by aromatic amines and requires thermal curing. The maximum heat deformation temperature of DGEBA is 120°C [37]. Since the aliphatic amine is cured at room temperature and provides excellent properties with heat resistance up to 100°C once it cured, therefore this resin is used here for tribological applications. However, curing speed depends on the type, amount of amine and also the type of epoxy resin (E51).

![Figure 1.6: Chemical Structure of DGEBA](image)

**Table 1.1**: Properties of epoxy resin

<table>
<thead>
<tr>
<th>Properties</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy Equivalent Weight (EEW)</td>
<td>184-210 gm/eq</td>
</tr>
<tr>
<td>Viscosity (25°C)</td>
<td>11000-16000 m.Pa.s ≈ cp</td>
</tr>
<tr>
<td>Molecular weight (MW)</td>
<td>380 gm/mol</td>
</tr>
</tbody>
</table>
**Table 1.2:** Properties of curing agent

<table>
<thead>
<tr>
<th>Properties</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine value</td>
<td>460-500 mg/gm</td>
</tr>
<tr>
<td>Viscosity (25°C)</td>
<td>11000-13000 m.Pa.s ≈ cp</td>
</tr>
</tbody>
</table>

EEW is the weight of resin required to obtain one equivalent of the epoxy functional group. It is widely used to calculate reactant stoichiometric ratios for reacting or curing epoxy resins. It is related to the epoxide content (%) of the epoxy resin through the following relationship:

$$EEW = \frac{43.05}{\% \text{Epoxide}} \times 100$$

where 43.05 is the molecular mass of the epoxide group.

A wide range of epoxy curing agent or functional groups is used based on which type of epoxy used to cure the epoxy resin. But to cure the epoxy at low or ambient temperature aliphatic amines are greatly used because it offers fast curing rate, moisture insensitive, electrical and mechanical properties. Also, it provides strong, and are excellent in bonding properties. They have resistance to alkalis and some inorganic acids and have good resistance to water and solvents [37, 38].

For thorough crosslinking, the hydrogen’s of the primary and secondary amines should be matched 1:1 with the epoxy groups. The amounts of curing agent and epoxy resin needed in order to obtain the 1:1 stoichiometric quantity are calculated as follows:

*Parts by weight of amine to be used with 100 parts by weight of epoxy resin (phr) = \( \frac{\text{Amine Equivalent Weight}}{\text{Epoxy Equivalent Weight}} \times 100 \) (1)*

In these cases, the amine equivalent weight can be determined in the following two ways i.e. from the molecular weight of amine or amine value.

\( Amine \ Equivalent \ weight = \frac{\text{Molecular weight of amine}}{\text{No. of available H}_2 \text{ per molecule}} \) (2)

The amine value gives the active hydrogen (NH) content of an amine hardener. It is expressed the weight of KOH in milligrams that will neutralize the NH in 1 gram of hardener. The equivalent weight of KOH is 56.1, hence,

\( Amine \ Equivalent \ Weight = \frac{56.1 \times 1000}{\text{Amine Value}} \) (3)

Here, epoxy equivalent weight (gm/eq) of epoxy E51 is 184-210 [7]. The amine value (KOH mg/gm) of T31 curing agent is 460-500. The viscosity at 25°C and relative density at 20°C are 1100-1300 m.Pa.s and 1.01-1.10 respectively [39, 40].
So based on equation (1), the amount of curing agent in 100 parts is 25. So, in the perfect mixing, the amount of base polymer is 80% while the hardener is 20%.

1.6 Filler Materials

The two different carbon-based filler materials like multi-walled carbon nanotube (MWCNT) and graphene (GP) are incorporated into pure polyimide because of its excellent characteristics as already mentioned in the background section. Some of the important features of these two fillers are discussed here.

1.6.1 Multi-Walled Carbon Nanotubes (MWCNTs)

Carbon nanotube is one of the allotropes of carbon. It is made up by rolling a single layer of graphite strips into multiple layers. In the multi-walled carbon nanotube (MWCNT), comprising of several concentrically interlinked nanotubes [41]. In this project, I used MWCNT of 25-30 nm diameter, 3-12 µm in length and 95% purity. A typical photograph of used MWCNT is portrayed in figure1.7 in nanoscale. The carbon nanotubes have a unique strength because of its orbital hybridization, where the adjacent carbon atoms form a chemical bond of $sp^2$ type. This exclusive characteristics align MWCNTs into ropes held together via van der Waals forces, resulting in ultra-high strength, and low weight with highly conductive electrical and thermal properties. It is claimed that the mechanical strength and density of MWCNTs are 100 times and one quarter that of steel respectively. MWCNTs thermal conductivity is comparable to diamond [41, 42].

![Multi-walled Carbon Nanotube (MWCNT)](image)

**Figure 1.7:** Multi-walled Carbon nanotube (MWCNT) [43]

One of the important features of this MWCNTs is hollow interior which can be filled with different nanomaterial, isolating and protecting from the neighboring environment [44]. Because of these excellent properties MWCNTs are recommended as filler materials or reinforcing additives in the polymer composites, to increase the load-carrying capacity and tribological performance simultaneously. Although the strength of individual CNT shells is extremely high, weak shear interactions between adjacent shells and tubes lead to a significant reduction in the effective strength of multi-walled carbon nanotubes [45]. Catalytic chemical vapor deposition (CCVD), laser ablation and arch discharge are the growth method for CNTs [46].
1.6.2 Graphene (GP)

Graphene is also an allotrope of carbon like MWCNTs and considered as a semi-metal. It is one atom thick and two-dimensional hexagonal honeycomb lattice structure. Graphene is highly stable because of its $sp^2$ orbital hybridization. Each atom consists of four bonds, one sigma ($\sigma$) bond ($s$, $p_x$, $p_y$) with its three neighbors and one pi ($\pi$) bond ($p_z$) oriented out of the plane. The typical distance between the atoms is 1.42 Å [24, 46].

![Graphene structure](image1.jpg)

**Figure 1.8:** Graphene (GP) is an atomic scale [24]

The common growth methods of graphene are epitaxial growth on SiC, exfoliation, chemical vapor disposition (CVD) on metal catalysts. In this thesis, the graphene as shown in figure 1.8 which was dissolved in N-methyl-2-pyrrolidone (NMP) solvent because GP forms homogeneous dispersion in it.

1.6.3 Boron Nitride (BN)

Boron nitride is also known as white graphite basically a refractory compound of boron and nitrogen with the chemical formula BN. The h-BN structure is similar to graphite and has the properties of heat and chemically resistant and is therefore used as a lubricant and an additive to cosmetic products. Furthermore, h-BN has a lamellar or layered crystalline structure as graphite and MoS$_2$ in which the bond between molecules within each layer, boron, and nitrogen atoms are bound by strong covalent bonds, while the binding between layers is almost entirely maintained by means of weak Vander Waals forces as shown in figure 1.9 [47, 48].

![Hexagonal boron nitride structure](image2.jpg)

**Figure 1.9:** h-BN structure analogous to graphite [49]
Considered to be more efficient than CNTs, shows good mechanical properties, high thermal conductivity, resistance to UV radiation, resistance to oxidation and possesses thermal stability; exhibits 20% greater interfacial adhesion to the epoxy matrix than CNTs [50]. Another important advantage of h-BN are that its lubricity does not depend on water or gas molecules trapped between the layers. As a result, this h-BN can be used in a vacuum, e.g. in space applications. The h-BN used with epoxy was in powder form of size is 1 micron and the density is 2.29 g/ml at 25°C.

**Table 1.3:** Details of h-BN used as filler with epoxy [47, 48]

<table>
<thead>
<tr>
<th>Properties</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Density</td>
<td>2.3 gm/cm³</td>
</tr>
<tr>
<td>Particle size</td>
<td>1.5 µm (average)</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>1000°C (air) and 1400°C (vacuum)</td>
</tr>
</tbody>
</table>

1.6.4 **Expanded Graphite**

The expanded graphite is also known as “intumescent flake graphite,” expandable graphite is a synthesized intercalation compound of graphite that expands or exfoliates when heated. This material is manufactured by treating flake graphite with various intercalation reagents that migrate between the graphene layers in a graphite crystal and remain as stable species.

![Figure 1.10: Expanded graphite slurry](image)

Exfoliation of the flake graphite results in an overall decrease in bulk density, increase in the volume of graphite of up to 300 times and an approximately 10 fold increase in surface area. Typically the increased surface area results in a material that has increased chemical reactivity. This reactivity is especially apparent in the oxidation rate of uncompressed material [1]. The properties and potential applications of expanded graphite are followed: good film-forming and anti-stick properties on a wide range of substrate and high aspect ratio of graphite particles for optimized thermal and electrical conductivity.
Table 1.4: Typical material data of expanded graphite slurry supplied by SGL Group

<table>
<thead>
<tr>
<th>Typical Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET (Specific surface area) (m^2/g)</td>
<td>20</td>
</tr>
<tr>
<td>Acid content (%)</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>Oxygen content (%)</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>Sulfur content (%)</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Ash content (DIN 51903)</td>
<td>≤ 1.3</td>
</tr>
</tbody>
</table>

1.7 Research Gap

A lot of works carried out to improve the mechanical, thermal and surface properties of polyimide coatings with nanofiller materials like MWCNTs and graphene by the researchers. But no one used these nanofillers for high-temperature tribological applications. So, in this thesis the MWCNTs and GP are incorporated into polyimide matrix to improve the mechanical characteristics, thermal properties and more importantly make it possible to use in high-temperature contact interfaces with low friction and high wear-resistant.

Also the hexagonal boron nitride (h-BN) and expanded graphite (EG) are the new inclusion into epoxy polymers. Finding the proper weight percentage (wt%) of this ceramic and carbon-based fillers into the epoxy and test the tribological performance is the new addition.

1.8 Objectives

The main purpose of this thesis is to find the proper filler materials of the polymers which will improve the tribological performance of polyimide coatings at elevated temperatures and will act as self-lubricating coatings. However, the broad objectives of this thesis can be listed as follows:-

1.8.1 Polyimide coatings:

a) Study of the thermal gravimetric analysis of the polyimide composite coatings to determine thermal stability.

b) Analysis of microhardness and nanoindentation behavior of prepared coatings.

c) Study of the tribological performance (friction and wear) of polyimide (PI) coatings at elevated temperatures ranging from RT to 200°C.

d) Investigation of the effect of MWCNTs and GP fillers in polyimide composite coatings.
1.8.2 Epoxy coatings:

a) Investigating the effect of boron nitride (BN) and expanded graphite (EG) on the performance of epoxy coatings;

1.9 Organization of thesis

In this project report, the tribological performance of polymer-based self-lubricating coatings is presented. On the basis of theoretical analysis and literature review, the performance results are explored.

- **Chapter 1** describes the general introduction of tribology, background of polymer coatings, self-lubricating coatings and the base materials polyimide, epoxy & filler materials properties. Also, this chapter comprises the aim of the study.
- **Chapter 2** comprises the experimental work of polymer coatings i.e. how coatings are made. The brief description of materials and the test apparatus used in this study for thermal, mechanical and other tribological test are also included.
- **Chapter 3** results and discussions section includes the thermal gravimetric analysis, micro-hardness, nanoindentation and tribological test results prepared polyimide composite coatings with the addition of MWCNTs and GP fillers.
- **Chapter 4** illustrates the results and discussions of epoxy coatings with filler materials. Also, it describes the comparison of h-BN and EG coatings.
- **Chapter 5** designates the conclusions of the objectives and experimented results of prepared polyimide composite coatings.
- **Chapter 6** provides the provision of future work of this study.
Chapter 2: Experimental Work

This section provides information about the materials selection, polymer coatings preparations and their tribological testing for the application in high temperature. Moreover, some of the tests which indicate the thermal and mechanical properties of the polyimide coatings also included in this section.

2.1 Materials

2.1.1 Materials for polyimide coatings

The aromatic polyimide precursors 4, 4 oxydianiline (ODA) with 97% purity, 200.24 gm/mol molar mass & N, N-dimethylacetamide (DMAc) with 87.12 gm/mol molar mass and aprotic solvent pyromellitic dianhydride (PMDA) with 97% purity, 218.12 gm/mol molar mass were purchased from Sigma-Aldrich. Also, the filler materials multi-walled carbon nanotube (MWCNTs) with an average 3-12 μm length, 25-30 nm diameter, purity 95%, and Graphene (GP) dissolved in N-Methyl-2-pyrrolidone (NMP) solvent were brought from China.

2.1.2 Materials for polyimide coatings

Basically, two types of filler materials e.g. expanded graphite (EG) and hexagonal boron nitride (h-BN) were used with epoxy E51 with an epoxide equivalent weight of 184-210 gm/eq. for their extensive mechanical, chemical and other properties. As a curing agent T31 (with amine value of 460-500 mg KOH/gm) was used. All the materials were bought from China. The steel of grade SS233 was used as substrate material (dimension: 60 × 30 × 3 mm³ and hardness: 205 ± 5HV₁₀₀) whose composition is Table 2.1.

Table 2.1: Chemical composition of steel substrate

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Fraction (wt%)</td>
<td>Max</td>
<td>Max</td>
<td>Max</td>
<td>Max</td>
<td>Max</td>
<td>17.0-19.0</td>
<td>8.0-11.0</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>1.0</td>
<td>2.0</td>
<td>0.045</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.2 Coating preparation

2.2.1 Steps for preparation of polyimide coatings

Figure 2.1: Diagram of polyimide coatings preparation

Figure 2.1 shows the diagram of polyimide coating preparation. It is depicted that the filler materials either MWCNTs or Graphene (GP) first dispersed in N N-dimethylacetamide (DMAc) solvents and then polyimide precursor 4, 4'-oxydianiline (ODA) dissolved into it. After that, the total solution is sonicated in 1 hour until the elements properly distributed. Then polyimide monomer Pyromellitic dianhydride (PMDA) is added into the solution and stirred 6 hours in an ice bath as it releases heat and ultimately produces poly amic acid (PAA). Here, the pure polyimide produces yellow or orange color PAA where with MWNT and GP shows mostly black PAA.

The PAA solution is poured on steel disc (100CR6 ESU hardened, Ø24 mm × 7.9 mm, and surface roughness (Ra) 120 nm, supplied by Optimal Instruments Prüftechnik GmbH, Germany, were washed with acetone and ethanol before using) and used a bar to make smoother coatings which is known as lab wound technique. The coatings were placed in a vacuum chamber at 80ºC for 10 hours to remove the moisture and solvents. To cross-linked the polyimide with filler materials the prepared coatings were heated in an oven at 100ºC and hold for 1 hour, heated from 100ºC to 200ºC and hold for 1 hour, and finally heated from 200ºC to 300ºC and hold for 1 hour. In the end, the coatings were cooled at room temperature and resulting 30 µm to 50 µm thickness coatings ready for tribological testing. The various weight percentage of prepared coatings are illustrated in table 2.2.
### Experimental Work

#### Table 2.2: Prepared coatings in terms of weight percentage (%) of MWCNTs and GP

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Mass of ODA (gm)</th>
<th>Mass of PMDA (gm)</th>
<th>Mass of DMAc (gm)</th>
<th>Filler Materials (CNT/GP) (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI</td>
<td>0.20</td>
<td>0.21</td>
<td>2</td>
<td>---</td>
</tr>
<tr>
<td>PI/0.1MWCNT</td>
<td>0.20</td>
<td>0.21</td>
<td>2</td>
<td>0.00042</td>
</tr>
<tr>
<td>PI/0.5MWCNT</td>
<td>0.20</td>
<td>0.21</td>
<td>2</td>
<td>0.0021</td>
</tr>
<tr>
<td>PI/1MWCNT</td>
<td>0.20</td>
<td>0.21</td>
<td>2</td>
<td>0.0042</td>
</tr>
<tr>
<td>PI/3MWCNT</td>
<td>0.20</td>
<td>0.21</td>
<td>2</td>
<td>0.0130</td>
</tr>
<tr>
<td>PI/5MWCNT</td>
<td>0.20</td>
<td>0.21</td>
<td>2</td>
<td>0.0221</td>
</tr>
<tr>
<td>PI/0.5GP</td>
<td>0.20</td>
<td>0.21</td>
<td>2</td>
<td>0.0021</td>
</tr>
<tr>
<td>PI/1GP</td>
<td>0.20</td>
<td>0.21</td>
<td>2</td>
<td>0.0042</td>
</tr>
<tr>
<td>PI/3GP</td>
<td>0.20</td>
<td>0.21</td>
<td>2</td>
<td>0.0130</td>
</tr>
<tr>
<td>PI/5GP</td>
<td>0.20</td>
<td>0.21</td>
<td>2</td>
<td>0.0221</td>
</tr>
</tbody>
</table>

#### 2.2.2 Steps for preparation of epoxy coatings

a) The details process of epoxy coatings preparation are followed-
b) First the base epoxy like Diglycidyl ether of bisphenol A (DGEBA), E51 and curing agent T 31 was poured in one transparent cup in 4:1 (80%:20%) ratio respectively by weight.
c) Two parts should be correctly mixed to get properly cross-linked polymer. So mixing is very important and for this, the mixer was stirred by a straw first and then sonicated around 40 minutes until it was dispersed each other. It is very important to aware during mixing to avoid the formation of any bubble.
d) To remove the air bubble in the mixer, a vacuum pump was used.
e) Once the coating was ready and then it was poured on the steel surface following the doctor blade technique. The steel substrate was placed on the wooden mold which was extended 1 mm above from the steel surface. This ensures the thickness of the final coating was 1 mm. Of course, the steel surface should be cleaned with acetone in an ultrasonic bath for 30 minutes and then it was again sonicated another 10 minutes with heptane (non-polar solvent) and finally dried at room temperature.
f) In a similar way, the boron nitride powder (h-BN) of 5wt%, 10wt% and 15wt% thoroughly mixed with epoxy E51 by stirring rod and then the mixture was sonicated 40 min to get proper dispersion of h-BN in the mixture. The curing agent T31 was added and mixed 5-6 minutes and the mixture was vacuumed to remove the bubbles before applying to coat on the steel substrate.
g) For the expanded graphite (EG), the weight percentage of 5wt%, 10wt%, and 15wt% were added to epoxy resin. For the proper dispersion of EG, ethanol was added to reduce the viscosity and sonicated for 30 min. Rest of the step was the same as earlier.
For proper curing, the coatings were kept 24 hours at room temperature.

Once the coatings were cured it’s ready for testing in micro-macro Tribometer.

The composition of epoxy coatings with various amount of h-BN and EG filler materials is depicted in table 2.3.

Table 2.3: The composition of prepared epoxy coatings in 2 gm mixture

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Mass of Epoxy (gm)</th>
<th>Mass of Curing agent (gm)</th>
<th>Mass of filler materials (h-BN/EG) (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E51-T31</td>
<td>1.60</td>
<td>0.4</td>
<td>0</td>
</tr>
<tr>
<td>E51-T31-5BN</td>
<td>1.52</td>
<td>0.38</td>
<td>0.1</td>
</tr>
<tr>
<td>E51-T31-10BN</td>
<td>1.44</td>
<td>0.36</td>
<td>0.2</td>
</tr>
<tr>
<td>E51-T31-15BN</td>
<td>1.36</td>
<td>0.34</td>
<td>0.3</td>
</tr>
<tr>
<td>E51-T31-5EG</td>
<td>1.52</td>
<td>0.38</td>
<td>0.1</td>
</tr>
<tr>
<td>E51-T31-10EG</td>
<td>1.44</td>
<td>0.36</td>
<td>0.2</td>
</tr>
<tr>
<td>E51-T31-15EG</td>
<td>1.36</td>
<td>0.34</td>
<td>0.3</td>
</tr>
</tbody>
</table>

2.3 Test apparatus and experimental procedures

To select the best polymer coatings various test apparatus were used to measure friction, wear and other instruments for emphasizing the selected tribological performance. Following instruments were used for tribological, mechanical and thermal testing of prepared coatings as shown in table 2.2 and table 2.3.

2.3.1 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) of pure PI and PI with filler materials were performed under nitrogen (N₂) atmosphere with a TGA, TA instrument Q500 thermal analyzer from 34°C to 900°C with a heating rate of 10°C /min.

2.3.2 Micro-hardness

Micro-hardness of prepared polyimide coatings were performed by the Matsuzawa MXT-α micro-hardness tester. For each specimen, five tests were conducted under the load of 10 gram and lasting for 10 seconds. Vickers method and indenter were considered for the measurement.

2.3.3 Nanoindentation

A nanoindentation test of polyimide coatings was carried out for hardness measurement by Nanoindenter by slowly increasing the load up to 20 mN and after holding for a certain time the load was gradually released. This hardness provides local or grain
Experimental Work

The hardness of the coating surfaces and Berkovich indenter was used for this. The mark of this indenter on different coatings is shown in figure 2.2. For each sample, ten different tests were conducted and the average value of ten tests was considered in this report.

![Figure 2.2: Berkovich Nanoindenter mark on a) Pure PI, b) PI/3MWCNTs and c) PI/3GP coatings surfaces](image)

2.3.4 **SRV reciprocating friction tester**

Friction test was carried out in reciprocating type ball on disc SRV (Schwingung Reibung Verschleiß) machine. A contact schematic diagram of SRV machine is shown in figure 2.3. The polyimide coatings surface were used as the lower specimens and commercially available 100Cr6 steel, Ra 20 nm with a diameter of 5 mm provided by SKF, Sweden were used as the upper specimens. The sliding was performed with a load of 10 N, frequency 5 Hz, stroke length 1000 µm and duration of 30 minutes. Before doing each test, the steel balls were cleaned with ethanol to remove the dust, dirt from the surfaces. A computer is connected to the SRV tester recorded the friction curve automatically.

![Figure 2.3: Contact geometry of reciprocating type SRV sliding friction](image)

2.3.5 **Optical Profilometer**

The wear scar produced on polymer coatings surface by steel ball during friction testing was measured in 3D optical surface profiler called Zygo New View™ 7300, USA to
measure the volume of wear loss. The wear volume loss of polymer coatings directly measured from Zygo profiler and a typical photograph of it is shown in figure 2.4.

Three repeated friction and wear tests wear carried out for each run and an average of this value was taken into calculation for this report.

![Image](image.png)

**Figure 2.4:** A photograph of a 3D optical surface profiler (Zygo New View™ 7300)

### 2.3.6 Scanning Electron Microscopy (SEM)

The type of wear occurred by the steel ball on the coating surfaces and the size of MWCNTs, GP was measured by a high-resolution bench-top scanning electron microscope (JCM- 6000 Neoscope, Jeol) at different magnifications. For this, the coating surfaces were coated with platinum to make the surface conductive. Only 3 wt% of filler materials with PI coatings has been examined for SEM as it has low friction and wear than other composite coatings. Pure polyimide coatings microscopy also observed for comparison with composite coatings.

### 2.3.7 Micro-macro tribometer

To evaluate the friction coefficient of prepared epoxy coatings at room temperature, the coating samples were kept in the lower part while the upper specimen was a 52100 bearing steel ball of 6 mm diameter and \( R_a \approx 20 \) nm surface roughness. In every test the ball was cleaned with ethanol and dried in the air as well as find a new location for the next experiment. The coatings surface was also wiped with ethanol and dried before the test begins. All the coatings are tested at two different loading i.e. 2 N and 4 N at atmospheric temperature conditions. The testing conditions for coatings are: sliding time of 30 minutes, reciprocating sliding frequency 15 Hz, rpm of 300. Figure 2.5 shows the micro-macro tribometer.
2.3.8 Wear dimensions measurement

The wear dimensions (length and width) of the tested epoxy coatings were calculated by using the appropriate scale as shown in figure 2.6. Proper scale ratio was chosen to avoid an experimental error.

Figure 2.6: Wear dimensions measurement using a scale
This chapter clearly describes the outcome of the prepared coatings i.e. thermal (thermal gravimetric analysis) performance, mechanical (micro-hardness, nanoindentation) tribological performance (friction, wear), and also the morphology of coatings wear tract.

### 3.1 Thermal Properties

The thermal properties of the prepared coatings indicate the heat-resisting limit of that coatings and this was investigated by the thermal gravimetric (TG) analysis.

#### 3.1.1 Thermal gravimetric (TG) Analysis

The thermal gravimetric analysis of pure polyimide and polyimide with different concentrations of MWCNTs were tested using a TG apparatus. 4.34 mg to 10 mg specimen was heated from 34°C to 900°C at a heating rate of 10°C/min in nitrogen ($N_2$) atmosphere as shown in figure 3.1.

![Figure 3.1](image.png)

**Figure 3.1:** (a) TG and (b) DTG curve of PI coating filled with various MWCNT contents

Whenever a polymer composite coating samples are heated, the mass of this polymer samples losses in two main ways during the thermal gravimetric analysis. In figure 3.1, it shows that in the temperature range of 34°C to 350°C, all the TG curves of polymer composite coatings follows the same change trend. But further increased of temperatures, the weight of the samples is slowly decreased due to the evaporation of moisture, water and
Results and Discussions

some organic matter of polymer matrix. This is taken place in the temperature range of 350°C to 550°C. When the temperature is increased from 550°C to 700°C, the weight loss rises sharply with this temperature range. The breakdown of the polyimide chains occurred at these temperatures which are called thermal decomposition of polymer main chain. But the degradation rate of the polyimide and polyimide composite coatings after 700°C is slow. However, the thermal stability of PI/MWCNTs composites is bigger than that of pure polyimide at high temperatures ranging from 600°C to 900°C. The red circled mark indicating the high-temperature stability of composite coatings and this is inserted in the inset of figure 3.1 in a widen view. At 60% weight residue, the corresponding temperatures are 730°C for pure PI, PI/0.5MWCNTs and PI/1MWCNTs, while for PI/5MWCNTs is 685°C and for PI/3MWCNTs is 887°C. So, MWCNTs can be enhanced the heat resistant properties of PI/MWCNTs composite coatings. Since the thermal stability of the composite coatings also depends on the proper dispersion of MWCNTs [4], it can be concluded that the 3MWCNT properly cross-linked and dispersed with the polyimide chain as its’ showing high thermal stability.

Figure 3.2: (a) TG and (b) DTG curve of PI coating filled GP dispersed in NMP

Figure 3.2, also shows the TG curve of PI/GP composite coatings and it also follows the same trend like the TG curve of PI/MWCNTs composite coatings. All the TG curves, from 34°C to 100°C follows the same pattern and then up to 425°C the trends also alike but slightly varied the values. From 425°C to 700°C, the weight losses rises abruptly. In the high-temperature range from 600°C to 900°C, the PI/3GP composites showing the high-temperature resistant properties which are 845°C because of the well-dispersion of the graphene into polyimide networks. While the thermal stability for pure PI and PI/0.5GP is 730°C; for PI/5GP is 788°C and 811°C for PI/1GP. The thermal decomposition rate of the polymer composite coatings is slow in the temperature ranging from 700°C to 900°C but decline sharply from 550°C to 700°C.
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The differential thermal gravimetry (DTG) graph in figure 3.1 (b) and 3.2 (b) shows the maximum degradation temperature at which the sample loses its maximum weight. So, in both of the graph, it’s about 600°C.

3.2 Mechanical Properties

The mechanical properties of the polyimide coatings have been determined by the micro-hardness and nanoindentation results. The micro-hardness define the average hardness of the coating surfaces where the nanoindentation indicates the local or grain hardness of that coating faces. In these cases, only PI/3MWCNTs and PI/3GP coatings investigated for nanoindentation test as it was showing good tribological performance along with PI for comparison.

3.2.1 Micro-hardness

Figure 3.3 shows the micro-hardness of polyimide coatings containing various weight percentage of multi-walled carbon nanotubes. It is shown that the hardness is gradually increasing with MWCNTs contents ranging from 0.0% to 4%. At the low percentage of MWCNTs such as 0.1%, 0.5% and 1% the hardness are 19.42 Hv, 20.56 Hv, and 21 Hv respectively while at higher percentage the hardness is also high 22.38 Hv at 5% MWCNTs. The addition of 5 wt% of MWCNTs into the polyimide matrix increases around 22% micro-hardness than pure PI.

![Figure 3.3: Effect of MWCNTs content on the micro-hardness of PI coatings](image)

On the other hand, figure 3.4 demonstrates that the addition of graphene into a polymer matrix has a little contribution to hardness improvement. Even at 1% GP the hardness decreases than the pure polyimide. This can be caused by the NMP solvent in graphene solution which provides the elastic behavior in the coating. Undoubtedly, NMP improves the graphene dispersion but removing the NMP solvent is also the challenging
task which can play a role in reducing the strength of the coatings. At 5% GP content the micro-hardness of polyimide coatings slightly increases than pure polyimide coating.

![Graph showing effect of graphene (GP) content on the micro-hardness of PI coatings](image)

**Figure 3.4:** Effect of graphene (GP) content on the micro-hardness of PI coatings

The addition of the coupling agent can effectively enhance the adhesive strength between the polyimide and fillers. However, the hardness of the polymer coatings is highly dependent on the homogeneous dispersion of fillers into the polyimide [4]. Even an astounded distribution and dispersion of fillers i.e. MWCNTs or GP into the polyimide matrix form a three-dimensional structure which ultimately contributes to improving the hardness of coatings.

3.2.2 *Nanoindentation*

Table 3.1 shows the mechanical properties of the polyimide (PI) and PI coatings with fillers MWCNTs and GP. It can be shown that the hardness of the PI/3MWCNT is higher approximately 272 MPa than 253 MP of pure PI i.e. it reduces the penetration depth. This proves that the addition of multi-walled carbon nanotube (MWCNT) into the polymer increases the hardness which ultimately contributes to carrying higher load-carrying capacity.

**Table 3.1:** Mechanical properties of PI and PI coatings with fillers via nanoindentation

<table>
<thead>
<tr>
<th>Type</th>
<th>Max. Depth (nm)</th>
<th>Plastic Depth (nm)</th>
<th>Hardness (GPa)</th>
<th>Plastic Work (nJ)</th>
<th>Elastic Work (nJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI</td>
<td>2190.267</td>
<td>1870.187</td>
<td>0.253405</td>
<td>10.99134</td>
<td>6.053784</td>
</tr>
<tr>
<td>PI/3MWCNT</td>
<td>2105.694</td>
<td>1790.466</td>
<td>0.272444</td>
<td>10.29065</td>
<td>5.973679</td>
</tr>
<tr>
<td>PI/3GP</td>
<td>2235.957</td>
<td>1887.159</td>
<td>0.249622</td>
<td>10.65366</td>
<td>6.565034</td>
</tr>
</tbody>
</table>
Results and Discussions

For better understanding, it can be shown in figure 3.5 of the nanoindentation curve of pure PI and PI/3MWCNT. The load slowly increases on the coating surface causing the surface deforms but at maximum load 20 mN, the pure PI has a higher displacement or penetration than PI/3MWCNT as shown in two dotted lines with an arrow. The main reason for the escalation of hardness is the inclusion of MWCNTs in polyimide which actually contributes to cross-link the polymer matrix with fillers and therefore increases the bond between the chains. Moreover, in the unloading curve, it is also shown that the PI/3MWCNT has a wider elastic region than pure PI i.e. MWCNTs increases the elasticity into the polymer with greater young modulus. Just before the end of unloading, there is a sudden recovery of materials in the curve for both PI and PI/3MWCNT which is occurred due to the viscoelastic behavior and thermal contraction of the polymer. PI/3MWCNT has higher value of these two properties than pure polyimide.

![Nanoindentation curve of pure PI and PI/3MWCNTs](image)

**Figure 3.5:** Nanoindentation curve of pure PI and PI/3MWCNTs

In a similar way, the nanoindentation curve of pure PI and PI/3GP can be explained as shown in figure 3.6. At the maximum load of 20 mN, the PI/3GP has a little higher deformation than pure PI. This can be happened due to the improper removal of NMP solvent into graphene which causes the coatings softer. But graphene into polyimide increases the elastic property than pure PI which can be seen in the unloading curve of figure 3.6. PI/3GP coatings recover the load little bit faster or more than pure polyimide and this is due to the increase of elasticity of PI/3GP as shown in table 3.1 where the elastic work of this coating is 6.56 nJ and the pure PI has 6.05 nJ. This high elastic work of this PI/3GP helps to recover from maximum deformation like 2235.96 nm as in table 3.1.
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Figure 3.6: Nanoindentation curve of pure PI and PI/3GP

3.3 Tribological Performance

Tribology means the study of friction and wear of contact interfaces of steel ball and coating surfaces which are included here.

3.3.1 Friction

Figure 3.7 illustrates the friction coefficient of PI and MWCNTs contents of PI coatings at different temperatures. It can be seen that the friction coefficient of neat polyimide at room temperature is 0.817, then it increases with temperature rises but at 150°C the friction becomes like room temperature (RT) and again it becomes high 0.874 at 200°C. Overall the friction coefficients of pure PI at higher temperature are relatively large than RT. This trend is also similar to friction behavior of 0.1% MWCNTs but the value of friction (0.755 to 0.849) is lower than the neat PI. At 0.5%, 1%, 3% and 5% MWCNTs content into PI the friction behavior are almost same to all i.e. at RT polyimide coatings has higher friction but with increasing temperature first, the friction reduces and then again increases. Normally at 50°C and 100°C, polymer coatings show lower friction value but PI/3MWCNTs coatings have the lowest friction 0.677 at 200°C. So, MWCNTs addition to the polymer matrix reduces the friction and also has a contribution to improving tribological performance at high temperature.
Results and Discussions

Figure 3.7: Friction coefficient of (a) PI; (b) PI/0.1MWCNT; (c) PI/0.5MWCNT; (d) PI/1MWCNT; (e) PI/3MWCNT and (f) PI/5MWCNT at different temperatures

Polyimide is a viscoelastic material and its friction mainly depends on the adhesion between the steel surface area and polyimide. At proper heat and shear stress the lessening of the polyimide chain is occurred due to the rubbing action in the direction of sliding resulting decrease in friction [50]. Therefore the pure polyimide has a lower friction value at 150°C. But further increased the temperature, decline the hardness of the coatings which enlarge the contact surface area due to the severe wear on the contact interface. As a result of the friction coefficient of PI again increased at 200°C.

However, the mechanism of friction reduction for the polyimide coatings with MWCNTs depends on the rolling of embedded particles which is generated from the coating surfaces at high temperature since viscous polyimide cannot hold it at this temperature. Also, MWCNTs forms a transfer film on the counterpart surface steel ball and hence, the friction coefficient reduces.
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Figure 3.8: Friction coefficient of (a) PI; (b) PI/0.5GP; (c) PI/1GP; (d) PI/3GP; and (e) PI/5GP at different temperatures

Similarly, the friction behavior of the polyimide coatings with and without graphene as shown in figure 3.8 can be described. The figure displays that the PI/3GP has a comparatively lower coefficient of friction than PI, PI/0.5GP, PI/1GP, and PI/5GP. The reasons for or mechanism of high friction of pure PI and low friction behavior of PI/GP with increasing temperature is similar to the mechanism that already mentioned in the previous part for polyimide coatings with MWCNTs. From the figure, it is clear that at room temperature neat polyimide coating and PI coatings with graphene, the friction is high whereas the polyimide with graphene the friction reduces with increasing temperature. Normally at the temperatures of 100°C and 150°C friction is low for graphene contents polyimide coatings.
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3.3.2 Wear

Figure 3.9 illustrates the wear volume of the worn surfaces varies with the content of MWCNT at various temperatures ranging from RT to 200°C for each coating sample. Also, the figure describes that with increasing temperature the wear volume first reduces and then again increases with increasing temperatures. The minimum wear volume of the pure polyimide coating is $1.42 \times 10^{-3}$ mm$^3$ at 50°C while the maximum wear volume reached $4.82 \times 10^{-3}$ mm$^3$ at 200°C. However, with the addition of MWCNT, the wear volume significantly reduces. It can be shown from the figure that PI/0.1MWCNT has higher wear than pure PI at 50°C, 100°C and 150°C which could be the improper dispersion of the MWCNT and not sufficient to enhance the wear-resistant properties of the polyimide coatings. This statement can be assured by looking at the results of other wt% of the MWCNT into the PI matrix. The 3.0 wt% of MWCNT has the higher wear-resistant than other coating compositions and also at 50°C, 100°C and 150°C the wear-resistant phenomena of the composite coatings are superior.

![Wear volume of worn coating surfaces of PI and PI/MWCNT](image)

**Figure 3.9**: Wear volume of worn coating surfaces of PI and PI/MWCNT

Whenever this carbon-based filler materials are incorporated into PI, they form an organic-inorganic hybrid structure and this structure helps to inhibit the heat flow to the polyimide matrix which actually lessens the thermal degradation of the composite structure. Therefore the polyimide composite coatings are significantly enhanced the wear-resistant properties at high temperatures step.
The 3D optical photo of the worn surfaces of the polyimide and polyimide composite coatings are demonstrated in figure 3.10. It is easily understandable that the pure polyimide coating surface at 200°C worn out more than any other surfaces which also showed in figure 3.9. The pure PI coating surfaces smoothly worn out because there was no filler material added and with increasing temperatures the volume of the scar also increases.

![Figure 3.10: 3D wear scar of (a) PI; (b) PI/0.1MWCNT; (c) PI/0.5MWCNT; (d) PI/1MWCNT; (e) PI/3MWCNT; (f) PI/5MWCNT where 1, 2, 3, 4 and 5 denotes RT, 50°C, 100°C, 150°C and 200°C respectively](image)

In the 3 wt% and 5 wt% of MWCNT coating surfaces literally has a very small scar as compared to others. The high wear scar area in high temperature for the surfaces of the composite coatings could be the reasons of losing the covalent bonds between PI matrix and the filler materials which increases the removal of stoke of material from the surfaces and hence enhance the wear volume on the surfaces.

Figure 3.11 shows the wear volume of worn coating surfaces of PI and PI/GP and their corresponding coating surfaces in figure 3.12. The results follow a similar trend of polyimide-MWCNT composite coatings as shown in figure 3.9 and figure 3.10.
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Figure 3.11: Wear volume of worn coating surfaces of PI and PI/GP

Figure 3.12: 3D wear scar of (a) PI; (b) PI/0.5GP; (c) PI/1GP; (d) PI/3GP; (e) PI/5GP where 1, 2, 3, 4 and 5 denotes RT, 50°C, 100°C, 150°C and 200°C respectively
3.4 Morphology

The morphology of wear tract of polymer coatings describes the nature of wear, type of dominant wear behavior and also the surface properties. All these phenomena were investigated by scanning electron microscopy (SEM).

3.4.1 Scanning Electron Microscopy (SEM) Analysis

Figure 3.13 shows the SEM micrograph of wear tract of pure PI at 50 µm magnification and at five different temperature ranging from room temperature (RT) to 200°C. The figure also depicts the sliding direction. At RT and 50°C, the surfaces are quite smooth and considered with many furrows which indicates the dominant nature of abrasive wear mechanism. At 100°C, both of furrows and spalling points are observed on the worn surface, designates the abrasive and fatigue wear mechanism. Moreover, severe cracks and peel of the materials from the surface of the coating occurred, perpendicular to the sliding direction, representing fatigue wear at 150°C & 200°C temperatures. The result of this SEM micrograph of pure polyimide coatings at high temperatures are agreed with Dong, Fengxia, et al. [13]. As we know from the friction test section that the pure polymer is a viscoelastic material and its friction depends on the adhesion between steel ball and coating surface area which ultimately plays an important role for wear mechanism. At RT there is crack or scar on the coating surface means the surface itself does not resist the load applied on it. But with the increasing temperature like at 50°C and 100°C the surface becomes smoother and appears very low scar as on worn surface as compared to other coating surfaces. It can be explained in the way that these temperatures help to relax the polyimide chain and branches which helps to reduce friction as well as wear. However, with increasing temperatures like at 150°C and 200°C the coating hardness decreases and that leads to severe wear or removal of stock of materials as we can see the on coating surfaces at these temperatures. Also, at these two temperatures, more wear debris or lot of separated chunk of materials appeared on the worn surfaces. This is also the reasons for the increase of friction coefficients at high temperatures as shown in figure 3.7 due to the augmented roughness of PI worn surface and higher strength between polyimide and steel ball.
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Figure 3.13: SEM micrograph of worn surfaces of pure polyimide coatings at different temperatures

The SEM micrograph of the addition of MWCNTs into the polyimide coatings is shown in figure 3.14. If we compare this SEM photographs with pure PI coating surfaces as in figure 3.13 it is observed that the PI/3MWCNT coating surfaces are smoother than PI because of the addition of MWCNTs into it. Overall, with the same applied load, the surfaces have a higher high load carrying capacity since there is no crack or major breaking off materials from the worn surfaces at RT to 150°C. It means that at these temperatures and load, a layer of microscopic materials from the coating surfaces transferred to the contact interfaces (steel ball and polymer coating surfaces) which ultimately produces a film which acted as a lubricating layer and helped to resist severe wear. But further increased temperature increased the number of materials transferred and aggravated into contact interfaces leading to sever crack or fatigue wear which is easily visible at 200°C in figure 3.14.
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The worn surface of the PI/GP composites is shown in figure 3.15. It is found that the worn surface of PI/GP composites at RT was characterized by some broken and swelling of the coating surface. This discloses that the load or stress applied on the PI/GP composites during the sliding process generated a crack in the sub-surface and this propagated to the top surface. But at the temperatures of 50°C and 100°C, the presence of loose particle and pulled-out of the surface respectively, parting several holes on the worn surface proves the creation of lubrication layer in the contact interfaces, which ultimately reduces the friction as well as wear of the coatings as shown in figure 3.11 and figure 3.12 respectively. Remarkably, the holes and furrows on the worn surface seemed to vanish at increased temperature 150°C and therefore, the worn surface looked smooth in the sliding direction resulting in low wear. However, further increased temperature produces several flakes on the worn surfaces, indicating a higher degree of wear, especially fatigue wear, aggravated, resulting in the increased friction coefficient and wear volume at 200°C.

Figure 3.14: SEM micrograph of worn surfaces of PI/3MWCNTs coatings at different temperatures
Results and Discussions

Figure 3.15: SEM micrograph of worn surfaces of PI/3GP coatings at different temperatures

Overall, the graphene is added into the polyimide matrix, damage of the coating surfaces decreases because the stress in the contact interfaces is carried by the graphene filler and part of the load moved to the matrix network. However, the tribological performance of the coatings depends on the well-dispersion of graphene and formation of polyimide-graphene structure.
Chapter 4: Epoxy Coatings Results

The epoxy coating results are divided into three parts. In the first section 4.1, the friction and wear results of epoxy with hexagonal boron nitride coatings are discussed. In a similar way, the epoxy with expanded graphite coatings is depicted in the second section 4.2. The third section 4.3 compared the results of between h-BN and EG coatings.

4.1 Tribology of Epoxy coatings with h-BN

![Figure 4.1: Coefficient of friction of Epoxy with h-BN](image)

In figure 4.1, the coefficient of frictions of epoxy with filler h-BN is shown in a combined way, where it shows the pure epoxy has a low coefficient of friction as compared to epoxy with fillers h-BN. This figure clearly depicted the variation of COF at 2 N and 4 N where the friction coefficient at 2 N is higher than 4 N.
Figure 4.2: Average COF of epoxy with filler h-BN

From figures 4.2, it can be shown that the pure epoxy has relatively low COF compared to various wt% of BN. This is because of the pure epoxy has low thermal conductivity around 0.2 W/m.K and as a result, heat is easily accumulated in the sliding interfaces during rubbing action resulting in increased stress which ultimately causes
cracking or failure of the materials. That is why the wear rate of epoxy without filler is also high as shown in figure 4.3 and COF is low. But adding the boron nitride (BN) as a filler material into the epoxy matrix increases the thermal conductivity and when the mass fraction of h-BN reaches 15% thermal conductivity goes up to 0.6264 W/m.K, increased by 223.72% than the pure epoxy. With the increasing amount of BN, contact mutually with epoxy resin and form a thermally conductive path, which spreads the heat and therefore epoxy-BN composite shows high heat transfer efficiency [52, 53]. Therefore with an increasing amount of BN, the wear rate is decreases and correspondingly friction increases.

However, with the excessive addition of BN, an incomplete dispersion of BN occurs, and more gas bubble and stress concentration points are formed. The mechanical properties of the composites decrease accordingly [54].

4.2 Tribology of Epoxy coatings with h-BN

Figure 4.4 is the graph of COF with run time for epoxy with expanded graphite at two different loading conditions i.e. 2 N and 4 N. The friction coefficient of pure epoxy at 4 N load has the lowest COF and the highest peak for friction is epoxy with 5wt% EG at 2 N load conditions. Overall, the friction coefficient is constant throughout the run time and the COF at 4 N load is low as compared to load 2 N.

![Figure 4.4: Coefficient of friction of epoxy with expanded graphite at different loads](image)
Figure 4.5: Average COF of epoxy with filler EG

Figure 4.5 shows the average coefficient of friction of epoxy with expanded graphite filler materials. With the increasing amount of expanded graphite, the wear dimensions decrease as the epoxy composite becomes harder and harder. So expanded graphite shows incredible mechanical properties i.e. increases the Young Modulus of the composites. The pure epoxy has a low COF 0.5063 and 0.4103 at 2N and 4 N respectively. The reason can be the accumulation of materials on the ball surface from the epoxy substrate at running conditions as shown in figure 4.6.

Figure 4.6: Accumulation of materials on the ball surface

In figure 4.7, it is showed that the pure epoxy has higher wear and this high shear off of materials stick to the ball surface as shown in figure 4.6 and formed a layer on it which helps to reduce the friction coefficient. With increasing wt% EG the COF also increases but the coefficient of friction at 10wt% (COF = 0.5643 and 0.4980 at 2N and 4N respectively) EG is lower than 5wt% (COF = 0.5797 and 0.5060 at 2N and 4N respectively) and 15wt% (COF = 0.5702 and 0.5097 at 2N and 4N respectively) EG. This phenomenon follows the same as that of 2N and 4N loads.
The wear dimensions of epoxy with various wt% of expanded graphite shown in figure 4.7. As we know the expanded graphite has more chemical reactivity so with the increasing wt% of EG the hardness of the epoxy increases. Therefore the wear dimensions of the composite epoxy also decrease. The same results were recommended by researchers [55].

4.3 Friction and wear comparison of epoxy with h-BN & EG

Figure 4.8: Comparison of COF between h-BN and EG as filler in Epoxy coatings
The comparison of the average coefficient of friction of epoxy with h-BN and EG at 2 N and 4 N is denoted in figure 4.8. It can be seen that the h-BN has low friction both at 2 N and 4 N applied load than expanded graphite. But the value of COF at 4 N load is lower for both of h-BN and EG than at 2 N load. The figure also shows the increasing behavior of friction with increasing wt% of filler materials since the coating hardness and thermal conductivity rises along with this.

On the other hand, this figure is reciprocal to wear dimensions case as displayed in table 4.1. The h-BN has high wear dimensions both at 4 N and 2 N applied load than EG. So it can be said that the EG has a very good wear-resistant properties as filler than h-BN.

**Table 4.1**: Comparison of wear between h-BN and EG as filler in Epoxy coatings

<table>
<thead>
<tr>
<th>Load/Filler (wt %)</th>
<th>2 N</th>
<th>4 N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>h-BN</td>
<td>EG</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>W</td>
</tr>
<tr>
<td>Pure</td>
<td>5.07</td>
<td>2.25</td>
</tr>
<tr>
<td>5 wt%</td>
<td>5.00</td>
<td>1.29</td>
</tr>
<tr>
<td>10 wt%</td>
<td>4.50</td>
<td>1.07</td>
</tr>
<tr>
<td>15 wt%</td>
<td>5.00</td>
<td>1.29</td>
</tr>
</tbody>
</table>

After the friction test of the prepared seven samples of epoxy coatings at 2 N and 4 N loading, the wear dimensions of each load for every coatings were measured by the stainless scale. The dimensions of this wear scar of h-BN and EG are also drawn in a bar chart as shown in figure 4.3 and figure 4.7 respectively. Here in figure 4.9, the photograph of wear scar with length and width of epoxy coatings are represented.

**Figure 4.9**: Wear Dimensions of Epoxy with various wt% of EG and h-BN at 2N and 4N
Chapter 5: Conclusions

5.1 Polyimide Coatings

In this study, the multi-walled carbon nanotubes (MWCNTs) and graphene (GP) were incorporated into polyimide (PI) to prepare PI/MWCNTs and PI/GP composites and successfully deposited on the steel surfaces by lab wound method. Also, the sliding friction and wear behaviors of composite coatings were examined at different temperatures (RT, 50°C, 100°C, 150°C and 200°C) along with pure PI as a comparison. In addition, other optical, thermal and mechanical characterization tests were performed to select the best coatings and the effects of filler materials into polymer had been discussed. The main conclusions of this project can be drawn as follows:

a) The thermal gravimetric (TG) analysis of composite polyimide coatings illustrates the thermal stability of the prepared coatings. At 60% weight residue, the composite coatings PI/3MWCNTs and PI/3GP show higher working temperatures i.e. 887°C and 845°C respectively than other pure PI and composite coatings.

b) The addition of the MWCNTs into polyimide coatings increases the micro-hardness and the curve is always rising with increasing the weight percentage of fillers. PI/5MWCNTs shows 22.22% more micro-hardness than pure PI. The filler graphene (GP) dissolve in NMP solvent initially with low wt% has no role to increase micro-hardness but at higher wt% like 5%GP slightly increase the micro-hardness of the composite coatings.

c) The nanoindentation test of PI and PI/3MWCNTs coatings proves that the composite coatings reduces the penetration depth and also helps to recover the materials rapidly as compared to PI coatings. So, the MWCNTs increases the local hardness of the composite coating surfaces. However, NMP dissolve GP in polyimide coatings slightly increases the deformation depth but oppositely upsurges elasticity of the composite coatings PI/3GP.

d) The friction coefficient of the polyimide composite coatings PI/MWCNT and PI/GP significantly reduces due to the addition of these carbon-based filler materials. At 50°C, 100°C, and 150°C, the composite coatings have excellent tribological properties. Overall, 5 wt% MWNCT into PI has the lowest friction trend but this is not always true as other coatings sometimes show low friction in 200°C like PI/3MWCNT. On the other hand, the PI/3GP significantly reduce the friction after
Conclusions

RT. In this composite coatings, 150°C temperature plays a critical role to reduce friction.

e) With the increase of fillers MWCNT and GP, the wear rate of the composite coatings is gradually reduced. PI/3MWCNT shows better wear-resistant behavior among the prepared coatings because of proper intercalation and dispersion of the fillers into the PI matrix.

f) The GP based PI composite coatings has also a significant role in reducing wear volume especially in 1 wt% and 3 wt% because in given load graphene produces a self-lubricating film/transfer film into contact interfaces at 50°C and 100°C.

g) The SEM micrograph analysis of the prepared coatings shows the wear mechanism and surface properties of the worn surface. The predominant wear mechanism of the pure and composite coatings is fatigue wear and adhesive wear sometimes play a role in it.

5.2 Epoxy Coatings

Epoxy coatings with fillers hexagonal boron nitride and expanded graphite were successfully applied on the steel substrate. The friction test, as well as wear volume measurement, were conducted and the effect of the filler on polymer coatings had been discussed. The following conclusions were reached:

a. The coefficient of frictions of epoxy with fillers h-BN and EG are lower at 4 N load as compared to 2 N load.

b. In both loading conditions, the COF increases with increasing fillers while the wear dimensions decrease.

c. Due to the low thermal conductivity heat is accumulated in the interface during rubbing action in pure epoxy. Therefore pure epoxy has high wear.

d. With an increasing amount of h-BN and EG the strength or hardness of coatings increases which decreases wear but rises friction coefficient.
Chapter 6: Future Work

6.1 Polyimide Coatings

Though the tribological performance and other mechanical, thermal are sufficient to study the effect of fillers MWCNTs, NMP dissolves GP into polyimide coatings, there is still room for future work of this polyimide composite coatings.

a) The NMP solvent present in graphene can be the cause of low micro-hardness and nano hardness in nanoindentation test of the polyimide composite coatings. So, the removal of the solvent can effectively improve the mechanical properties of the surfaces of the composite coating and also can increase the thermal stability. Therefore, suitable methods need to be found out for the removal of NMP solvent from the graphene.

b) Other composite coatings can be made by the inclusion of MWCNTs and GP together with same weight percentage that made out from MWCNTs and GP individually with pure PI. Careful study and literature review needs to be carried out to determine the dispersibility of these fillers together with pure polyimide.

c) The friction test for this work was conducted for 30 minutes, single load (10 N) and a stroke length (1000 µm). This test conditions can be varied to get to know them better performance and better working mechanisms of the composite coatings.

d) The analysis of the aging of the prepared coatings was not possible in this study due to the short time frame. So, this examination can be possible to test the coatings immediately after the preparation and after a long wait like two or three months later to see the tribological performance.

e) Glass transition temperature \( T_g \) is an important factor for determining the thermal stability of the polymer coatings. This is also indicate the range of solid and glassy state of the polyimide composite coatings. So, Dynamic Mechanical Analysis (DMA) needs to be carried out for this.

6.2 Epoxy Coatings

The following things need to be considered for further improvement of the epoxy coatings with filler materials: Measurement of hardness of the epoxy coatings with h-BN/EG fillers; Curing process at room temperature and elevated temperature, Effect of dispersibility of filler materials into epoxy, Surface Roughness of the coatings and morphology of coatings (SEM).
References


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