Introduction

1.1. Tribology

Tribology is derived from the Greek word tribos, meaning rubbing, and focuses on the science and engineering of rubbing surfaces in relative motion.[1] Basically, it includes the phenomena of friction, wear, and lubrication. Friction and wear result in simultaneous loss of energy and material, respectively, leading to detrimental effects like frequent component failures and increased greenhouse gas emissions. An effective lubricating system can prevent such undesirable happenings. Because of the complexity of surface interactions, tribology requires a broad understanding of disciplines, including chemistry, physics, mechanical engineering, material science, machine design, thermodynamics, heat transfer, etc. Tribology is crucial for many activities in the human body, in addition to the world of materials and machinery.

1.1.1. Friction

The frictional force resists the relative motion of the interacting surfaces under the applied load, leading to energy loss. Some common examples of friction are; driving a car on the road, friction between the floor and shoes during walking, and skin and blade while shaving. Frictional force (F_f) is directly proportional to the applied normal load (F_n) except for exceptionally hard and soft materials.

According to the laws of friction for common materials, $F_f = \mu \times Fn$, where μ the coefficient of friction (COF) depends on the properties of the material, working conditions, etc. The values of μ lie between 0 to somewhat greater than 1.

As long as surfaces are not extremely smooth, the frictional force is independent of the contact area.

1.1.2. Wear

Wear is the gradual removal of material from rubbing surfaces when a normal load is applied. Removal of material causes dimensional changes, which eventually result in subpar performance. So, replacement of the worn component is necessary. The degree of wear loss is influenced by the material's characteristics, such as surface roughness, mechanical strength, environment, hardness, operating circumstances, and the geometry of proximal surfaces. The types of interactions governing wear may be abrasion, adhesion, surface fatigue, chemical reaction, etc.

- **Abrasive wear**

It occurs when the hardness of the contacting surfaces differs significantly. When a hard rough surface slides across a soft surface**,** the harder surface causes abrasion of the soft surface resulting in furrows and scratches. There are two types of abrasive wear.

- **Two-body abrasive wear**

Two-body abrasive wear occurs when the hard asperity of one of the contacting surfaces gives cutting action on the softer body.

- **Three-body abrasive wear**

Three-body abrasive wear occurs when hard particles come between the two surfaces in relative motion.

- **Adhesive wear**

Adhesive wear occurs when the lubricating film becomes very thin, and asperities on the opposing surfaces can make contact through the film. In this type of wear, there is a mutual transfer of materials. These transferred particles come off later as loose debris. It happens when surfaces that come into contact with each other through asperities deform irreversibly and stick to one another, causing severe wear, galling, scuffing, or seizure**.**

- **Chemical wear**

Chemical wear is also known as oxidative wear. The Chemical reactivity on the metallic surfaces is combined with the rubbing action that scuffs off the metal. Various chemical agents like H_2O, H_2S, and acidic compounds formed in the lubricating system can cause this type of wear on metals. Due to the higher reactivity of the chemicals, corrosion of metal also occurs. The most common example of corrosive wear is rusting of moving steel parts.

- **Surface fatigue wear**

The above three types of wear are associated with sliding friction. Rolling conditions produce surface fatigue-type wear, which is characterized by pitting and appears suddenly after a large number of revolutions. Fatigue wear occurs where the lubricating film is intact and metallic contact is negligible. The very high load involved in rolling contact bearings develops sub-surface shear stress, creating and propagating cracks upwards, which leads to the removal of metal, forming characteristic pits. Rolling element bearings and gears undergo surface fatigue wear as there is a high degree of rolling, while adhesive wear associated with sliding is negligible. The result of fatigue wear is severe plastic deformation.

1.1.3. Lubrication

Lubrication is the process or technique employed to reduce the wear of one or both of the adjacent surfaces moving relative to each other by interposing a substance called lubricant. Poor lubrication results in significant energy and material losses. Lubrication is necessary for other functions like cleaning, preventing corrosion, and dissipating heat from the contact surfaces.[2,3] In addition to playing important roles in manufacturing processes and machine designs, lubrication is equally important in the human body, including artificial joints, hip replacements, and other body parts.[4] One of the single largest applications of lubricant, in the form of motor oil, is to protect the internal combustion engines in motor vehicles and powered equipment. A good lubricant is characterized by high viscosity index, non-corrosiveness, good fluidity at low temperatures, strong oxidative and thermal stability, and low volatility.[5]

Three crucial factors that regulate various lubrication regimes are speed, applied normal load, and lubricant viscosity. Based on the thickness of the lubricant film between the interacting tribo-surfaces, the Stribeck curve provides a better understanding of these regimes. The thickness of the lubricant film is determined mainly by the bearing parameter [(speed × viscosity)/load]. The changes in the coefficient of friction (COF) as a function of the bearing parameter are demonstrated in Figure 1.1, Stribeck curve.[6]

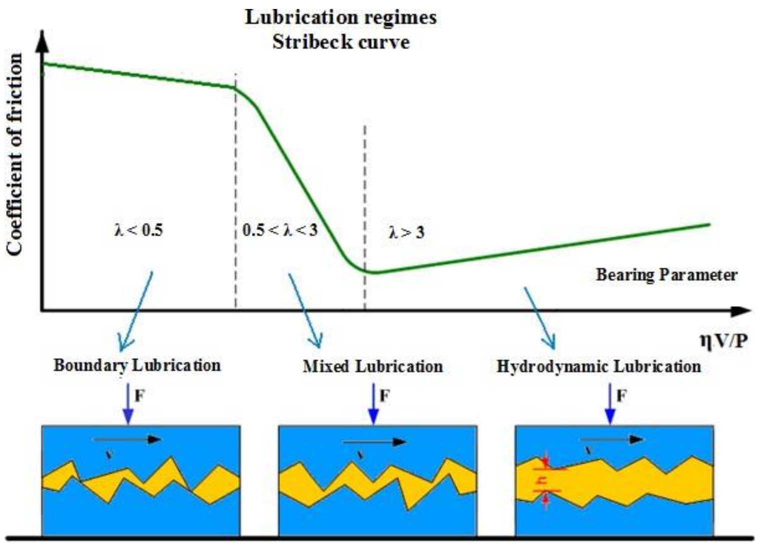


Figure 1.1. Stribeck curve showing the dependence of the COF on viscosity, speed, and loadfor a sliding lubricated system

Depending upon the lambda ratio, which is the ratio of minimum film thickness (h) to composite roughness (σ*), i.e., average roughness of mating surfaces, the Stribeck curve may be classified into the boundary, mixed, and hydrodynamic lubrication regimes.

$$Lambda\ ratio\ \lambda\ = \frac{h}{\sigma *}$$

Where, h = Minimum film thickness, σ* = Composite roughness

- **Boundary lubrication**

Low viscosity, low velocity (less than 0.1cm/s), and high load contribute to boundary lubrication. Due to the thin fluid film formation in the boundary lubrication regime, there is significant contact between the tribo-surfaces. Direct contact between the asperities of interacting surfaces, which results in a high COF, bears the load. The lambda ratio for this lubrication regime is less than 0.5. The high COF causes a significant loss of energy and resources; as a result, the regime is the most harmful.[7]

- **Mixed lubrication**

A mixed lubrication regime is an intermediate of elastohydrodynamic and boundary lubrication; therefore, it can be seen as a combination of these two, having the properties of both regimes. In mixed lubrication, the load is supported by the elastohydrodynamic or hydrodynamic lubrication mechanism and boundary lubrication as well. Thus, in this case, the lubricant film can only separate the contact surfaces at a few points while some asperities are in contact with each other. Consequently, friction is relatively much more than hydrodynamic lubrication, and the value of the lambda ratio lies between 0.5-3.0.[7]

- **Hydrodynamic lubrication (HL)**

This type of lubrication is also called thick film lubrication. Reynolds proposed the theory of this type of lubrication. He postulated that one of the rubbing surfaces is displayed relative to the other, forming a wedge-shaped oil film between the two surfaces. The pressure of the oil film prevents direct contact between the rubbing surfaces. Hydrodynamic lubrication occurs when speed, viscosity, and load are moderate. Under these conditions, the lubricant film bears the load entirely, so there is no direct contact between the metallic surfaces.[7] Hence, hydrodynamic lubrication is the safest mode, with extremely low friction and negligible wear. The value of the lambda ratio for hydrodynamic lubrication is greater or equal to 5.

- **Elastohydrodynamic lubrication (EHL)**

Elastohydrodynamic lubrication (EHL) is a development of hydrodynamic lubrication to consider the elastic deflection of the surfaces in contact. Film thicknesses are much smaller (0.25-1.25 µm) than conventional hydrodynamic lubrication. The value of the lambda ratio for EHL lies between 3 and 4.

In this region, components of the machine are in nominal point or line contacts. The lubrication mechanism is the same as HL, but the pressure developed in the lubricant is much higher. With an increase in the pressure on the oil, the viscosity also increases. The pressure of the lubricant causes the elastic deformation of the two surfaces, and the lubricant is carried into the convergent zone approaching the contact area, forming a hydrodynamic film.

1.2. Lubricants

Lubricant is any substance that lowers friction and wear when placed between two moving surfaces. Typically lubricants contain 90% of base oil and 10% of additives for different purposes. In addition to reducing friction and wear, lubricants prevent corrosion, avert the entry of dirt and moisture, carry away contaminants and debris, and act as coolants and sealing agents. Depending upon the physical state, the lubricants may be categorized as follows.

1.2.1. Liquid Lubricants

According to their origin, liquid lubricants can be categorized as animal, vegetable, mineral, or synthetic oils. The base oil should generally have low viscosity and a high viscosity index. Still, it also needs to have adequate viscosity to maintain a lubricant film under the necessary working conditions. Oil should have high fluidity to remove heat, minimize power loss due to viscous drag, and control friction and wear. Besides, it should have high oxidation and thermal stability and low volatility. The liquid lubricants are valuable due to their adaptability to a wide range of temperatures, cooling characteristics, and cleaning action.

Mineral oils are readily available, stable under severe conditions, inexpensive, and reusable. Structurally, they contain 20-40 carbon atoms in the form of either straight or branched chains, aliphatic or aromatic hydrocarbons.

Animal oils or vegetable oils are derived from animals and plants, respectively. Chemically these are fatty acid triglycerides. Examples of animal oils include seal oil, sperm oil, lard oil, and whale oil; on the other hand, cottonseed oil, palm oil, rapeseed oil, olive oil, and castor oil are examples of vegetable oils. Due to their decomposition at high temperatures, the usage of animal or vegetable oils is limited. These oils have a distinctive quality called oiliness, making them tenaciously adsorbed on metallic surfaces providing lower COF and higher load-carrying capacity when supplemented with mineral oils like paraffin and naphthenic oils. Synthetic oils are produced using more sophisticated methods than mineral oils; they are purer and more expensive. The structure of synthetic oil can be specifically designed to meet a specific application's needs for thermal or chemical stability, insulation, high viscosity index, and low volatility. Examples of synthetic oils include polyalphaolefins, polyalkylene, silicones, glycols, polyphenylene, and ethers.

1.2.2. Semi-solid Lubricants

Soap suspended in lubricating oil is the main component of semi-solid lubricants. The most typical examples of semi-solid lubricants are greases and petroleum jelly. The benefit of utilizing semi-solid lubricant is that it sticks to contact surfaces and remains intact, offering a superior mechanical lubrication cushion under extreme circumstances. A significant disadvantage of semi-solid lubricants is their poor heat dissipation. Dust, filth, and wear debris are always present with greases. Grease is made by emulsifying fats or oils with water and metallic soap, whereas petroleum jelly is a semi-solid mixture of hydrocarbons with carbon numbers mainly higher than 25.

1.2.3. Solid Lubricants

Solid lubricants are solid bulk materials or thin films that can be placed between the contact surfaces offering low shearing under a specific load. It is impossible to utilize liquid lubricants or greases for bearings in a vacuum at high temperatures. Solid lubricants are preferred in these circumstances. Because of their crystalline lamellar structure, these materials are easier to shear and reduce friction. Materials like graphite, zinc oxide (ZnO), molybdenum disulfide (MoS_2), tungsten disulfide (WS_2), ceramic coatings, etc., are typical solid lubricants. Aside from the layered structure, the important requirements for solid lubricants are low shear strength, high mechanical strength, and high thermal and chemical stability. The main disadvantages of solid lubricants are their low self-healing capacity and high friction coefficient compared to liquid lubricants.

1.2.4. Gaseous Lubricants

Gaseous lubricants like air, nitrogen, oxygen, helium, etc., are needed for aerodynamic or aerostatic lubrication. For wide temperature ranges, they are recommended. Gaseous lubricants have an advantage over liquid lubricants because their viscosity increases with a temperature rise. Gaseous lubricants, however, are extremely difficult to store.

1.3. Lubricant Additives

Lubricant additives are conventional inorganic/organic chemical compounds or nanomaterials added to lubricants in small amounts to improve their specific properties.[8] Today's market offers a variety of lubricant additives, including corrosion inhibitors, viscosity modifiers, viscosity index improvers, antioxidants, friction modifiers, pour point depressants, antiwear, extreme pressure additives, etc. Depending on the application, a fully formulated lubricant may contain one or more additives. Various kinds of lubricants and additives have been developed to increase the service life of machinery. Detailed information about these substances is given below.

1.3.1. Inorganic/Organic compounds as conventional additives

These additives are usually added to base oils as lubricant additives such as viscosity modifiers, viscosity index improvers, foam inhibitors, pour point depressants, etc., to modify the respective physical properties of the base lube. On the other hand, extreme pressure, antiwear, and antifriction additives containing tribologically active elements; P, S, N, Cl, Zn, Mo, and B or their mixtures enhance their tribological characteristics. The additives, in general, may be categorized as aliphatic/aromatic nitrogen, oxygen, sulfur, phosphorus, boron, and halogens compounds.

The excellent tribological properties of heterocyclic compounds containing N and O, such as pyrazines, pyridines, furans, pyrimidines, pyrans, pyridazines, oxadiazoles, tetrazoles, dioxanes, imidazolines, pyrroles, triazines, pyrazoles, oxazoles, imidazoles,[9–11] and Schiff bases[12–14] etc. have been documented for their remarkable tribological characteristics.

Sulfur-containing compounds are vital in improving antifriction, antiwear, and extreme pressure performances. Organic sulfur compounds such as fats, sulfurized olefins, esters, dithiocarbamates,[15,16] thioamides,[17] isodithiobiurets,[18] thioacetamides[19], phenylacetothioamides,[20] molybdenum/tungsten complexes of thiobiurets,[21] dithiocarbamates, thiosemicarbazides[22] etc. have been well recognized for their tribological properties.

Various phosphates and dithiophosphates such as dialkyl dithiophosphates,[23] dithiophosphate disulphide,[24] triarlyphosphorothionates,[25], etc. have been investigated for tribological applications. Zinc dialkyl dithiophosphates (ZDDPs) are the most promising antiwear additives among them. However, owing to their significant environmental harm due to the release of large volumes of phosphorus, sulfur, and zinc and their indirect impact on the exhaust emission system by blocking the catalysts, their excessive use is still restricted.

Various boron compounds have been used as lubricants, including boric acids, oxides, and esters. Borates that exhibit tribological behavior include zinc borate, sodium metaborate, potassium borates, aluminum borate, titanium borate, strontium borate, magnesium borate, cerium borate, lanthanum borate, calcium borate, and ferrous octoxyborates.[26–29]

Among halogen compounds, chlorine compounds were the first extreme pressure and antiwear additives used in the lubricant industry.[30] Chlorine-containing compounds generally pose problems for the environment and human health. Consequently, they are not regarded as suitable substitutes for conventional lubricants.

Ionic liquids (ILs) are liquid salts, a particular class of compounds, having large asymmetric cations and anions. The characteristic properties of ionic liquids like low volatility, non-flammability, thermal stability, and miscibility with organic solvents make them potential antiwear/antifriction lubricant additives. There are several cation-based ILs, such as imidazolium, pyridinium, ammonium, phosphonium, etc.[31] anion-based such as hexafluoro phosphate $[PF_6]^-$, $[\text{Sulfonate}]^-$, $[\text{sulfate}]^-$, tetrafluoro borate $[BF_4]^-$, (trifluoromethyl sulfonyl) imide $[Tf_2N]^-$, trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate [DEHP], etc. and mixed ILs, which have been utilized in the application of lubrication.[32]

Lubricant additives get adsorbed on the rubbing surfaces in boundary or mixed lubrication regimes generating a protective tribofilm. The tribofilm shields the interacting surfaces from direct metal-to-metal interactions. The typical way that additive compounds are adsorbed is through lone pairs of electrons on heteroatoms, aromatic ring electrons, negatively charged centers, and π- electrons. Due to the high affinity of adsorbed compounds to nascent steel surfaces, tribofilms formation occurred, which impart tribological properties.[33] A tribochemical film will not develop if an additive has an inert behavior. In contrast, the extreme activity of the additive will promote a corrosive attack on the surface, which will cause tribochemical wear. Optimizing the reactivity of additive with the surface for maximum performance is essential. The chemical interactions between two or more interacting surfaces, especially under the boundary or mixed lubrication regimes, are studied under tribochemistry.[34] Tribochemistry refers to the chemistry of the lubricant/environment with the rubbing surfaces under tribological conditions.[35] Understanding the nature of tribochemical reactions and their process is essential for understanding the function of lubricants in lowering friction and wear. The contact asperity temperature and the nascent metal surface often catalyze the tribochemical reaction of an additive with a surface. The contact temperature rises due to heat generated by friction between the sliding asperities.[36] The contact temperature (flash temperature) is around 400 ºC or more, but short-lived. On the other hand, very high surface energy and active sites are present on the nascent surface. Due to the combined effect of the active surface site and heat, many chemical reactions such as surface oxidation, surface catalysis, lubricant oxidation and degradation, polymerization, and the growth of inorganic and organometallic compounds on the sliding surfaces take place.[37] The nature of tribochemical products depends upon the reactivity, structure, and composition of the additive. For example, sulfur-containing additives decompose and get adsorbed chemically and physically to the steel surface, forming an iron sulfide coating that avoids direct metal-metal contact and reduces friction and wear.[38] While phosphates containing additives are firstly adsorbed on the surface, breaking down at a higher temperature to produce alkyl-acid phosphates. Alkyl-acid phosphates then interact with the metal surface to form high-melting salts, which enhance lubrication and shield the metal surface from wear and friction. In practical applications, the reactivity of antiwear, antifriction, and extreme pressure additives is influenced by the nature of the surfaces, the type of base oil, and other additives present in the system.

1.3.2. Nanoadditives

The failure of conventional additives under extreme conditions restricts their use in tribology. Additionally, these additives are non-biodegradable, inherently toxic, extremely reactive, and ineffective at low temperatures. These traits greatly limit their tribological uses. Therefore, creating lubricants that are both environmentally benign and highly tribologically effective is vital. The development of nanotechnology has made it possible to create such successful engineering materials. Nano lubricants are stable colloidal solutions of nanoscale components such as quantum dots, nanoparticles, nanorods, nanotubes, nanosheets, and composites. Because of their small size, nanomaterials demonstrate exceptional tribological efficiency when applied in low quantities (<1 wt %). Moreover, because of their chemical stability, emissions are reduced.[39] The high thermal conductivity of nano lubricants facilitates heat dissipation by friction. Thus, in the present circumstances, nano lubricants meet the demands of green tribology, a developing area for tribologists.

1.3.2.1. Quantum Dots and their Functionalization

Quantum dots (QDs), a novel class of semiconductor particles with a diameter of less than 10 nm, have received much attention due to their exceptional optical capabilities, excellent biocompatibility, and a high degree of chemical inactivity.[40] Carbon-based quantum dots (CQDs) can be synthesized from any carbon source, such as biomolecules, chemical reagents, or foodstuff.[41] CQDs with functional groups on their surface are used as lubricant additives in tribology.[42] Graphene/oxidized graphene(GO) has been used to produce the carbon quantum dots known as graphene quantum dots (GQDs), a sheet-like, spherical nanostructure. Due to layered structure, GQDs show unique physicochemical and tribological behavior.[43] Zhang et al. have explored the peculiar tribological behavior of graphene quantum dots that convert to fullerene-like quantum dots due to interface sliding.[44] CQD composites with ionic liquid are effective lubricant additives.[39,45] Highly dispersed MoS_2 QDs have been investigated as a lubricant additive on the ball-on-disc machine.[46] Nitrogen-doped CQD (N-CQDs) were added to MoS_2 nanofluid to enhance its tribological properties.[47] Zhu et al. investigated the tribological application of the 2D Ni-BDC nanosheets decorated with N-CQDs.[48] Wang et al. studied the silver-doped CQDs as a lubricant additive.[49]

1.3.2.2. Nanoparticles

Nanoparticles (NPs) are characterized by their high surface-to-volume ratio, which increases their surface reactivity.[50] The existence of a lot of surface atoms provides a surface modification of the nanoparticles, which is suitable for stable dispersion in particular lubricants.[51–54] The inorganic nanoparticles including metals like palladium,[55] nickel,[56] copper,[57] and silver,[58] metal oxides such as TiO_2,[59] Fe_3O_4,[60] Al_2O_3,[61] ZrO_2,[62] CuO,[63] CeO_2,[64] ZnO,[65] V_2O_5,[66] SnO_2,[67] metal sulfides, for example, CuS,[68] Ag_2S,[69] MoS_2,[70] WS_2,[71] metal halides like lanthanum fluoride.[72]

Dispersion stability of nanoparticles in base lube is enhanced by the functionalization of the NP surface, which in turn, upsurges the lubrication properties.[73] The functionalization process prevents NP aggregation in a non-polar base oil.[50] By steric or electrostatic stabilization, a polymer or surfactant coating significantly reduces aggregation.[50] Due to the functionalization of NPs, material transfer between them and cold welding between the shearing surfaces is prevented.[50]

The tribological efficacy of stearic acid-stabilized calcium copper titanate NPs,[74] calcium-doped ceria (CCO) NPs stabilized by sodium dodecyl sulfate (SDS), and 1-decyl-3-methyl imidazolium bis (trifluoromethylsulfonyl) imide in paraffin oil have been evaluated in our laboratory.[75] Recently tribological properties of m-$LaVO_4$ nanoparticles have been studied in our lab.[76] Enhanced tribological activity has been noted for a metal salt lattice doped with various metal ions, possibly due to the creation of defects that create slip systems and reduced shear strength.[74,77] Kalyani and her colleagues have investigated improved tribological performances of the SDS-stabilized magnesium and aluminum-doped zinc oxide nanoparticles.[77] Recently from our laboratory, ceria-doped zirconia,[78] magnesium-doped zinc oxide,[79] and lanthanum-doped yttria nanoparticles[80] have exhibited promising lubricant behavior in paraffin oil.

Numerous mechanisms, including tribosinterization (self-repairing or restoration, mending) rolling, polishing, and the formation of tribofilms, have been proposed to explain the lubricating efficacy of nanoparticles. The polishing and mending processes are related to indirect mechanisms, but the tribofilm and ball-bearing mechanisms are considered direct.

- **Rolling mechanism**: Due to the almost spherical shape of nanoparticles, they act as tiny ball bearings that roll into the contact zone and change sliding friction as a mixture of rolling and sliding friction.
- **Tribosinterization:** Tribosinterization is the process of healing the surfacesby filling nanoparticles in the grooves and scars.
- **Polishing mechanism:** Since nanoparticles are hard to cause abrasion of the rough

surfaces resulting in polished surfaces.

- **Tribofilm formation:** The formation of a protective tribofilm may result from interactions between additives and tribo-surfaces. Tribofilm formation should prevail over wearing for better surface protection.

1.3.2.3. Nanorods

Nanorods are rod-shaped, solid, nanoscale structures produced via chemical synthesis. In addition to nanoparticles, nanorod-structured morphology also exhibits encouraging results in tribology. Recently, TiO_2,[81] ZnO,[82] MnO_2,[83] Fe_2O_3[84], CuS,[85] Fe_3O_4,[86], and Al_2O_3[87] nanorods have been well-recognized for their tribological behavior. According to a study by Akbulut and his coworkers, ZnS nanorods exhibited better tribological outcomes due to a synergistic interaction between their shape and surfactant (octadecyl amine) coating, which makes it easier for nanorods to roll and slide between the interacting surfaces.[88] Zhang and his colleagues investigated the tribological characteristics of the WS_2 nanorod.[89] Yang et al. examined the friction and wear-diminishing behavior of WSe_2 nanorods in base oil (HVI500).[90] The greater aspect ratio (length/breadth ratio) of nanorods offers favorable tribological results.[91] Due to rolling and sliding effects, enhanced lubricity of copper oxide nanorods over nanoparticles was reported by Khatri et al.[91] Like ball bearings, nanoparticles can be certainly stuck between asperities, while nanorods being relatively harder, are not easily trapped.[88]

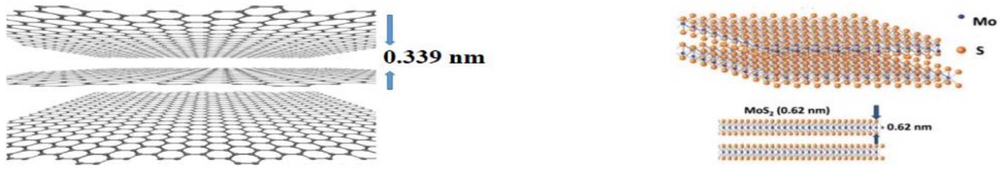
1.3.2.4. Nanotubes

A single-walled carbon nanotube (SWCNT) is formed when a layer of graphene rolls up, whereas a multi-walled carbon nanotube is formed when layers of graphene roll up

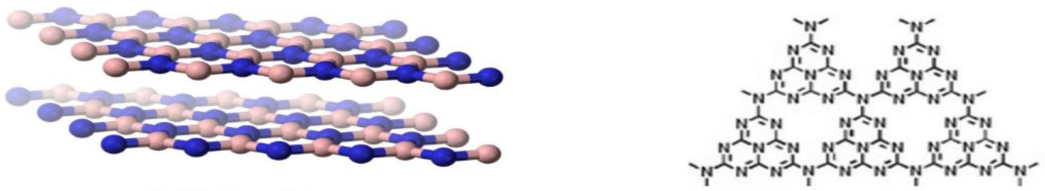
(MWCNT). There are numerous industrial applications for these nanotubes. They make excellent lubricant nano additives or solid lubricants due to their shape, superior mechanical properties, high length-to-diameter ratio, and significant flexibility to improve tribological properties.[92,93] Using a pin-on plate wear tester, Chen et al. examined the tribological properties of multi-walled carbon nanotubes (MWCNTs) modified with stearic acid that had enhanced dispersibility.[94] According to Khalil and his group's research, the tribological activity of paraffin oils and Mobil gear 627 was enhanced when carbon nanotubes were added.[95] The SDS functionalized multi-walled carbon nanotubes improved the load-bearing capacity of the water-based lubricants in addition to the extreme pressure, antiwear, and antifriction properties.[96] There may be a correlation between increased dispersibility and significant activity. For the same reason, the ionic liquid/MWCNTs hybrid showed unusual behavior in reducing friction and wear.[97] Cu-matrix composite reinforced by CNT was studied by Dong et al. for its antiwear and antifriction properties.[98] Zhang and his associates reported the tribological behavior of the composite CNT/MoS_2.[99] The tribological performance of ZnO/MWCNTs composite dispersed in 10w40 engine oil as a lubricant additive was investigated by Vardhaman and colleagues.[100] Recently, copper phthalocyanine nanotubes have been used to functionalize amino borate-functionalized reduced graphene oxide for reducing friction and wear in our laboratory.[101]

1.3.2.5. Nanosheets

Inorganic two-dimensional layered nanomaterials, like graphene, polymeric graphitic carbon nitride, transition metal dichalcogenides (TMDs), and hexagonal boron nitride, have acclaimed tribological importance due to the high specific surface area. Weak van der Waals-type forces existing in between proximal layers of a layered structure facilitate the lubricating propensities. Some of the nanosheets are shown in Figure 1.2.[102]



Graphene nanosheets **MoS_2 Nanosheets**



BN Nanosheets **g- C_3N_4 Nanosheets**

Figure 1.2. Different nanosheets

- **Graphene**

Graphene looks like a honeycomb crystal lattice having a planar layer sheet of sp^2-hybridized carbon atoms. Electrons easily migrate across it with minimal resistance, conducting electricity more effectively than in conductors like copper. The exceptional chemical stability, mechanical strength, optical characteristics, inertia to allow the entrance of liquids or gases, and superior electrical and thermal conductivity of graphene make it a particularly suitable material.[103–105] Theoretically, a single sheet of graphene has a surface area of 2630 m^{2}g^{-1}, which is extremely high. Interestingly, it has Young's modulus of 1.06 TPa and therefore is stiff and stretchy (like rubber) and can be stretched up to 20-25% without breaking.[106] There has been plenty of investigations into the potential uses of graphene in various fields, including sensors, gas storage and adsorption, solar cells, Li-ion batteries, supercapacitors, catalysis, fuel cells, and tribology.[107–109]

Graphene exhibits significant friction and wear-reducing characteristics only at lower concentrations; at higher concentrations, it aggregates and causes abrasive wear. By using graphene as a nano lubricant, the tribological efficiency of the engine has been improved.[106–108,110] Dangling carbon bonds help graphene adhere to a steel surface. Because it adheres to the surface, it prevents metal-metal contact and reduces friction.[111] Graphene's usefulness is recognized in micro and nano electro-mechanical systems (MEMS and NEMS) with rotating, oscillating, and sliding contacts for minimizing friction and wear because it is ultrathin even with multilayers.[106,112] At lower concentrations, graphene can reduce friction and wear; at higher concentrations, Graphene is prone to aggregate and return to its graphitic state because of its high surface area and surface energy.[113] Consequently, abrasive wear occurs.

Graphene oxide (GO), usually synthesized by the exfoliation of graphite oxide, is an important intermediate between graphite and graphene. Although structurally different, it has chemical similarities to graphite oxide. It is often prepared by ultrasonically stirring or mechanically agitating graphite oxide in aqueous media or polar organic solvents.[114] Graphene oxide, compared to graphene, shows higher friction and wear under a moist environment, but under dry conditions, just the opposite trend happens. The most widely used technique for producing large amounts of reduced graphene oxide (rGO) is the reduction of graphene oxide (GO), often by hydrazine. According to Gupta et al., rGO and GO act as base oil additives that reduce wear and friction, and [115] and rGO is easier to disperse in non-polar solvents than GO.[114] On the other hand, functionalities on the surface of GO lead to greater dispersion.[114] The rGO dispersions have much superior thermal conductivity and mechanical properties than GO.[114]

According to Kuila et al., the chemical functionalization of graphene improves its adherence to surfaces and prevents agglomeration.[114] A further advantage of functionalization is the ease with which it may be dispersed over different media.[39,106,114,116,117]

Due to the synergistic effect of the components, composites typically perform better than individual ones. As a result, the non-covalent functionalization of graphene resulted in the formation of composites with exceptional tribological characteristics. Molecules are physically adsorbed on the surface of graphene during non-covalent functionalization via weaker types of interactions, including electrostatic, π-π, or van der Waals forces.[114,117]

For the non-covalent functionalization of graphene, several nanoparticles have been employed. A sandwich-like nanostructure of Mn_3O_4 and graphene has been investigated for its lubricating characteristics.[118] Zhou and co-workers studied a nanohybrid of rGO with zirconia as a lubricant additive.[119] The tribological studies of chemically capped zinc borate nanocomposites with graphene oxide (2.0 wt.% of ZB/GO) were reported by Cheng et al.[120] In our laboratory, TiO_2-reinforced boron and nitrogen co-doped reduced graphene oxide,[121] zinc oxide and magnesium-doped zinc oxide nanoparticles decorated nanocomposites of reduced graphene oxide,[79] amino borate-functionalized reduced graphene oxide further functionalized with copper phthalocyanine nanotubes,[101] ZrO_2/rGO/MoS_2,[78] and La-doped Y_2O_3-MoS_2-methionine functionalized GO[80] have been reported as friction and wear modifiers in PO using a four-ball lubricant tester.

- **Polymeric graphitic carbon nitride (g-C_3N_4)**

Polymeric carbon nitride, a metal-free n-type semiconductor, possesses a graphitic structure (g-C_3N_4) with weak van der Waals forces.[122] Its high thermal stability and unique optical and electrical properties led to g-C_3N_4-based nanomaterials, a new category of multifunctional nanoplatforms for electronic, catalytic, and energy applications.[122–124] Photocatalytic applications include water oxidation and reduction, carbon dioxide reduction, and degradation of pollutants.[122] Zhu et al. have studied the tribological behavior of bulk g-C_3N_4 with polyvinylidene difluoride (PVDF).[125] Ajay Kumar and his colleagues investigated the antifriction and antiwear performance of the nanosheets of octadecyl amine grafted g-C_3N_4.[126] The carbon nitride composite with MoS_2 (MoS_2/g-C_3N_4) exhibited synergistic friction and wear reduction properties.[127] Lubricating behavior of a composite of copper nanoparticles with g-C_3N_4 has been noted for improving the wear resistance of polyimide composite.[128] Wu and his coworkers have used CuO/g-C_3N_4 composite.[129] They have also investigated the tribological behavior of phenolic coatings with different concentrations of g-C_3N_4.[130] Zhang and his associates studied the antiwear performance of the hybrid g-C_3N_4 /TiO_2.[131]

- **Transition metal chalcogenides (TMDs)**

2D transition metal dichalcogenides (TMDs) with the general formula MX_2 (M = Mo, W, V, Nb, etc., X= S, Se, Te, etc.) possess a similar lamellar structure to graphene, withhold adjacent layers by van der Waals interactions. TMDs are highly desirable in the fields of nanoelectronics, electrochemical reactions, optoelectronics, and energy storage.[132] In the literature, there are several research papers and reviews on tribological studies of TMDs.

MoS_2 consists of a hexagonal close-packed structure in which molybdenum is present in a trigonal prismatic manner with six sulfur atoms. The existence of weak van der Waals forces amid molecular S-Mo-S tri-layers is responsible for its lubricity. The tribological evaluation of thiol-functionalized MoS_2 nanosheets in water has been studied.[133] Xu et al. investigated the synergistic tribological behavior of MoS_2 and graphene dispersed in esterified bio-oil.[134] The tribological activity of hydrothermally synthesized graphene oxide-MoS_2 nanocomposite has been studied by Song and co-workers.[135] Chemically capped zinc borate/MoS_2 nanocomposite in grease and oil has shown excellent tribological properties.[136] Recently, Liu et al. investigated the lubricating properties of Fe_3O_4/MoS_2 composite in addition to significant photocatalytic degradation.[137] The synergistic tribological activity of ternary nanocomposites of molybdenum disulfide nanosheets with nanohybrids; zirconia/cerium-doped zirconia nanoparticles with nano lamellar reduced graphene oxide[78], methionine-functionalized GO/La-doped Y_2O_3 nanoparticles[80] have been reported from our group.

Tungsten disulfide (WS_2), having a layered structure like MoS_2, is a conventional solid lubricant additive. Jiang et al. reported the excellent tribological activity of ultrathin

WS_2 nanosheets in polyalphaolefin.[138] A nanohybrid of titanium dioxide and WS_2 (WS_2/TiO_2) was synthesized by Lu et al. and studied its synergistic effect on the lubricity in di-iso-octyl sebacate.[139] Xu et al. investigated the tribological properties of WS_2 nanosheets adorned with homogeneously dispersed Cu nanoparticles.[140]

The tribological properties of some metal selenides, including mono- and di-selenides ZnSe,[141] WSe_2,[142] $NbSe_2$,[143], and $MoSe_2$,[144] have been recently studied. Zhao et al. examined the superlubricity of $MoS_2/MoSe_2$ heterostructures at the macroscale.[145] Meister and colleagues investigated the lubricating properties of MoS_2 and WSe_2-based nanocomposite coatings.[146] The composite of a copper matrix reinforced with Ni/$NbSe_2$ has been used in tribological applications.[147] Cao et al. studied the tower-like morphology of ultrathin WSe_2 nanosheets as an additive in paraffin oil.[142] In addition to the selenides mentioned above, VSe_2 has a layered hexagonal lamellar structure and is well known for its ability to undergo hydrogen evolution reactions[148] and energy storage applications.[149] Since $NbSe_2$ and VSe_2 are congeners, VSe_2 is considered to have a comparable lubricant additive ability to $NbSe_2$.

- **Boron nitride (h-BN)**

The lattice structure of the 2D-hexagonal boron nitride (h-BN), also known as "White graphite," has an equal amount of boron and nitrogen atoms alternately organized in a honeycomb pattern. The presence of distinct covalent bonds of B-N is responsible for excellent thermal stability, anti-oxidation, mechanical strength, and self-lubricating properties compared to graphite.[150,151] In oil-lubrication and water-lubrication systems, the BN nanosheets as an additive show good tribological performance.[152,153] Because of its chemical inertness, modifying the BN surface through physical adsorption or chemical functionalization is necessary for achieving high dispersibility in lubricating media.[150] Through π-π overlap interaction, aromatic organic substances are readily adsorbed on the surface of h-BN.[154] The nanohybrids of chemically functionalized h-BN with different nanomaterials like graphene, Fe_3O_4,[155] NPs,[156] MoS_2,[152] carbon nanotubes (CNTs),[150], etc., are exceptionally tribologically active due to synergistic interactions.

- **Metal Organic Framework (MOF)**

Metal-Organic Frameworks (MOFs) are a new class of crystalline materials consisting of 2D/3D networks formed by nucleating the metal centers and bridging organic ligand(s).[157] Recently, MOFs have been widely utilized in the field of energy conversion,[158] energy storage,[158] catalysis,[159] sensor,[159] gas separation,[160], and direct electrochemical applications.[161]

Moreover, MOFs have been explored in tribology due to their attractive properties like large surface area, tunable porosity, and excellent thermal and chemical stability.[162] Zeolitic imidazolate framework (ZIF- a MOF sub-class) has recently been employed in tribology.[163,164] The 3D-structure MOFs such as ZIF-8 has exhibited significant antiwear and load-carrying properties.[165] However, the friction reduction of the 3D-structured MOF materials is limited due to poor dispersion in a base oil.[166] Gao et al. have demonstrated that the mechanical and tribological performances of 2D Ni-Fe MOF-assisted poly (vinyl alcohol) hydrogels were much better due to enhanced dispersibility.[167] Ultrathin Zn-BDC[166] and mesoporous Cu-BTC-MOFs[168] have also shown good lubricating behavior. Thus, the lamellar structure of 2D MOFs is favorable in upgrading dispersibility in the base oil, resulting in improved mechanical and tribological performance.

1.4. Statement of the Problem

Friction and wear-related failures are major sources of the issue in mechanical systems where mating surfaces move relative to one another. Energy consumption rises as a result of friction between proximal surfaces. Wear, on the other hand, makes the instrument less durable. Therefore, in order to improve efficiency, durability, and environmental compatibility, the system must be sustainable. To accomplish the purpose, friction and wear must be controlled. The use of lubricants makes the prevention of friction and wear possible. The lubricant creates a low-shear, durable layer on the tribo-surfaces to prevent metal-to-metal contact. Additives may be added to enhance the antiwear/antifriction characteristics of base oil. Compounds containing nitrogen, boron, phosphorus, chlorine, and sulfur have been reported as tribological additives for boundary lubrication. The most widely utilized antiwear additives were zinc dialkyl dithiophosphates (ZDDPs). On the contrary, because of the high levels of sulfated ash, phosphorous, and sulfur (SAPS) concentrations, current environmental regulation has restricted the use of these multifunctional additives. It is well-recognized that excessive SAPS concentrations contaminate vehicle exhaust and have a negative impact on the environment. In order to replace ZDDP-based lubricant additives in a more environmentally responsible manner without sacrificing effectiveness or having any negative effects on the surfaces that interact, specific environmental regulations are being followed. The needs of green tribology, which is now an emerging field for tribologists, are fulfilled by nano lubricants. Various nano lubricants, such as nanoparticles, nanorods, nanotubes, and nanosheets, have been added to base oil as tribologically beneficial additives.

1.5. Aims and Objectives

From the discussion so far, the most suitable methodology for enhancing the tribological efficacy of nanomaterials appears to prepare their nanohybrids. The synergistic effects of the constituting nanomaterials are of utmost importance for the purpose. Therefore, the present research commenced with synthesizing various nanomaterials and developing their nanohybrids as efficient friction and wear modifiers.

Further, doping by various nonmetals/metals in the host lattice exhibited superior tribological efficiency due to the creation of defects that developed slip systems and lowered shear strength. Therefore, doped nanomaterials have been preferred to fabricate nanohybrids.

The main objectives of the present research are-

1. To synthesize, characterize, and assess the tribological behavior of
    - ❖ Nitrogen-doped zinc oxide nanorods, g-C_3N_4 nanosheets, and their nanohybrids
    - ❖ Bulk and ultrathin Mn-MOF
    - ❖ Zinc borate, lanthanum-doped zinc borate matrix, and their binary composites with vanadium selenide nanosheets
    - ❖ Bismuth vanadate, Mo-doped bismuth vanadate nanorods and their binary

composites with Ni/Mn-MOF nanosheets

2. To examine the surface morphology of worn surfaces using Scanning Electron Microscopy (SEM) and contact mode Atomic Force Microscopy (AFM) techniques.
3. To explore the lubrication mechanism and tribochemistry of these nanomaterials using X-ray Photoelectron Spectroscopy (XPS) and Energy Dispersive X-ray spectroscopy (EDX) techniques.

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