Chapter 1

Introduction

1.1. Tribology

Phenomena of friction and wear are the significant sources for concurrent loss of energy and material, leading to negative impacts such as extensive energy utilization, the recurrent collapse of engineering components, and enhanced emission of greenhouse gases. The efficacious lubricant system can lower such unpleasant happenings. Friction, wear, and lubrication are collectively represented by tribology. Tribology is originated from "*tribos*," a Greek word meaning rubbing. It is considered the science and engineering of rubbing surfaces in relative motion [Bhushan et al. (2001)]. Surface interactions in tribology are highly complex and require an understanding of diversified subjects like physics, chemistry, material science, mechanical engineering, machine design, heat transfer, thermodynamics, etc. Their applications are ranging from spacecraft, automotive to household appliances [Bhushan et al. (1999)]. Tribology is not only for the materials and machinery world but also equally important for several activities in the human-body [Zhou et al. (2015)].

1.1.1. Friction

During the relative motion of the interacting surfaces under the applied load, the force that resists their movements is called frictional force. Consequently, there is a loss of energy due to friction. Some common examples of friction are; friction between the floor and shoes during walking, skin, and blade while shaving and driving a car. According to the laws of friction for common materials except for exceptionally hard and soft materials, frictional force (F_f) is directly proportional to the applied normal load (F_n)

$F_f = \mu . F_n$, where μ is 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.

The frictional force is independent of the contact area provided surfaces are not exceptionally smooth. Kinetic friction is independent of the sliding velocity when speed is not very high.

1.1.2. Wear

Wear is the progressive loss of material from the contacting surfaces under the applied normal load, leading to dimensional changes, eventually causing poor performance. Sometimes, the replacement of the worn component is urgently required. The magnitude of wear banks on the properties of material like surface roughness, environment, operating conditions, mechanical strength, hardness, and geometry of proximal surfaces. The types of interactions leading to wear may be adhesion, abrasion, chemical reaction, surface fatigue, etc.

- **Adhesive wear** occurs when surfaces in contact through asperities deform irreversibly and adhere to each other resulting in tremendous wear, scuffing, galling, or seizure.
- **Abrasive wear** takes place when the hardness of the proximal surfaces is widely different. The harder surface causes abrasion of the softer material resulting in scratches and furrows.
- **Chemical or corrosive wear** is caused by chemical agents formed in the oil. The anticorrosive agent in lubricant can reduce corrosive wear. The extreme pressure

lubrication may be considered as an example of controlled corrosive wear.

- **Surface fatigue wear** is characterized by pitting or cyclic crack growth that appears suddenly after a large number of revolutions. The material weakens because of structural modifications leading to subsurface cracks that propagate and result in flaking, spalling, and peeling.

Surface and fatigue wear is produced by rolling and sliding motions, while the types of wear are associated with sliding friction

1.1.3. Lubrication

Lubrication is meant to introduce a foreign substance, i.e., lubricant, between two or more moving bodies, which reduces friction and wear by preventing direct contact between the interacting surfaces. Poor lubrication is responsible for heavy energy and material losses. The lubrication is also required to accomplish other purposes, such as dissipation of heat from the contact surfaces, corrosion inhibition, and cleaning action. [Dorinson et al. (1985), Jones et al. (1983)]. In addition to vital roles in manufacturing processes and machine designs, lubrication is equally essential in the human body, e.g., artificial joints, hip replacements, etc. [Grupp et al. (2010), Davim et al. (2010)]. A good lubricant should exhibit low volatility, excellent thermal and oxidative stability, good fluidity at low temperature, non-corrosiveness, and high viscosity index [Kuratomi et al. (2009)].

The viscosity of the lubricant applied normal load and speed are critical parameters that control different lubrication regimes. These regimes are better understood by the Stribeck curve, based on the thickness of lubricant film between the interacting tribo-surfaces. The thickness of lubricant film is mainly determined by the bearing parameter given by [(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 [Hubson et al. (1955), Wang et al. (2006)]. Based on the lambda ratio, which is the ratio of minimum film thickness (h) to composite roughness (σ*), i.e., average roughness of interacting surfaces, the Stribeck curve may be divided into boundary, mixed and hydrodynamic lubrication regimes.

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

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

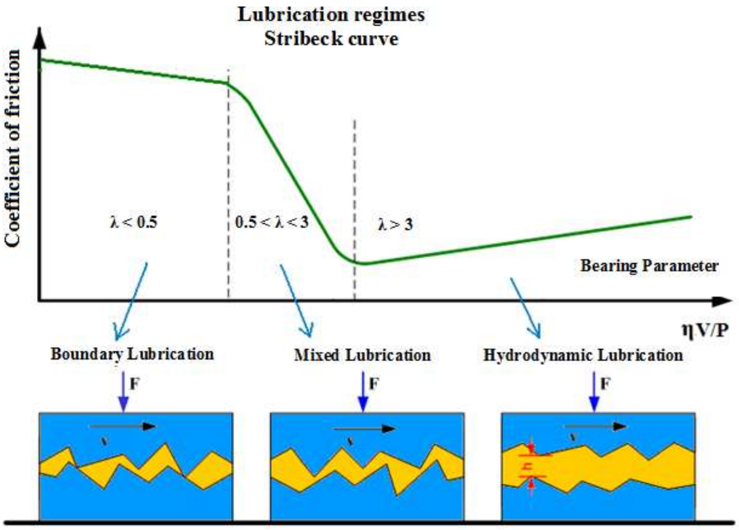

Figure 1.1. Stribeck curve showing the dependence of the COF on viscosity, speed, and load for a sliding lubricated system.

Boundary lubrication exists under the conditions of low viscosity, low velocity, and high load. The fluid film thickness is negligible under the boundary lubrication regime; therefore, considerable contacts are developed between the tribo-surfaces. The load is supported by direct contacts between asperities of interacting surfaces leading to a high COF. The value of the lambda ratio is less than 0.5 for this lubrication regime. Because of the high COF, there is an immense loss of energy and material; the regime is, therefore, the most damaging. [Myshkn et al. (1997)].

The hydrodynamic lubrication occurs when speed, viscosity, and load are moderate; lambda ratio is greater than 3.0, and lubricant film is sufficiently thick to prevent any direct contact between lubricated surfaces. Under these conditions, the load is borne entirely by the film of lubricant. Hence, hydrodynamic lubrication is the safest regime where friction is incredibly low, and wear is almost negligible.

A mixed lubrication regime is an intermediate of hydrodynamic lubrication and boundary lubrication. In this case, the lubricant film can separate the contact surfaces at a few points only 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 [Myshkin et al. (1997)].

1.2. Lubricants

Any material which reduces friction and wear when interposed between two moving surfaces is called lubricant. The primary function of a lubricant is to abstract heat and thus to increase mechanical efficiency. Besides this, it acts as a sealing agent and prevents dirt and moisture entry between the moving parts. The ever-progressing development of mechanical systems operating under arduous conditions calls for the improvement of the lubricants to withstand high temperatures and pressures. Based on the physical state, the lubricants may be classified as follows:

1.2.1. Liquid Lubricants

The base oil generally should have low viscosity and high viscosity index, but it should possess enough viscosity to maintain a lubricant film under the required working conditions. The fluidity of oil should be high to remove heat, minimize power loss due to viscous drag, and control friction and wear. Besides, it should have low volatility and high thermal and oxidation stability. The liquid lubricants are advantageous for their applicability over a wide range of temperatures, cooling properties, and cleaning action.

Liquid lubricants can be classified as vegetable oil, animal oil, mineral oil, or synthetic oil.

Vegetable oils are natural fatty acid triglycerides from agricultural produce, such as cottonseed oil, palm oil, rapeseed oil, olive oil, and castor oil. These oils have a very characteristic property, oiliness, by virtue of which they are adsorbed on metallic surfaces tenaciously and offer a lower COF and higher load-carrying capacity.

Animal oils like sperms oil, whale oil, seal oil, lard oil can be used as lubricants. The use of these oils is limited due to their decomposition at high temperatures.

Mineral oils like paraffin and naphthenic oils have primarily replaced animal or vegetable oils. These are inexpensive, readily available, stable under severe conditions, and reusable. Structurally, these are composed of straight or branched carbon chains of 20-40 carbon atoms. Aromatic or aliphatic rings, sulfur, oxygen, nitrogen, etc., may also be found.

Synthetic oils are made from the more advanced refining crude oil processes and, therefore, are purer and more expensive than mineral oils. The synthetic oil structure can be tailor-made as per requirements in a particular application for insulation, thermal or chemical stability, high viscosity index, and low volatility. Examples of synthetic oils are; polyalphaolefins, polyalkylene glycols, silicones, polyphenylene ethers, etc.

1.2.2. Semi-solid Lubricants

Greases, the semi-solid lubricants, are emulsified oils or fats with metallic soap and water. The advantage of using semi-solid lubricant is that it adheres to contact surfaces and remains at the application point to provide a better mechanical lubrication cushion under extreme conditions. However, again poor heat dissipation is a major drawback of using semi-solid lubricants. Greases are always accompanied by impurities like dust, dirt, and wear debris.

1.2.3. Solid Lubricants

Solid lubricants are solid bulk materials or solid thin films that can be placed between the contact surfaces and provide low shearing under a given load. Liquid lubricants or greases cannot be used for bearings under vacuum at elevated temperatures. In such cases, solid lubricants are used. The crystalline lamellar structure of these materials facilitates shearing and diminishes friction. Typical examples of solid lubricants are graphite, molybdenum disulfide (MoS_2), tungsten disulfide (WS_2), zinc oxide (ZnO), and ceramic coatings, etc. Apart from the layered structure, the critical requirements of solid lubricants are; high mechanical strength, low shear strength, high thermal, and chemical stability. The poor self-healing and high friction coefficient compared to liquid lubrication are the main drawbacks associated with solid lubricants.

1.2.4. Gaseous Lubricants

Aerodynamic or aerostatic lubrication requires gaseous lubricants such as air, nitrogen, oxygen, helium, etc. These can be recommended for extended temperature ranges. The gaseous lubricants are advantageous compared to liquid lubricants because their viscosity increases with increasing temperature. However, it is very tough to store gaseous lubricants.

1.3. Lubricant Additives

Lubricant additives are chemical compounds/materials, mostly organic, inorganic, and nanomaterials added to the lubricant in a small amount for enhancing the specific properties of lubricants [Ludema et al. (1996)]. Different types of lubricant additives are commercially available in today's market like viscosity improver, corrosion inhibitor, antioxidant, pour point depressant, friction modifier, and antiwear and extreme pressure, etc., and a fully formulated lubricant contains few of them, depending on the targeted application. During the past several decades, different categories of lubricants and additives have been evolved to improve the service life of machines.

1.3.1. Conventional Additives

The additives are added to base oils at low concentrations. The additives like viscosity modifiers, foam inhibitors, and pour point depressants are concerned with modifying the physical properties of the base oil. In contrast, antiwear, extreme pressure, and corrosion inhibitors improve the tribological properties of the lubricant. Generally, antiwear, antifriction, and extreme pressure lubricant additives are organic or inorganic compounds containing tribologically active elements (P, S, N, Cl, Zn, Mo, and B) or combinations of compounds with these elements. These are further classified into the following types based on their chemical compositions: sulfur compounds, ashless phosphorus compounds, dialkyl dithiophosphate complexes of metals (MDTPs), dialkyl dithiocarbamate complexes of metals (MDTCs), heterocyclic compounds, halogens, borate esters, and ionic liquids (ILs). Out of all these, ZDDPs have been the most promising antiwear additives. Still, their excessive usage is limited because of their direct negative impact on the environment based on massive amounts of sulfur phosphorus, zinc, and indirect effect on the exhaust emission system by blocking the catalysts.

The chemical interactions between two or more interacting surfaces, particularly under the boundary or mixed lubrication regimes, are studied under tribochemistry [Hutchings et (1992)]. In fact, tribochemistry is the chemistry between the lubricant/environment with the rubbing surfaces under tribo-conditions [Hsu et al. (2002)]. The nature of tribochemical reactions and their mechanism is gaining considerable interest in understanding the role of lubricant in reducing friction and wear. In boundary or mixed lubrication regimes, lubricant additives get adsorbed on the interacting surfaces. This adsorbed layer of the additive molecules minimizes the contact between moving surfaces. At higher load and elevated temperature, these additives undergo decomposition forming a protective tribofilm. This tribofilm prevents direct metal to metal contacts, thereby protecting the interacting surfaces. The reactivity of the additive with surfaces is crucial and must be optimized for the best performance. Inert behavior of additive will not favor the formation of a tribochemical film. Conversely, hyperactivity of the additive will promote the corrosive attack on the surface resulting in tribochemical wear. The reactivity of antiwear, antifriction, and extreme pressure additives in real applications depends on the nature of surfaces, the type of base oil, and other additives present in the system. A tribochemical reaction of an additive with a surface is generally catalyzed by the nascent metal surface and the contact asperity temperature. The contact temperature (flash temperature) is around 400 ºC or more, but short-lived. The frictional heat between the sliding asperities increases the contact temperature [Hsu et al. (2005)]. The nascent surface possesses very high surface energy and active sites. A variety of chemical reactions may occur due to the active surface and effect of heat together. These reactions mainly include oxidation of surfaces, oxidation and degradation of the lubricant, surface catalysis, polymerization, and the formation of inorganic and organometallic products on the sliding surfaces [Hsu et al. (1996)]. The reactivity, structure, and composition of the additive affect the nature of tribochemical products.

1.3.2. Nanoadditives

Failure of the conventional additives at high temperatures and pressures often obstructs their usage in tribology. Besides, these additives are inherently toxic, non-biodegradable, highly reactive, and ineffective at low temperatures. These characteristics strictly limit their tribological applications. Therefore, the need of the hour is to develop eco-friendly lubricants but with high tribological efficiency. With the advent of nanotechnology, it has become possible to achieve such fruitful engineering materials. Nano lubricants are stable colloidal suspensions of nano-sized materials, such as quantum dots, nanoparticles, nanofibers, nanotubes, nanowires, nanorods, and nanosheets. Nanomaterials, when added in a minimal amount (<1 wt%), exhibit tremendous tribological efficiency because their small size activates prompt tribological action at the surface. Simultaneously, emissions are minimized due to their chemical stability [Zhang et al. (2017), Xie et al. (2019), Zhai et al. (2019)]. Nano lubricants possess high thermal conductivity, which promotes the dissipation of heat generated by friction. Thus, nano lubricants meet the requirements of green tribology, an emerging area for the tribologists in the present scenario.

Carbon-based materials are known to possess high conductivity, thermal, mechanical, and chemical stability [Wang et al. (2016)]. Among these materials, fullerenes [Turan et al. (2018)] activated carbon, mesoporous carbon, carbon spheres [Kumar et al. (2020), Kumar et al. (2019)], carbon nanotubes [Moghadam et al. (2015)], carbon nano-onions, and graphene [Liu et al. (2019), Paul et al. (2019), Sun et al. (2019)] are considered to be of paramount significance for reducing friction and wear. Multifarious activities of carbon spheres (CS) have been acknowledged in different areas like a supercapacitor, electrode materials, catalysis, fuel cell, hydrogen storage, picolitre container, electromagnetic devices, and tribology. The amorphous carbon has been found in these spheres due to the low degree of graphitization. These are capable of bearing high pressures [Pesika et al. (2011)]. Their spherical morphology and chemical composition are retained as such under tribological test conditions in boundary and mixed lubrication regimes. Therefore, the mechanism of lubrication is considered to be rolling motion. Mistry et al. (2015) have studied the efficiency of the ultrasmooth submicron carbon spheres as a lubricant additive. The remarkable enhancement in tribological activity of carbon sphere-oil hybrid lubricant has been explained by considering carbon spheres as a third body material, which fill the minute gaps between surfaces asperities. The filling of gaps increases the area of actual contact. As a result, the contact pressure is reduced. The rigid carbon/ Fe microspheres have proved to be the lubricant of high-performance [Mistry et al. (2015), Cheng et al. (2016)]. Alazemi et al. (2016) used CS-MoS_2 as an oil additive to minimize friction loss. The tribological properties of polyether ether ketone were found to enhance by carbon spheres [Zhang et al. (2009)]. The nanohybrids of carbon spheres, copper@C, and ionic liquid stabilized Ag@C have been reported from our laboratory to give excellent tribological properties [Kumar et al. (2020), (2020)].

1.3.2.1. Nanoparticles

The characteristic feature of nanoparticles (NPs) is their large surface to volume ratio, making them more chemically reactive [Tang et al. (2014), Uflyand et al. (2019)]. The presence of a large number of surface atoms facilitates the surface modification of the nanoparticles, which is beneficial for stable dispersion in a particular lubricant [Philip et al. (2019), Chen et al. (2020), Tang et al. (2014), Uflyand et al. (2019), Srivyas et al. (2018), Singh et al. (2020), Hong et al. (2020), Xiong et al. (2012), Zhang et al. (2014), Sánchez-López et al. (2011)]. The inorganic nanoparticles include metals like nickel [Chou et al. 2010)], palladium [Kumara et al. (2018)], copper [Viesca et al. (2011), Guo, Zhenqi, et al. (2020), and silver (Ma et al. (2009), Kumara et al. (2017)] metal oxides such as Fe_3O_4 [Zhou et al. (2013)], TiO_2 [Ingole et al. (2013) Wu et al. (2017), Zhang et al. (2018)], Al_2O_3 [Luan et al. (2012), Pena-Paras et al. (2015)], CuO [Pena-Paras et al. (2015), Battez et al. (2008)], ZrO_2 [Battez et al. (2008), Liu et al. (2002), Rylski et al. (2020)], MgO [Liu et al. (2002)], ZnO [Battez et al. (2008), Battez et al. (2006), Nainaparampil et al. (2001)], CeO_2 [Shen et al. (2016)], SnO_2

[Bonu et al. (2016)] V_2O_5 [Dai et al. (2017)], metal sulfides, for example, Ag_2S [Ma et al. (2019)], CuS [Kang et al. (2008)], MoS_2 [Xie et al. (2016), Koshy et al. (2015)], WS_2 [Ratoi et al. (2014)], metal halides like lanthanum fluoride [Zhou et al. (2001), Li et al. (2014)].

Functionalization of the NP surface results in increased stability of the NP dispersion, which in turn, increases the lubrication properties [Qian et al. (2012), Xu et al. (2018), Chen et al. (2020)]. Aggregation of NPs is prevented in non-polar base oil after functionalization [Uflyand et al. (2019)]. A polymer or surfactant coating severely reduces aggregation by steric or electrostatic stabilization [Uflyand et al. (2019), Philip et al. (2019), Chen et al. (2020), Singh et al. (2020), Hong et al. (2020)]. The functionalized NPs prevent the transfer of material between them and cold-welding between the shearing surfaces [Uflyand et al. (2019)].

Liu and his team have reported excellent tribological performance of oleic acid stabilized lead sulfide NPs [Liu et al. (2006)]. Silver nanoparticles functionalized by organic compounds have been studied as lubricant additives [Qu et al. (2017)]. Valbe and co-workers have documented the antiwear performance of phosphonium based ionic liquids mixed with stabilized oxide nanoparticles in PAO and 5w40 [Valbe et al. (2017)]. Recently from our laboratory, tribological efficiency of stearic acid stabilized calcium copper titanate NPs [Jaiswal et al. (2014)], and sodium dodecyl sulfate (SDS) stabilized 1-decyl-3-methyl imidazolium bis(trifluoromethylsulfonyl) imide modified calcium-doped ceria (CCO) NPs have been evaluated in paraffin oil [Kumar et al. (2020)].

A metal salt lattice doped with different metal ions has resulted in increased tribo-activity due to the formation of defects that form slip systems and lower shear strength [Kalyani et al. (2016), Jaiswal et al. (2014), Li et al. (2017)]. The SDS stabilized magnesium- doped zinc oxide NPs and aluminium doped zinc oxide NPs are known to improve the tribological properties [Kalyani et al. (2016)]. Zinc-doped calcium copper titanate and has been reported to give promising results regarding tribological behavior [Jaiswal et al. (2014)]. Doping of zirconia by magnesium, calcium, aluminium, and yttrium, etc., in a mechanically more robust tetragonal phase is known to enhance its tribological properties [Jaiswal et al. (2014)]. Nanopowders containing alumina- ceria-zirconia have been documented for catalytic activity [Kim et al. (2009)]. Philip et al. (2016) investigated surface morphology, stability analysis of ceria-zirconia hybrid nanoparticles, and proposed fcc-fluorite structure based on XRD results. They endorsed the application of these nanoparticles as lubricant additives. Li et al. (2017) have studied friction and wear characteristics of $ZrO_{2,}$ and Y_2O_3 stabilized ZrO_2.

Different mechanisms have been proposed for the lubrication efficiency of nanoparticles; rolling, self-repairing or restoration, polishing, and tribofilm formation. The ball bearing and tribofilm mechanisms are considered direct mechanisms, whereas the mending and polishing mechanisms are related to indirect mechanisms.

- **Rolling mechanism:** Since nanoparticles are usually spherical, they behave as small ball bearings that roll into the contact zone and change sliding friction to a mixture of sliding and rolling types of friction.
- **Tribofilm formation:** Interactions between additives and tribo-surfaces may lead to the formation of a protective tribofilm. For better protection of the surfaces, the formation of tribo-film should prevail over wearing.
- **Tribosinterization:** Tribosinterization eventually leads to the healing of the surfaces by filling NPs in the scars and grooves.
- **Polishing mechanism:** The NPs being hard cause abrasion of the rough surfaces leading to polished surfaces.

1.3.2.2. Quantum Dots and their Functionalization

A new type of semiconductor particles with a diameter less than 10 nm, quantum dots (QDs), have been widely studied because of their commendable biocompatibility, excellent optical properties, and high chemically inactive behavior [Tu et al. (2020)]. Carbon-based quantum dots (CQDs) are carbon nanostructures, which can be synthesized from any carbon source, including chemical reagents, biomolecules, or even foodstuff [Chimeno-Trinchet et al. (2020)]. The CQDs with functional groups on their surface derived from different carbon sources have found applications as lubricant additives in tribology [Ye et al. (2019)]. Because of strong polarity, their applications are limited to strengthen the lubricating properties of polar base oils. The unconventional carbon quantum dots, graphene quantum dots (GQDs) having sheet-like-spherical nanostructure, have been synthesized from graphene and oxidized graphene (GO). GQDs withhold the layered structure and show distinctive physicochemical and tribological performances [He et al. (2018), Yin et al. (2020)]. Interface-sliding-induced graphene quantum dots transferring to fullerene-like quantum dots and their unusual tribological behavior have been studied [Zhang et al. (2019)]. Composites of CQDs with ionic liquids proved to be an efficient lubrication additive [Wang et al. (2016) and Zhang et al. (2017)]

The tribological performance of highly dispersed MoS_2 QDs as a lubricant additive in paroline oil has been investigated on the ball-on-disc machine. [Guo et al. (2020)].

1.3.2.3. Nanosheets

Inorganic two-dimensional layered nanomaterials, like molybdenum disulfide, tungsten disulfide, hexagonal boron nitride, and graphene, have enhanced research due to their special characteristics, mainly high specific surface area. The presence of weak van der Waals-type forces between proximal layers in a layered structure facilitate lubricating tendencies. Some of the nanosheets are shown in **Fig. 1.2.** **[**Rao et al. [2014].

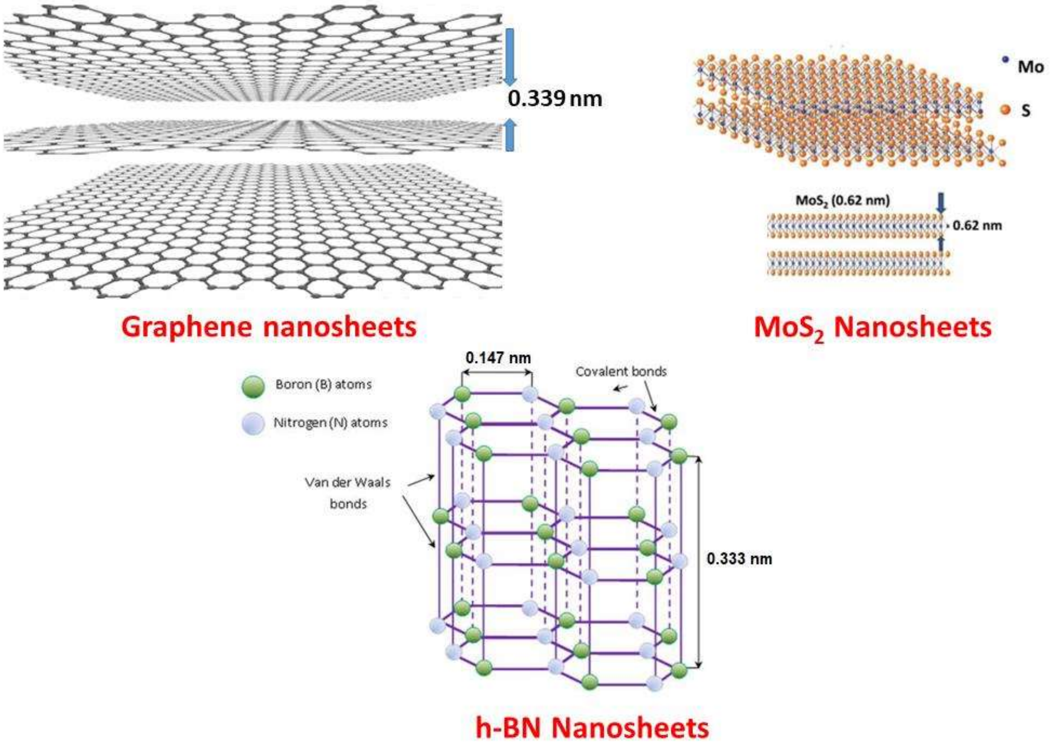

Fig. 1.2. Different nanosheets

Graphene is believed to be the strongest material yet discovered. It consists of a monoatomic thick planar sheet of sp^2-hybridised carbon atoms arranged in a compact honeycomb crystal lattice. It offers little resistance to electrons, which zip through it fast and easily carry electricity better than conductors like copper. The matchless mechanical strength, chemical stability, optical properties, resistivity to permit entry of gases or liquids, excellent thermal and electrical conductivity make graphene a very apt material [Geim et al. (2009), Zhu et al. (2010), Ferrari et al. (2015)]. A theoretically single sheet of graphene exhibits a very high surface area, i.e., 2630 m^2g^{-1}. Remarkably, it is stiff and elastic (like rubber), Young's modulus 1.06 TPa, can be stretched 20-25 percent of its original length without breaking

[Paul et al. (2019)]. Extensive research has been carried out to explore applications of graphene in different domains (**Fig. 1.3.**); gas adsorption and storage, sensors, solar cells, supercapacitors, fuel cells, Li-ion batteries, catalysis, and tribology [Liu et al. (2019), Paul et al. (2019), Sun et al. (2019), Eswaraiah et al. (2011)].

The graphene and functionalized graphene do not provide good lubrication properties at the macroscale level. The performance has been enhanced by synergistic interaction with other solid lubricants. According to Berman et al. (2018), graphene and nanodiamond particles have shown macroscale superlubricity when used against diamond-like carbon (DLC) coated steel ball.

In fact, graphene nanoscrolls formed by the wrapping of graphene flakes around nanodiamonds keep the contact surfaces far apart and account for macroscale superlubricity. The friction and wear-reducing properties of graphene are significant only at lower concentrations, higher concentrations of graphene cause agglomeration producing abrasive wear.

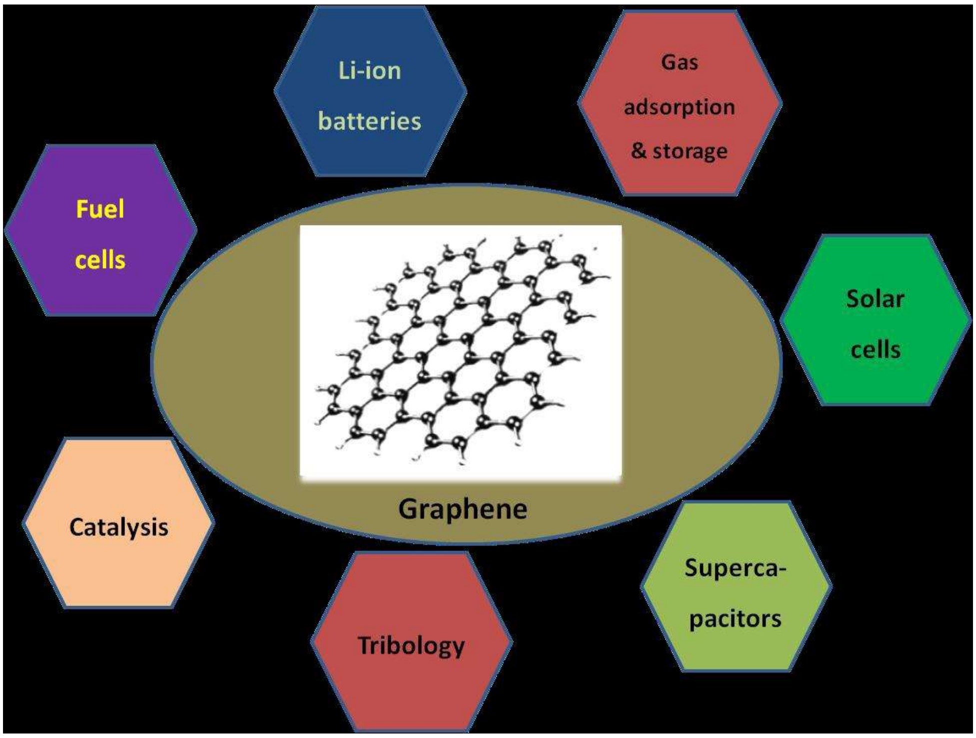

Figure 1.3. Potential of graphene in various applications

The tribological performance of the engine has been improved by graphene nano lubricant [Paul et al. (2019), Sun et al. (2019), Eswaraiah et al. (2011), Ali et al. (2018), Yang et al. (2014)]. Adherence of graphene to a steel surface is promoted by dangling bonds of carbon. Its adhesion to the surface acts as a barrier between metal-metal contact and is capable of reducing friction [Righi et al. (2016)]. Graphene being ultrathin even with multilayers, its importance is realized in micro-electro-mechanical systems (MEMS) and nanoelectromechanical systems (NEMS) with oscillating, rotating, and sliding contacts for reducing friction and wear [Kulia et al. (2012), Paul et al. (2019), Mungse et al. (2014)].

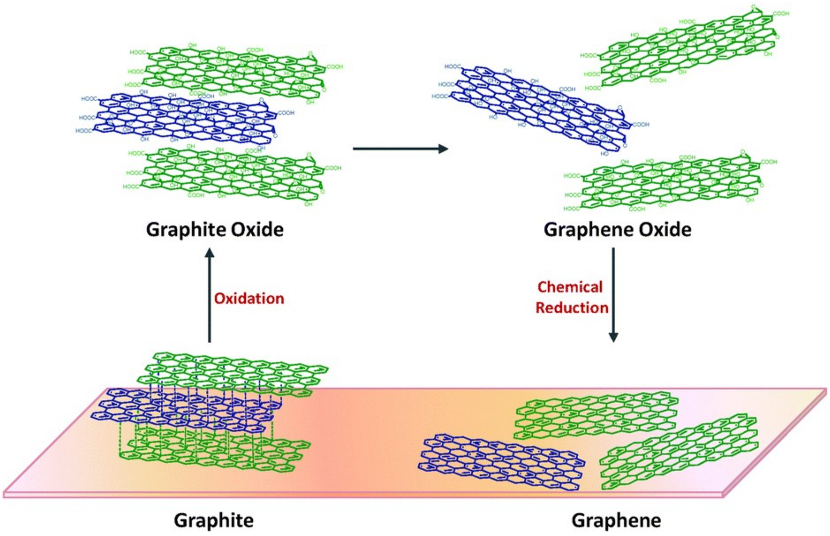

Fig. 1.4. Synthesis of graphite oxide, graphene oxide, and graphene from graphite [Chua et al. (2014)].

The graphene oxide (GO) is an important intermediate between graphite and graphene. It is generally prepared by the exfoliation of graphite oxide, **Fig. 1.4.** Structurally, it is different but exhibits chemical similarity to the graphite oxide. It is usually obtained *via* ultrasonication or mechanical stirring of graphite oxide in polar organic solvents or aqueous media [Kuila et al. (2012)]. The exfoliation of the graphite oxide is effectively and quickly achieved by the ultrasonication method. The efficiency of exfoliation of graphite oxide to form graphene oxide is related to the extent of oxidation of graphite, ultrasonic frequency, sonication time, and dispersion medium. It has been found that the degree of exfoliation increases as the extent of oxidation, ultrasonic frequency, and sonication time increase. Graphene oxide shows comparatively higher friction and wear under a moist environment than graphene, but the opposite happens under dry conditions. For mass-scale graphene production, the reduction of graphene oxide (GO), usually by hydrazine, is the most popular method, **Fig. 1.5**. Both rGO and GO act as antifriction and antiwear additives to the base oil [Gupta et al. (2016)]. The dispersion of rGO in non-polar solvents is more feasible than GO [Kuila et al. (2012)]. On the other hand, functionalities on the surface of GO favor functionalization, resulting in increased dispersion [Kuila et al. (2012)]. The mechanical and thermal conductivity properties of rGO dispersions are far better than those of GO [Kuila et al. (2012), Ota et al. (2015), Paul et al. (2019)].

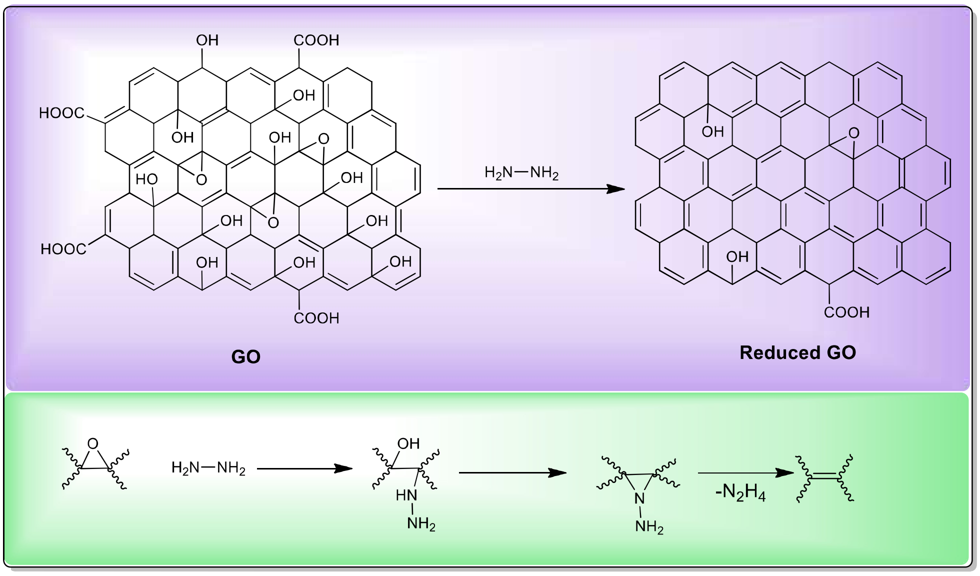

Figure 1.5. Schematic representation for reaction and mechanism of GO reduction by hydrazine.

Because of its high surface area and surface energy, graphene is prone to agglomerate and approach back to graphitic form [Ota et al. (2015)]. Graphene is chemically inert due to its structure, resulting in weak adsorption and rapid removal on the metal surface. Chemical functionalization of graphene provides an impeding effect to agglomeration [Kuila et al. (2012)] and enhances its adhesion on the surface. An additional benefit of functionalization has been realized in facilitating its dispersion in different media [Choudhary et al. (2012), Mungse et al. (2019), Kuila et al. (2012), Georgakilas et al. (2012), Zhang et al. (2017), Tang et al. (2018), Paul et al. (2019)].

A comprehensive literature survey reveals that covalent functionalization of graphene oxide can be brought about both at the end of the sheets or on the surface depending upon the nature of the modifier [Mungse et al. (2019), Kuila et al. (2012), Georgakilas et al. (2012), Zhang et al. (2017), Tang et al. (2018), Paul et al. (2019), Gusain et al. (2016), Mungse et al. (2014), Chouhan et al. (2018)]. Nucleophilic substitution occurs at the epoxy groups by the attack of ionic liquids, amines, amino acids, small molecular weight polymers, and silane compounds. On the other hand, substitution by an electrophile, for example, aryl diazonium salt, is edge selective and utilizes displacement of the hydrogen atom. The compounds like isocyanates, diisocyanates, and amines undergo a condensation reaction with -OH and -COOH groups forming carbamates and amides. Several reports are available for the functionalization of graphene by environment-friendly ionic liquids resulting in enhanced lubricating properties [Fan et al. (2015), Khare et al. (2013), Pu et al. (2011), Gusain et al. (2016), Pamies et al. (2018). Tribological investigations carried out on graphene 1-butyl-3 methyl imidazolium iodide hybrid material have shown its potential to reduce friction and wear. Gusain et al. (2016) have reported friction and wear reducing behavior of graphene-imidazolium-based ionic liquid hybrids with anions as bis(salicylato)borate, oleate, and hexafluorophosphate in polyethylene glycol (PEG 200). Dispersions of 1-ethyl-3-methylimidazolium dicyanamide or bis(trifluoromethylsulfonyl)imide ionic liquids with graphene improved their load-carrying properties [Pamies et al. (2018)].

Composites usually exhibit superior performance owing to the synergetic effect of more than one nanomaterial, compared to individuals. Thus, composites of graphene prepared by non-covalent functionalization also yielded excellent tribological properties. For non-covalent functionalization, molecules undergo physical adsorption on the surface of graphene via the weaker type of interactions such as electrostatic, π-π, or van der Waals forces [Kuila et al. (2012), Georgakilas et al (2012), Singh et al. (2011)]. Various conjugated polymers and aromatic compounds like poly (sodium 4-styrene sulfonate), sulfonated polyaniline, poly(3-hexylthiophene), conjugated polyelectrolyte, 7,7,8,8-tetracyanoquinodimethane anion, pyrene, perylene diimide, and macrocyclic ligands porphyrins, zinc phthalocyanine are reported to stabilize graphene structure in the composite materials through π-π interactions [Serra et al. (2019), Kuila et al. (2012), Georgakilas et al (2012)]. Recently, Haruna et al. (2019) and co-workers have prepared cyclodextrin-based functionalized graphene oxide and applied it as an effective corrosion inhibitor for carbon steel in an acidic environment.

A variety of nanoparticles have been employed for the non-covalent functionalization of graphene in nanohybrids. The lubricating properties of sandwich-like nanostructure of Mn_3O_4/graphene nanomaterial have been investigated [Zhao et al. (2019)]. Zhou and co-workers prepared a nanocomposite of reduced graphene oxide with zirconia. They used it as a lubricant additive [Zhou et al. (2015). SiO_2/graphene nanofluids contributed a better lubrication effect than pure nanofluids for magnesium alloy rolling [Xie et al. (2019)]. Antiwear properties of engine oil 5W-30 were improved in automobile engines by copper/graphene nano lubricants [Ali et al. (2019)]. Pu and coworkers (2011) have prepared thin films of non-covalently functionalized reduced graphene nanosheets on hydroxylated silicon surfaces with ionic liquids having a very high tribological activity like hydrophilic 1-butyl-3-methyl imidazolium tetrafluoroborate [BMIM][BF_4], hydrophobic 1-butyl-3-methyl imidazolium hexafluorophosphate [BMIM][PF_6] and discussed their applications in micro-electro-mechanical systems(MEMS)/nanoelectro-mechanical systems (NEMS) [Pu et al. (2011)]. TiO_2-reinforced boron and nitrogen co-doped reduced graphene oxide-based hybrid nanomaterials have been explored as efficient antiwear lubricant additives from our laboratory [Jaiswal et al. (2016)].

One-dimensional single and multi-walled carbon nanotubes [SWNT, MWNT] consist of the graphene layer embedded in one another. These have found numerous industrial applications. Their shape, high length-to-diameter ratio, superior mechanical properties, and great flexibility have made them useful solid lubricants or lubricant nano additives to improve the tribological activity [Zhai et al. (2017), Ali et al. (2019)]. Stearic acid-modified MWCNTs with increased dispersibility have been investigated for their tribological properties using a pin-on plate wear tester [Chen et al. (2005)]. The advancement of tribological activity of Mobil gear 627 and paraffin oils was observed when CNTs were blended [Khalil et al. (2016) and his team]. The SDS functionalized MWCNTs as lubricant additives besides improving antifriction, antiwear, and extreme pressure properties of the water-based lubricants, improved load carrying capacity also. [Peng et al. (2007)]

The tribological activity of the polyelectrolyte grafted MWCNTs, having a solid MWCNT base and a soft brush-like polyionic liquid (MWCNTs-g-PILs) as an additive to LP104 base lubricant (1-methyl-3-butylimidaaoliumhexafluorophosphate) were assessed using the Optimol SRV tester [Pei et al. (2008)] The substantial activity could be correlated with increased dispersibility. The ionic liquid/MWCNTs composite exhibited excellent wear and friction-reducing properties for the same reason [Zhang et al. (2015)]. Song et al. (2018) studied the friction and wear-reducing properties of dibutyl phthalate (DBP) containing SOCNTs, MoS_2, SOCNTs/MoS_2 mixture, and SOCNTs@MoS_2 composite. Synergic behavior was observed between CNTs and MoS_2. Vardhaman et al. (2020) investigated the tribological properties of ZnO/MWCNTs hybrid nanomaterials as additives dispersed in 10w40 engine oil. The nanocomposites of MoS_2 nanoparticles (NPs) grown on carbon nanotubes (MoS_2@CNT), graphene (MoS_2@Gr), and fullerene C_{60} (MoS_2@C_{60}) have been recommended as potential lubricant additives. Their considerable dispersibility in polyalkylene glycol (PAG) due to synergistic interaction between MoS_2 and carbon nanomaterials (CNMs) has been instrumental in enhancing the tribological behavior. Che, Qinglun, et al. (2020) reported the role of carbon nanotubes on the growth of a nanostructured double-deck tribofilm yielding excellent self-lubrication performance.

The hexagonal close-packed structure of MoS_2 consists of molybdenum in a trigonal prismatic arrangement of six sulfur atoms. The weak van der Waals forces existing between molecular S-Mo-S tri-layers owe to lubricity. Tribological studies of highly dispersed thiol-functionalized MoS_2 nanosheets in water have been carried out. [Wang et al. (2019), Zhao et al. (2016), Rajendhran et al. (2018)]. The nanosheets of MoS_2/graphene /their nanocomposites are added to the base oil for the advancement of lubrication [Song et al. (2018), Xu et al. (2017), Song et al. (2017), Zhao, Jun et al. (2016). MoS_2 and graphene dispersed in esterified bio-oil have shown the synergic tribological behavior [Xu et al. (2017)]. Song and co-workers have studied the tribological activity of hydrothermally synthesized composite, MoS_2-graphene oxide [Song et al. (2017)]. The GO-MoS_2 film reduced friction by 90% and 50% compared to the steel substrate and GO film. Wu and his associates have investigated tribological properties of the chemically capped zinc borate/ MoS_2 nanocomposite in oil and grease [Wu et al. (2018), Wu et al. (2018)]. The tribological behavior of Fe_3O_4/MoS_2 nanocomposite in water/oil was studied by Zheng et al. (2016). Recently, Fe_3O_4/MoS_2 nanocomposite has been reported to show enhanced lubricating properties in base oils together with significant photocatalytic degradation [Liu et al. (2018)].

WS_2 is a two-dimensional nanomaterial that is a traditional solid lubricant additive due to its layered lattice structure. Zhang et al. investigated the tribological performance of WS_2 nanosheets as an additive in poly alpha-olefin and gel lubricants. The excellent tribological activity of ultrathin WS_2 nanosheets in poly alpha olefin was demonstrated by Jiang et al. Lu et al. (2019) prepared a nanohybrid of WS_2 with titanium dioxide nanoparticles

(WS_2/TiO_2) and found their synergistic effect on lubricity in di-iso-octyl sebacate. The tribological studies of WS_2 nanosheets decorated by uniformly dispersed Cu nanoparticles have been reported by Xu et al. (2019).

The 2D-hexagonal boron nitride (h-BN) possesses the lattice structure most similar to that of graphite and has equal numbers of boron and nitrogen atoms alternatively arranged in a honeycomb configuration. It is also termed as "white graphite." Its superior mechanical strength, thermal stability, anti-oxidation, and self-lubricating properties compared to graphite have been attributed to the presence of special covalent bonds of B-N [Zhang et al. (2019), Yuan et al. (2019)]. The BN nanosheets with the thickness of tens of nanometers as an additive in oil-lubrication and water-lubrication systems provided encouraging performance [Wu et al. (2020a), (2020b)]. Hexagonal Boron nitride shows excellent antifriction behavior under extreme conditions in the presence of organic vapors and high temperature, which could be ascribed to the weakening of the interlayer interaction. Because of the chemical inertness of the h-BN surface modification via chemical functionalization or physical adsorption is essential to achieve high dispersibility in lubricant media [Yuan, Junya, et al. (2019)]. Aromatic organic substances could be readily adsorbed on the h-BN surface through π-π overlap interaction [Kumari et al. (2014), Kumari, et al. (2016)] and alkyl [Wu et al. (2020a)] [Zhang et al. (2019), Yuan et al. (2019)]. Chemically functionalized h-BN and their nanocomposites with differents nanomaterials like Fe_3O_4 NPs, CNTs, Graphene, MoS_2, etc., have been found to be highly tribologically active due to synergistic interactions between the components [Bondarev et al. (2020), Zhao et al. (2019), Liu et al. (2018), Yuan et al. (2019), Wu et al. (2020b), Zhao et al. (2019)].

1.4. Statement of the Problem

In mechanical systems where interacting surfaces are in relative motion, friction and wear-related failures are great trouble sources. Friction between proximal surfaces leads to an increase in energy consumption. Wear, on the other hand, reduces the durability of the device. Therefore, factors like efficiency, durability, and environmental compatibility are to be improvised for the sustainability of the system. The subjugation of friction and wear is practically imperative to achieve the goal. The use of a lubricant paves the way to control friction and wear. The lubricant prevents metal-to-metal contact by forming a low-shear, durable film on the tribo-surfaces. The additives may be appended to the base oil to improve its antiwear/antifriction properties. Various boron, nitrogen, phosphorus, sulfur, and chlorine compounds have been recommended as tribological additives for boundary lubrication. Among these, zinc dialkyl dithiophosphates (ZDDPs) were the most frequently used antiwear additives. On the contrary, environmental legislation nowadays has limited the application of these multifunctional additives due to the high amount of sulfated ash, phosphorous, and sulfur (SAPS) contents. The high SAPS contents are known to poison the automotive exhaust and show damaging effects on the environment. The rigorous environmental legislations necessitate searching for better environment-friendly replacements for the ZDDP-based lubricant additives without compromising the efficiency and any harmful effect on the interacting surfaces.

Nano lubricants meet the requirements of green tribology, an emerging area for the tribologists in the present scenario. Several inorganic nanoparticles of metals, metal oxides/sulfides/halides, have been applied as tribologically active additives to the base oil. Among 2D-nanomaterials, graphene is well recognized for its exclusive friction and wear-reducing properties, but it is highly susceptible to agglomeration due to high surface energy causing poor dispersibility in the base oil, and it is feebly adhered to the surface due to chemical inertness. Chemical functionalization of graphene is a remedial measure to curb its agglomeration, restacking, and promote dispersion and adhesion to the interacting surface. Surface modification of graphene oxide can be achieved by covalent and non-covalent pathways.

1.5. Aims and Objectives

Given the above, the most appropriate approach to improve the tribological properties of graphene was considered by covalent/non-covalent functionalization or both together using their synergistic effects. Therefore, the present investigation was undertaken to develop graphene-based nanohybrids as highly efficient friction and wear modifiers using chemical functionalization.

The covalent functionalization of graphene was achieved by 2-aminoethyl diphenyl borate (ADB), expecting *in situ* formation of an additional triboactive layered material, boron nitride, in the tribofilm, which may improve tribological activity tremendously. Since metal oxides are relatively inexpensive, have high thermal stability, and the size of the nanoparticles can easily be regulated, these have been preferred for the non-covalent functionalization of graphene. Further, doping by some different metal ions in the host lattice of a metal oxide has yielded enhanced tribological performance due to the formation of defects that form slip systems and lower shear strength. Therefore, doped-metal oxide nanoparticles have been favored to develop nanohybrids. Besides, copper(II) phthalocyanine nanotubes (CuPc), another layered structure, and a polymer, polyaniline (PANI), have been deliberately chosen for the purpose.

The main objectives of the present investigation are-

1. To synthesize, characterize and assess the tribological behavior of

- zinc oxide and magnesium-doped zinc oxide nanoparticles and their nanohybrids with reduced graphene oxide
- yttrium and vanadium -codoped zinc oxide nanoparticles and their nanohybrids with reduced graphene oxide
- ternary nanocomposite containing vanadium and yttrium-codoped zinc oxide nanoparticles/ reduced graphene oxide nanohybrid and polyaniline
- binary nanohybrids of cerium-doped yttria nanoparticles with reduced graphene oxide and molybdenum disulfide
- ternary nanocomposite containing cerium-doped yttria nanoparticles /reduced

graphene oxide nanohybrid and molybdenum disulfide

- 2-aminoethyl diphenyl borate functionalized reduced graphene oxide and its nanohybrid with copper(II) phthalocyanine nanotubes

2. To study the relative adsorbing capacity of phthalocyanine and copper (II) phthalocyanine on the steel surface by molecular dynamics simulations

3. To analyze the surface morphology of worn surfaces using Scanning Electron Microscopy (SEM) and contact mode Atomic Force Microscopy (AFM) techniques

4. To investigate the action mechanism and tribochemistry of these nanomaterials using Energy Dispersive X-ray spectroscopy (EDX) and X-ray Photoelectron Spectroscopy (XPS) techniques