1 Introduction

This chapter introduces the role of lubricants in tribology, their classification, and the global and domestic market scenario. Moreover, the chapter describes nanomaterials and their potentials for the enhancement of lubricant performance. The chapter concluded with a brief introduction of green tribology and the need for green lubrication.

1.1 Tribology

The term tribology was first reported by Prof. H. Peter Jost in 1966, and it is Greek originated word *tribos*, means rubbing, and *logos*, implies science. The term tribology represents *the science of rubbing*, and it includes the study of friction, wear, and lubrication (Menezes et al., 2013). It is science and technology of interacting surfaces, which are in relative motion with each other and deals with friction, wear, and lubrication. The moving surfaces of engineering bodies experience friction and lead to progressive loss of material. The tribological interactions of rubbing surfaces are highly complex. To develop insight about tribological processes and the role of lubricants, the knowledge of multiple disciplines including solid mechanics, heat transfer, thermodynamics, fluid mechanics, lubrication, rheology, material science, chemistry, physics, applied mathematics, machine design, performance, and reliability are required.

In tribological interactions, friction plays a critical role in the performance of various systems. In many tribological situations, low friction is preferable and even indispensable for a daily routine life, i.e., ball bearing, gears, hip joints, hinges of doors, etc. High friction is desirable in many applications, such as in clutches and brakes, to transfer torque and dissipate kinetic energy. High friction also plays a vital role while we are walking and driving a car (interaction between tire and road) (Stachowiak and Batchelor, 2013).

The progressive loss of material is a common phenomenon; whenever two or more surfaces are in relative motion and directly contact each other. In many tribological situations, wear is maleficent to the service life and efficiency of the machinery. The progressive loss of material causes the failure or unwanted breakdown or can be a root cause of any engineering disasters. High wear rates are desirable in some tribological events such as polishing, grinding, machining, etc. Similarly, for writing purposes, a high wear rate and less friction are favorable between the pencil and paper (Hutchings and Shipway, 2017).

The requirement of minimum or maximum friction and wear depend on the tribological applications. The tribo–pairs have high sliding friction when they have interacted under an unlubricated condition. Therefore, high frictional heat is generated, which often leads to an increase in wear rate, and a significant amount of energy is required to overcome the frictional losses. The application of lubricant/grease between two interacting surfaces plays a vital role in reducing friction and wear. Lubricants form a thin film of low shear strength between the tribo–pairs which reduce friction and prevent wear.

1.2 Role of lubricants in tribology

Lubricants have an inherent lubricious property capable of reducing friction between the rubbing pairs and preventing surfaces from wear. Lubricant is an amalgamation of lube base stock and a package of additives. Additives are added to enhance the performance of the lube base stock. The percentage and composition of additives in the lubricants are varied according to their applications. Typically, a liquid lubricant constitutes lube base oil and additives in the range 1–25 wt% (Menezes et al., 2013).

Lubricants protect the tribo–surfaces against wear and minimize the risk of frequent breakdown. They also facilitate smooth sliding or rolling of machine parts and reduce the noise during the machinery operation. The lubricants decrease the friction and direct interaction of asperities by establishing a tribo–film on the interacting surfaces.

The lubricants have many different functions, which vary according to the tribological situations. The prime purpose of the lubricants is to protect the interacting surfaces, minimize friction and wear, expand the drain time, and dissipate the heat from contact surfaces. A wide range of lubricants encompasses the following functions:

- Cleaning and sweep away the debris and contaminations
- Protect against corrosion
- Reduce friction and wear
- Reduce vibrations and noise
- Seal for gases
- Separate interacting surfaces
- Dissipate heat
- Provide antioxidant properties
- Transfer of power, etc.

1.3 Classification of lubricants

The lubricants are categorized according to their (a) physical state, (b) the origin of lube base oil and, (c) applications (Mobarak et al., 2014). **Figure 1.1** shows the classification of lubricants. The lubricants are categorized into solid, semi–solid, and liquid, based on their physical state. In some cases, gases are also used as lubricants. As per the derived origin of lube base oil, the lubricants are classified as mineral oils (oil derived from crude oil), vegetable oils (oil derived from plant seeds or kernels), and synthetic oils (chemically processed oils). Apart from that, lubricants are divided based on their applications, such as industrial oils, automotive oils, marine, aviation, and special–purpose oils.

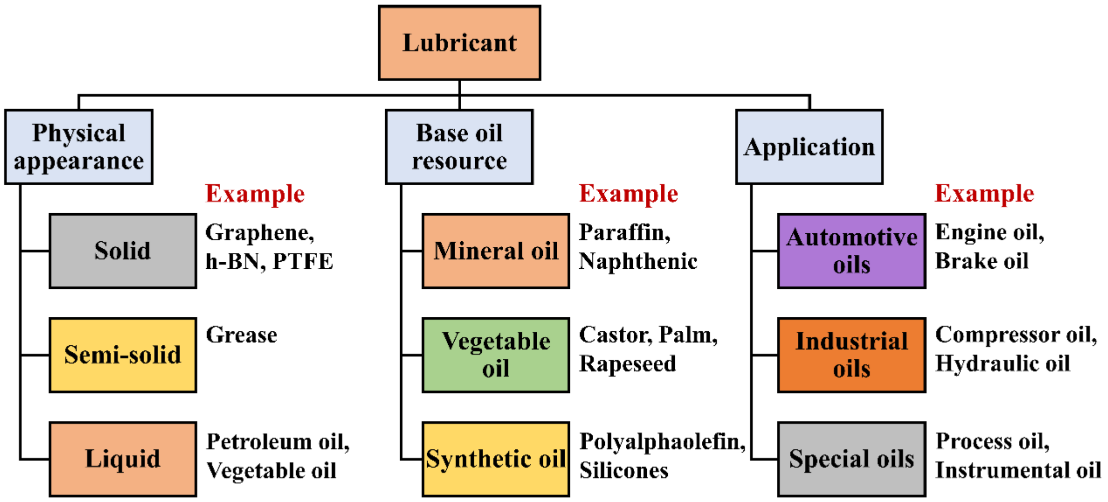

Figure 1.1: Classification of lubricants based on their physical state, sources, and applications

The American Petroleum Institute (API) has segmented the lube base oils into five categories according to their physicochemical properties and are presented in **Table 1.1**.

Table 1.1: Categorization of lube base oil as per API guidelines (Rizvi, 2009; Torbacke et al., 2014)

Category	Saturates (%)	Sulfur (%)	Viscosity index
Group I	< 90	>0.03	80 to 120
Group II	≥ 90	≤ 0.03	80 to 120
Group III	≥ 90	≤ 0.03	≥ 120
Group IV	PAOs		—
Group V	All other not included in Group I, II, III, and IV		—

1.4 Current status of lubricant market

Approximately 1700 small and large lubricant manufacturers exist worldwide. Around global demand of 60% of lubricants is met by less than 2% of lubricant manufacturers (Nagendramma and Kaul, 2012). BP, Chevron, Conoco Phillips, Exxon Mobil, Fuchs, Lukoil, Nippon oil, Petro China, Shell, and Valvoline are the major lubricants manufacturers worldwide. In India, Hindustan Petroleum Corporation Ltd. (HPCL), Bharat Petroleum Corporation Ltd. (BPCL), and Indian Oil Corporation Ltd. (IOCL) are the leading lubricant manufactures. Indian Institute of Petroleum, Dehradun, Indian Oil Corporation, Faridabad, and Indian Institute of Chemical Technology, Hyderabad, are premier research and development laboratories in India.

1.4.1 Global and domestic market of liquid lubricants

Table 1.2: Forecast medium–term oil demand for period 2018–2024 (OPEC–Report, 2019)

Year	World (mb/d)	India (mb/d)
2018	98.7	4.7
2019	99.9	4.9
2020	101.0	5.1
2021	102.0	5.3
2022	103.0	5.5
2023	103.9	5.7
2024	104.8	6.0
Growth 2018–2024	**6.1**	**1.2**

In the last 20 years, the global lubricant market has experienced significant demand due to the globalization of industries. In 1991, the worldwide demand for lubricants was ~35 million tonnes/year. In 2004, the global consumption of lubricants increased to ~37.4 million tonnes/year (Nagendramma and Kaul, 2012). According to the Organization of the

Petroleum Exporting Countries (OPEC) report 2014, the World and India's medium–term oil demand has increased from 90 to 96 mb/d (million barrels per day) and 3.7 to 4.6 mb/d, respectively. However, in 2018 the lubricants' demand increased by 4.7 and 98.7 mb/d in India and worldwide, respectively. At the end of the year 2024, the lubricant demand is expected to grow by 1.2 mb/d and 6.1 mb/d in India and worldwide, respectively. In the long term, global oil demand is expected to increase by ~12 mb/d, rising from 98.7 mb/d in 2018 to 110.6 mb/d in 2040 (OPEC–Report, 2019). The forecast growth of medium oil demand for the period 2018–2024 is summarized in **Table 1.2**.

1.4.2 Global and domestic market of greases

Table 1.3: Percentage share of different types of grease production based on the type of thickeners (Singh, 2020)

Type of thickener	World (%)	India (%)
Aluminum soap	0.29	2.31
Aluminum complex soap	3.95	0.13
Calcium hydrated soap	3.02	3.09
Calcium anhydrous soap	4.81	2.72
Calcium sulfonate soap	3.68	1.06
Calcium complex soap	0.80	0.11
Lithium soap	50.94	73.58
Lithium complex soap	21.31	9.44
Sodium soap	0.42	2.64
Other metallic soap	0.88	3.69
Polyurea	6.09	0.21
Organophilic clay	2.29	0.83
Other non–soap (except clay)	1.52	0.20

The major grease manufacturing companies in India are Balmer Lawrie & Corporation Ltd., Bharat Petroleum Corporation Ltd., Indian Oil Corporation Ltd., and Standard

Greases & Specialties. The total production of all types of greases at the global level is ~1174 TMT, with the India share of ~82 TMT in 2018 (Singh, 2020). The worldwide and India production of different types of greases based on variable thickeners are presented in **Table 1.3**. Conventional and complex lithium greases meet approximately 72% share of the total grease demand. **Table 1.4** exhibits the percentage excerpt of different kinds of base oils used to produce lubricating greases.

Table 1.4: Percentage excerpt of different kinds of base oils used for the production of lubricating greases (Singh, 2020)

Type of base oil	World (%)	India (%)
Mineral	88.97	97.53
Synthetic	5.77	1.79
Semi–synthetic	4.64	0.44
Bio–based	0.63	0.23

1.5 Nanomaterials

In the nanometer scale regime, the properties of materials are dramatically different from their bulk counterparts. The materials, with their size below 100 nm at least in one dimension, are referred to as *nanomaterials*. The surface–to–volume ratio and surface energy of nanomaterials are exceptionally higher in comparison to their bulk counterparts. The engineered nanomaterials are classified into seven categories according to their compositional features: metal oxides, sulfides, metal, carbon, and its derivatives, nanocomposites, rare earth compounds, and others (Dai et al., 2016).

The lubricants/greases with highly dispersible nanometer–size additives are known as *nanolubricants/nanogreases*. In recent years, nanomaterials have drawn significant interest as alternatives to conventional additives, and enormous nanomaterials have been explored as additives to lubricants and greases (Gulzar et al., 2016; Shariq and Charoo, 2019). The nanomaterials tend to agglomerate because of their high surface energy, resulting in poor dispersion stability in lube oils. Therefore, achieving the long–term dispersibility of nanoadditives in the lubricant is a great challenge. In this context, the surface modification of nanomaterials using surface–active molecules are gaining immense attention (Chouhan et al., 2018; Kumari et al., 2017). Nanocomposites comprise more than one type of material, and chemicals have shown a synergistic effect and extended the superior tribological performance than their constituent materials (Sun and Du, 2019; Verma et al., 2018). Therefore, in the recent past, nanocomposites are also gaining increasing attraction as lubricant additives.

1.6 2D lamellar materials

Two–dimensional (2D) nanostructured lamellar materials, viz. molybdenum disulfide (MoS_2), graphene, hexagonal boron nitrate (*h*–BN), tungsten disulfide (WS_2), carbon nanotubes (CNTs), are made of stacking of atomic/molecular lamella along the axis. The adjacent lamellae of each 2D material are connected with each other via weak van der Waals interaction (Xiao and Liu, 2017). The inherent properties of 2D nanomaterials make them advantageous materials compared to conventional spherical nanoparticles for lubrication applications via blending with lubricants. The weak van der Waals interactions between the adjacent lamellae ease the shearing due to interplanar slip and furnish low frictional properties. Moreover, the large surface area provides high coverage on the interacting tribo–surfaces and extends the antiwear properties. The ultralow thickness of 2D materials makes them easily enter the tribo–interfaces and effectively enhance the tribological properties. The real contact area decreases due to the entrapped 2D nanomaterials at the interacting tribo–surfaces (Ghaednia et al., 2016; Kashyap and Harsha, 2016).

MoS_2, a transition metal dichalcogenide, has a lamellar structure, in which each molybdenum atom is sandwiched between the two sulfur atoms in the trigonal prismatic geometry, as shown in **Figure 1.2**. The characteristic interlayer spacing between the molecular lamellae of MoS_2 is 0.62 nm. The molecular lamellae of MoS_2 are held together by the weak van der Waals interactions, which facilitate the shearing under the sliding stress and reduce the friction (Cizaire et al., 2002; Onodera et al., 2009). The mechanical properties of MoS_2 are summarized in **Table 1.5**. The strong covalent bonding between the atoms of each MoS_2 lamella provides remarkably high mechanical strength. The dangling sulfur atoms, particularly in the outer MoS_2 lamellae of each sheet, show good affinity with most metal surfaces and form the protective and lubricous thin film under the tribo–stress.

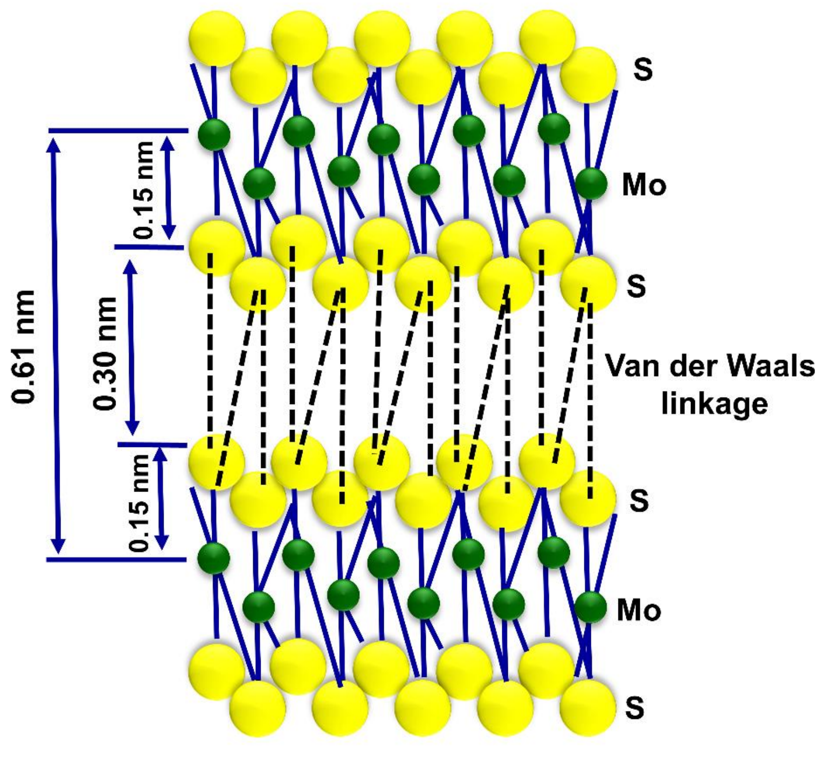

Figure 1.2: Structural model of MoS_2, representing the van der Waals interaction between (Chouhan et al., 2020a)

Table 1.5: Mechanical properties of 2D materials (Chouhan et al., 2020a)

2D Materials	Young's modulus (GPa)	Fracture strength (GPa)
MoS_2	246–282	16–30
Graphene	990–1060	130

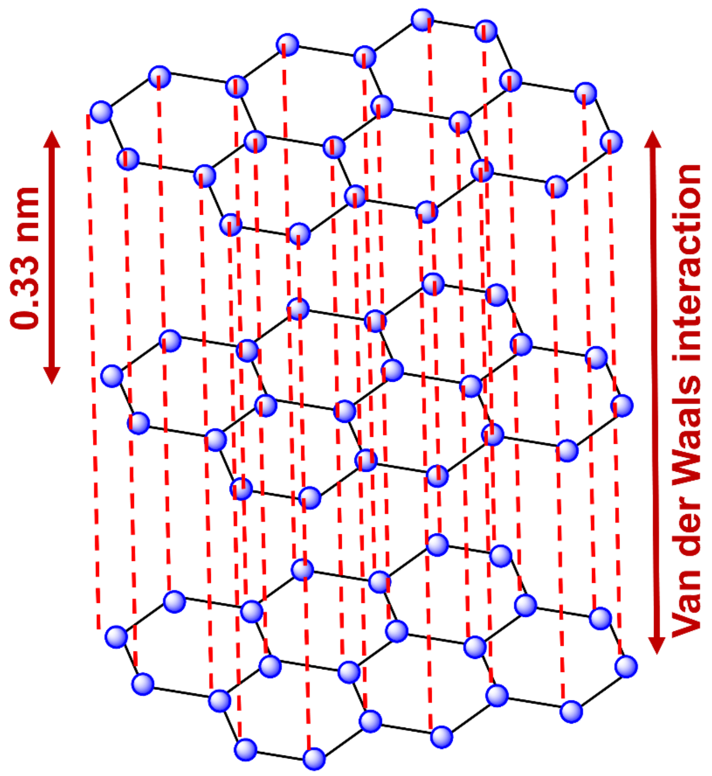

Figure 1.3: Structural model of graphene, representing the van der Waals interaction (Chouhan et al., 2020a)

Graphene is a 2D honeycomb lattice structure of sp^2–hybridized carbon and its structural model is shown in **Figure 1.3**. The characteristic interlayer spacing between the atomic lamellae of graphene is 0.33 nm. The mechanical properties of graphene are summarized in **Table 1.5**. The distinctive properties like remarkable thermal conductivity (5000 WmK^{-1}), good optical transparency, excellent mechanical strength, and large specific surface area (2630 m^2g^{-1}) make graphene a promising material for fundamental studies to several applications (Chouhan et al., 2020a). It has attracted enormous potential for numerous applications such as sensors, capacitors, fuel cells, batteries, adsorbents, catalysis, solar cells, filler to engineering composites, etc. (Choi and Lee, 2012; Georgakilas et al., 2016). The weak van der Waals interaction between adjacent laminates of graphene provides low resistance to shear and reduces friction.

1.7 Green tribology

Green tribology deals with the tribological aspects to maintain an ecological balance and environmental sustainability. The ultimate target of green tribology is to conserve energy resources and materials, minimize energy consumption, and reduce the causes of pollution and their adverse impact on the environment and ecosystem. The approaches of energy conservation, environment, and ecological sustainability by tribological interventions are referred to as *eco–tribology*. Green tribology is also an interdisciplinary approach encompassing various disciplines such as material science, green chemistry, green lubrication, green engineering, energy, and environmental science. The activities under the green tribology are broadly classified into the following three domains (Nosonovsky and Bhushan, 2012):

- Environment–friendly lubrication,
- Biomimetics for tribological applications, and
- Tribology of renewable energy application

The eco–tribology emphasizes to design the products and processes in such a manner that eliminate the generation of hazardous byproducts and maximize efficiency. In this context, the use of renewable and environmentally friendly products is an excellent approach towards the energy/environmental sustainability. The vegetable oils are renewable and eco–friendly. Therefore, vegetable oil–based lubricants are also referred to as *biolubricants*, *green lubricants*, or *eco–friendly lubricants*.

1.8 Need of green lubrication

The mineral oils are the preferred lube base stock in the formulation of lubricants/greases. Mineral oil–based lubricants/greases are non–renewable, and their biodegradability is very poor (Panchal et al., 2017). The disposal of drained out lubricants is a very challenging task, and their inappropriate disposal causes groundwater contamination, eco–toxicity, adverse impacts on aquatic and human lives. Non–sustainability, continuous depletion, and rising prices of petroleum products are important concerns associated with the use of crude oil–based lubricants. With the growing awareness about the environment, it is imperative to find an alternative base stock for lubricants development.

The non–toxicity, biodegradability, renewability, and eco–friendly nature of vegetable oils enfold immense attention to replace the conventional lube base stock. In the last few years, several tribological investigations have been made using various types of vegetable oils and demonstrated their potential for lubrication enhancement. The vegetable oils have out–performed the conventional lube oil and showed significant enhancement of tribological properties (Syahir et al., 2017; Zainal et al., 2018). The polar nature of vegetable oils confers a high affinity towards the metal surfaces, leading to superior lubrication performance (Mannekote and Kailas, 2009). Vegetable oils are also used to synthesize diesel, termed as *biodiesel*, a promising alternative to crude–based fuels. Biodiesel promotes reduced CO_2 emissions and global warming (Gerpen, 2005).

1.9 Summary of the chapter

This chapter presents an overview of tribology and conventional lubricants. Global issues related to crude oil are the finite source, continuous decline, rising prices, and environmental–related concerns. In this context, global efforts are made to minimize the dependence on crude oil products, which can add to the environmental values. Green tribology plays an important role, and its prime concerns are energy conservation and environmental sustainability. The suitable substitutes are required for conventional lubricants, which have at least equal or better lubrication performance and eco–friendliness. The vegetable oils have excellent lubrication properties and may substitute conventional lubricants by offering high renewability and biodegradability.