2 Literature survey

This chapter describes the fundamentals of greases and their composition. Large varieties of base oils and thickening agents are used in the formulation of lubricating grease. The blending of additives in the grease is a common practice to enhance physicochemical and tribological properties. In brief, the synthesis technique of grease is mentioned. This chapter also highlights the role of additives in the grease lubrication. Furthermore, this chapter discusses the review of previous studies reported on mineral oil–based, synthetic oil–based, and vegetable oil–based greases. The objective of the thesis work and methodology used in the thesis are included at the end of this chapter.

2.1 Introduction

Friction is a resistance, which opposes the relative motion of interacting surfaces. Many tribological situations desire low friction and wear, such as ball–bearing, gears, etc. High friction often leads to an adverse impact on the efficiency, wear rate, reliability, and life of the engineering components. It is a great challenge to minimize friction. Holmberg et al. have reported that, on average, a single–unit of truck consumes 1500 liters of diesel per year worldwide to overcome friction (Holmberg et al., 2014). Similarly, it has been reported that 15–25% of energy is consumed in paper mills to overcome friction (Holmberg et al., 2013). It indicates that a massive amount of energy is dissipated due to frictional losses. Therefore, the application of lubricants/greases is necessary to minimize the frictional energy losses between the tribo–pairs. The primary purpose of the lubricants is to minimize the friction and wear at the interacting surfaces of machinery. A large variety of lubricants are available in liquids, semi–solids, solids, or sometimes gases also used to lubricate the engineering surfaces. In a lubricated condition, the lubricant reduces the asperity interactions and reduces the adhesive forces between friction–pairs. Adequate lubrication reduces the overall friction in the system as well as minimizes heat generation. A reduction in frictional losses not only decreases the maintenance cost but also reduces the economic losses. The 10% reduction in rolling resistance in a passenger car can reduce 2% energy demand (Holmberg et al., 2012).

2.2 Advantages of greases over lubricants

Grease protects surfaces against wear and corrosion. The solid additives dispersed in the lubricating oil tend to settle down with time, while solid additives remain fully dispersed in the grease. Textiles, pharmaceuticals, and the food industry are required to maintain hygiene while developing the product. The use of lubricating oil in these industries causes splash or leak during operation, which is not desirable. This problem is well managed with the help of grease. The viscoelastic behavior of the lubricating grease imparts consistency that restricts leak out. Bearings lubricated with lubricating oils need a seal to prevent dirt, contaminations, and leakage. Grease acts as an inherent seal against dirt and foreign particles. Grease is more viscous, so it is more water–resistive as compared to lubricating oil. The viscosity of lubricating oil is affected by temperature, while grease has apparent viscosity, which has a comparatively lower effect of temperature. Along with these advantages, lubricating grease has some demerits as compared to lubricating oil. Grease has inferior thermal conductivity and high oxidative characteristics.

2.3 Grease composition

Grease is the Latin word that originated from *Crassus*, which means fat. Grease is semi–solid in physical appearance. Standard grease comprises 5–20% thickener, 80–90% lube oil, and 0–10% a package of additives. The lube base oil used in the grease formulation may be mineral, synthetic, or vegetable oil, while the thickening agent may be soap or non–

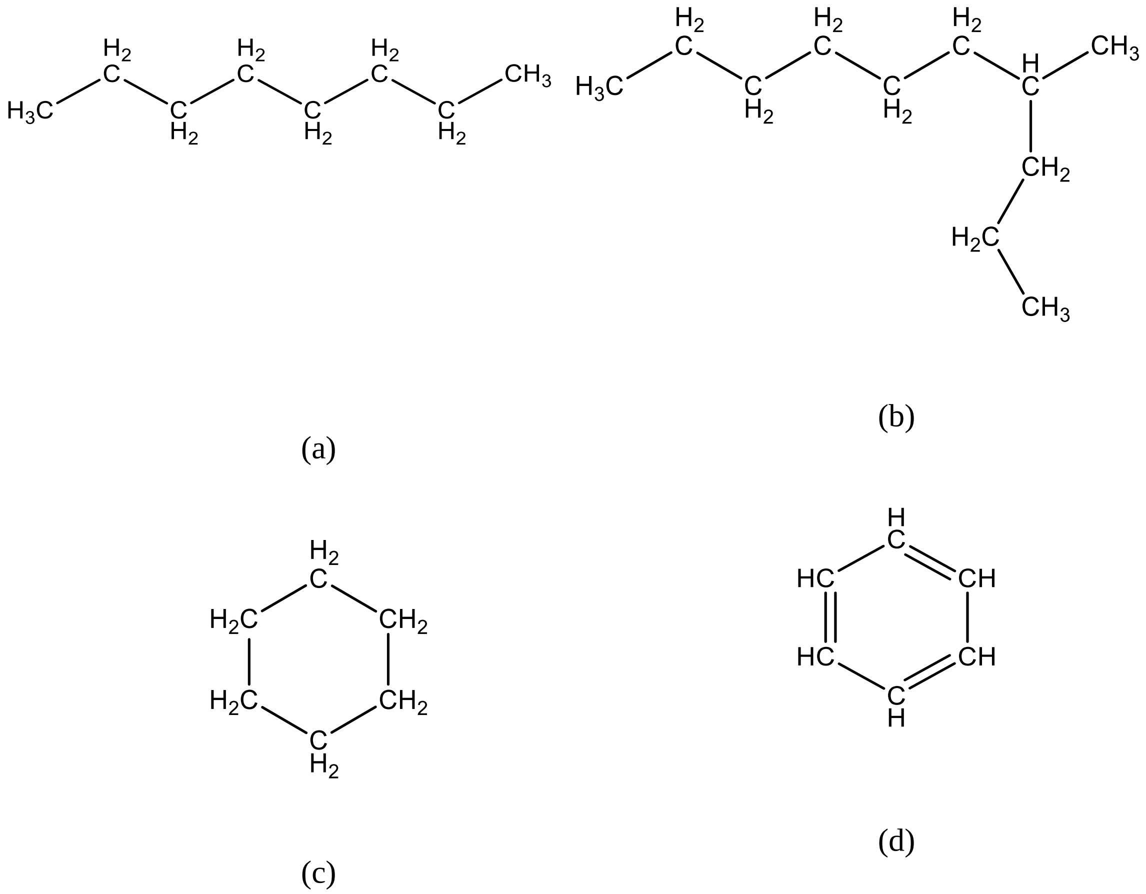
soap. It is a stable colloidal suspension in which lubricating oil is thickened through the dispersion of thickener. The fibrous network of the thickener forms the body structure of the grease. This network restrains the lubricating oil within the voids formed between the fibrous structures. The additives impart unique characteristics to the grease, which enhances the physicochemical and tribological performance of the grease. The fundamental requirement of the lubricating grease is to enhance the tribological properties and extend the and machinery lifetime. The lubrication performance and physical characteristics of the greases are dependent on the properties of the ingredients.

2.3.1 Lube base oil

The base oil is a hydrocarbon compounds extracted from biological and non–biological sources. The oil derived from the crude oil is under the non–biological oil category; if extracted from plant seeds, it falls into the biological group. The base oil is classified as mineral, synthetic, and vegetable oils. The physical properties such as viscosity, viscosity index (VI), oxidation stability, volatility, polarity, and solvency influence the tribological performance of lubricants/greases.

2.3.1.1 Mineral oil

Crude oil is a complex mixture of straight and branched paraffin, naphthenic, aromatic, alkenes, and heteroatom–constituted hydrocarbons. Mineral oil is obtained from crude oil through a fractional distillation process. They are preferred as a lube base stock to formulate a wide variety of lubricants and greases due to their low cost, abundant resources, and enormous viscosity grades. The mineral oils are made of paraffinic (branched and linear), naphthenic, and aromatic compounds, as shown in **Figure 2.1**.



(a) (b) (c) (d)

Figure 2.1: Structure of (a) straight chain paraffin (b) branched chain paraffin (c) naphthenic and (d) aromatic molecules, key constitutes of mineral lube base oils

Paraffin oil

The hydrocarbon chain contains a single covalent bond between each carbon (C) and hydrogen (H), also referred to as *saturated hydrocarbons*. The empirical formula of paraffinic hydrocarbon is C_nH_{2n+2}, where n represents the number of C atoms. They are also known as *paraffin*, comprised of linear (*n–paraffin*) or branched (*iso–paraffin*) chain hydrocarbons. The paraffinic hydrocarbons are extensively used components of mineral oil as a base stock for the formulation of lubricants/greases. These are non–polar and show higher viscosity, particularly the linear chain paraffin. The higher alkyl chain provides waxy form, associated with increasing the van der Waals interaction between straight chains of saturated hydrocarbons.

The alkenes are double bond/s–constituted hydrocarbon compounds and are known as *olefins*. The double bond between the carbon atoms is made of one sigma and one pi bonds. In this sigma bond is stable, whereas pi bond is reactive and also considered as unsaturated linkage. The empirical formula of alkenes is C_nH_{2n}. The olefinic–enriched lube base oil shows poor oxidation stability and higher pour point because of unsaturated hydrocarbon. Paraffinic oils are poor solvents than olefinic oils. If the number of branch–chain hydrocarbon contents increases in paraffinic oil, it decreases the viscosity of mineral oil.

If a hydrocarbon chain contains at least one triple bond, it is referred to as *alkynes*. The empirical formula of alkynes is C_nH_{2n-2}. The triple bond is made of two pi and one sigma bonds. Alkynes are highly unsaturated compared to alkenes.

Naphthenic oil

Naphthenic oils are made of cyclic rings of saturated hydrocarbons, and they mostly contain six and five–member rings. Therefore, they are also referred to as *cycloalkanes*. Naphthenic oil is free from wax and having high densities and low pour points compared to straight–chained hydrocarbons. Naphthenic oil has excellent solvency ability for grease thickeners. The metallic soap is less soluble in paraffinic oils than naphthenic oils. This merit of naphthenic oil makes the most favorable base stock for grease. Naphthenic oils have low–temperature flowability and low VI. At elevated temperatures, this oil demonstrates poor viscosity–temperature characteristics and oxidation stability. Paraffinic oil showed higher VI, pour point, and oxidation stability than naphthenic oil.

Aromatic oil

Aromatic oil is mainly made of six carbon atoms cyclic structures having alternate double and single bonds. These aromatic rings merge with each other and then make the polynuclear aromatic rings. This oil possesses excellent thermal stability, so it has widespread use in heat transfer fluids. Aromatic oils show high density and poor viscosity–temperature characteristics. Aromatic compounds are naturally free from wax; they have a low melting point and low–temperature fluidity. Aromatics also have high polarity. Therefore, it has a strong tendency to dissolve water. Aromatic compounds are excellent solvents; consequently, it is widely used in rubber compounding. In comparison with paraffinic and naphthenic oils, aromatic compounds have superior thermal stability.

Table 2.1: Basic physicochemical properties of different hydrocarbons–based mineral oils (Torbacke et al., 2014; Totten, 1992)

Property	Paraffinic	Naphthenic	Aromatic
Pour point	High	Low	Low
Oxidation stability	High	High	Low
Density	Low	Low	High
Viscosity index	High	Low	Low
Volatility	Low	Medium	High
Toxicity	Low	Low	Medium

The lube base oil properties depend on their molecular weight distribution and chemical structure (see **Table 2.1**). At high–temperature conditions, the volatility of base oil plays a crucial role, which affects the consumption of lubricants, particularly if the base oil having a low viscosity grade. The solvency (capability to dissolve additives) of the base oil depends on its chemical structure. A hydrocarbon with ring structures interacts better with additives in contrast to straight–chained hydrocarbon. The polarity defines the interaction ability of base oil with available surfaces and additives. Therefore, the polarity plays a vital role in forming the base oil adsorption layer over the lubricated surface. The viscosity of base oil is a function of hydrocarbon chain length. The viscosity of base oil increased with increasing of straight hydrocarbon chain length of paraffin. The viscosity of base oil is very sensitive to the operating temperature. The VI is a parameter that indicates the viscosity–temperature characteristics of base oil. The higher VI of the base oil suggests that the variation in viscosity at elevated temperatures is low.

2.3.1.2 Synthetic oil

Synthetic oils are synthesized from one or more base oil to acquire the desired properties. Generally, synthetic oils are made from petroleum base stock. The cost of synthetic lube is higher than mineral lube oils. Polyalphaolefines (PAO), polybutylene, polyisobutylene, polyalkylene glycols (PAG), polyphenyl ethers, perfluoropolyalkylether (PFPE), polyol esters, phthalate esters, synthetic polymeric esters, phosphate esters, synthetic hydrocarbon oils, silicones, polysiloxanes, etc. are common examples of synthetic lube base stock. Synthetic oils have higher VI, lower evaporation losses, high oxidation resistance, excellent low–temperature fluidity than mineral oils. Synthetic oils are not compatible with conventional thickeners, so fumed silica, polyurea, clay, Teflon are widely used as thickeners in synthetic oil–based greases. Synthetic greases are applied where mineral oil–based greases do not meet the desired service.

2.3.1.3 Vegetable oil

The seeds or kernels of the plants are crushed between the rollers to extract the vegetable oil. These oils are mainly of two types: non–edible and edible oils. The vegetable oils are comprised of triglycerides ester (also referred to as *natural oil*), primarily a glycerol molecule consisting of three long fatty acids chains through ester linkages (**Figure 2.2**). If the hydroxyl group of primary glycerol is replaced with one fatty acid, it is known as *monoglycerides*. Similarly, if any two–hydroxyl groups in glycerol are replaced by two units of fatty acids, it is called *diglycerides*. The triglycerides present as a major component

(98%) along with some minor components such as free fatty acids (0.1%), tocopherols (0.1%), sterols (0.3%), and diglycerol (0.5%) in vegetable oils (Zainal et al., 2018).

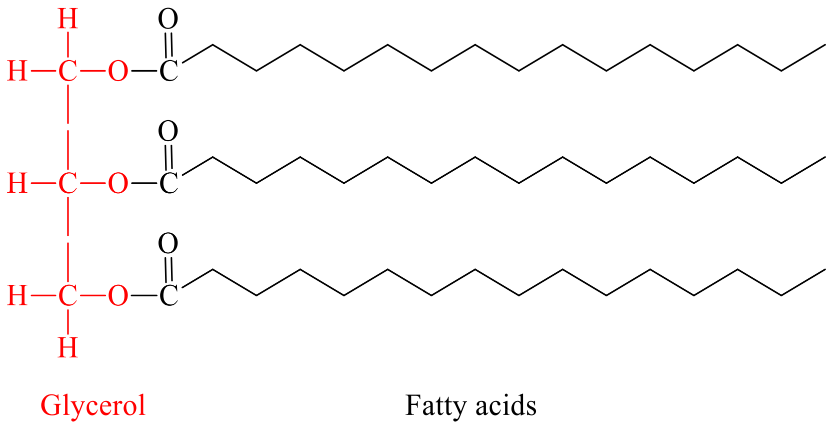


Figure 2.2: Schematic representation of triglyceride structure, a constituent of vegetable oil

The saturated fatty acids contain only single bond–based hydrocarbons (linear and branched), whereas unsaturated fatty acids contain double or triple bonded hydrocarbons. Based on the number of double/triple bonds in fatty acids, they are classified as monounsaturated (only one unsaturation site) and polyunsaturated (two or more unsaturation sites) fatty acids.

Vegetable oils are a mixture of saturated, monounsaturated, and polyunsaturated fatty acids. The composition of fatty acids in each vegetable is unique, and their physicochemical properties are governed by fatty acids. The oxidation stability of unsaturated fatty acids is low in contrast to saturated fatty acids. Nevertheless, saturated fatty acids have lower liquidity (higher melting point) than unsaturated fatty acids. For example, the pour point of coconut oil is ~21°C because it contains more than 90% saturated fatty acids (Jayadas and Nair, 2006), while castor oil demonstrates the pour point −10 °C because of the significant fraction of unsaturated fatty acids (Singh, 2011). The C–C single bonds are chemically stable than the C=C (double) and C≡C (triple) bonds. The pour point (liquidity at a lower temperature) improved with increasing unsaturation with increased in chemical reactivity. Therefore, unsaturated fatty acids are more chemically reactive in, consequence, exhibited poor oxidation stability. Vegetable oils have several advantages and few demerits over mineral oils. A comparative study on the physicochemical characteristics of vegetable oils and mineral oils are tabulated in **Table 2.2**.

Table 2.2: Comparison between physicochemical properties of mineral oil and vegetable oil (Rudnick, 2006)

Properties	Mineral oil	Vegetable oil
Biodegradability (%)	10–30	80–100
Cold flow behavior	Good	Poor
Density (@ 20^{o}C, kg/m^3)	840–920	890–970
Evaporation loss	Higher	Lower
Flash point, ^{o}C	Lower	Higher
Fire point, ^{o}C	Lower	Higher
Hydrolytic stability	Good	Poor
Load–bearing capacity	Low	High
Oxidation stability	good	Fair
Pour point, ^{o}C	–15	–22 to +12
Shear stability	More than vegetable oil	Minimum
Toxicity	Toxic	Non–toxic
Viscosity index	100	100–200
Volatility	High	Low

2.3.2 Thickener

The thickener is also termed as *soap*, a reaction product of fatty acid and a strong base (alkali). Water is obtained as a by–product in the neutralization process of fatty acid and base.

$$\text{FATTY ACID + BASE} \longrightarrow \text{SOAP + WATER}$$

For example–

$$CH_3\text{-}(CH_2)_5\text{-}CHOH\text{-}(CH_2)_{10}\text{-}COOH + LiOH \rightarrow CH_3\text{-}(CH_2)_5\text{-}CHOH\text{-}(CH_2)_{10}\text{-}COOLi + H_2O$$

12–hydroxy stearic acid	lithium hydroxide	lithium 12–hydroxy stearate	water

Lithium soap

$$CH_3\text{-}(CH_2)_5\text{-}CHOH\text{-}(CH_2)_{10}\text{-}COOH + Ca(OH)_2 \rightarrow [CH_3\text{-}(CH_2)_5\text{-}CHOH\text{-}(CH_2)_{10}\text{-}COO)]_2Ca + H_2O$$

12–hydroxy stearic acid	calcium hydroxide	calcium 12–hydroxy stearate	water

Calcium soap

$$CH_3\text{-}(CH_2)_{16}\text{-}COOH + Al(OH)_3 \longrightarrow [CH_3\text{-}(CH_2)_{16}\text{-}COO)]_3Al + H_2O$$

stearic acid	aluminum hydroxide	aluminum tristearate	water

Aluminum soap

The product of the neutralization process is soap, and it is mixed with a base oil to obtain the grease. The thickener imparts a unique property to the lubricating oil. The lubricating oil is reinforced by the thickening agent, which formed a three–dimensional network. The soap matrix behaves as a reservoir of the lubricating oil, releases the lubricating oil at the contact of friction surfaces. An enormous variety of thickeners are used for grease formulation. **Figure 2.3** shows the classification of thickeners. Thickeners are broadly classified into two categories (a) soap and (b) non–soap.

2.3.2.1 Soap thickener

Salt is a chemically neutralized product of an acid and base, and water is obtained as a by–product. When fatty acids are neutralized with alkali, the developed product is referred to as *soap*. Soaps are further divided into four groups: alkaline–earth metal (barium and calcium), alkali metal (lithium and sodium), heavy metals (zinc and lead), and aluminum–based soaps. Further, each group of soap is categorized into subgroups of straight and complex. The complexing agents are organic or inorganic materials and are added to the conventional metallic soap to develop complex grease. Metallic acetate, chloride, benzoate, and carbonate are typical examples of complexing agents. The primary purpose of adding a complexing agent in the grease is to enhance the dropping point. The dropping point of the complexing agent thickened the grease by 50–100 ^{o}C higher than the conventional soap thickened grease (Mang and Dresel, 2007). Conventional and complex lithium soap–based greases are preferred, and they meet ~70% of worldwide demand (Honary and Richter, 2011).

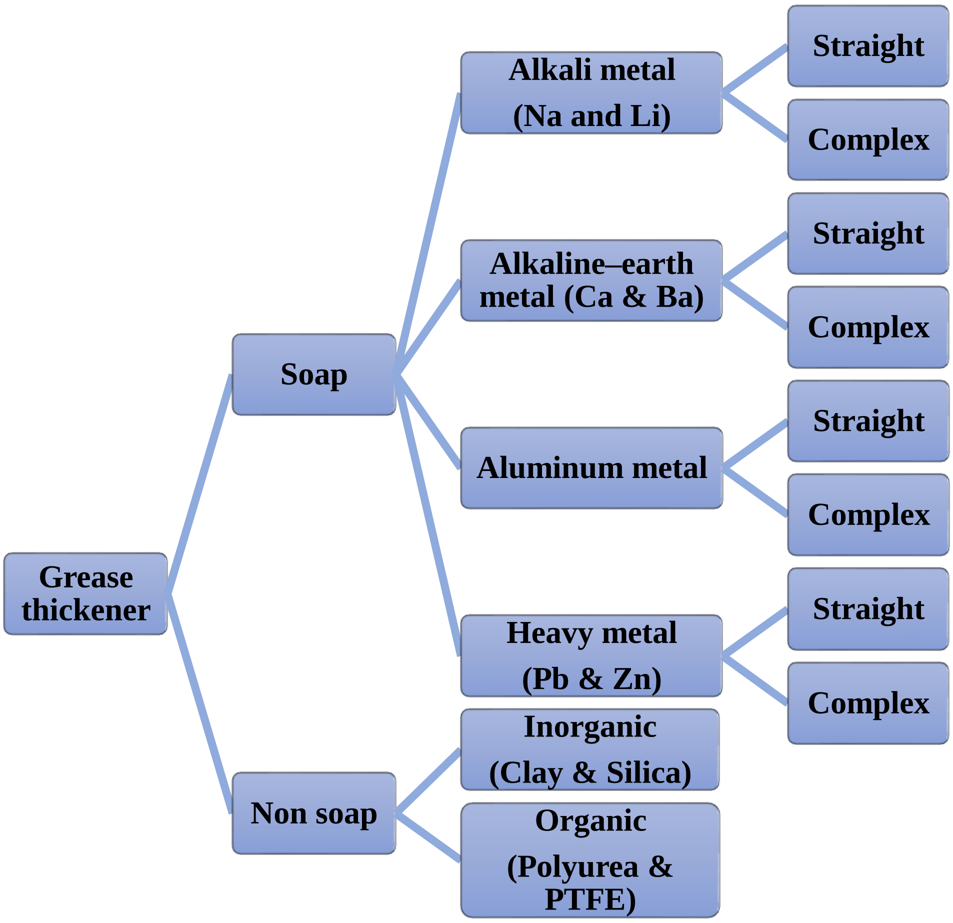


Figure 2.3: Classification of thickeners

Shorter and longer hydrocarbon chain lengths degrade the thickening capacity. The 12–hydroxystearic acid (having 18 carbon atoms) derived from vegetable oils show the maximum thickening effect (Mang and Dresel, 2007). The solubility of thickener in the lube base oil increases with increasing the carbon chain length, and solubility of thickener in the lube base oil decreases with decreasing the carbon chain length. The molecular weight of the base oil is a significant factor that affects the solubility of thickener. Unsaturated carboxylic acid is more soluble in mineral oils, lowers the drop point, and decreases thickening capacity. Their applications are limited due to poor oxidation stability (Mang and Dresel, 2007). The presence of a branched alkyl chain reduces the thickening capacity and melting point of the thickener. On the other hand, hydroxyl groups having a higher polarity increases the thickening capacity and melting point of the thickener (Lugt, 2013).

2.3.2.2 Non–soap thickener

Non–soap greases are organic or inorganic materials. Polyurea and polytetrafluoroethylene (PTFE) are typical examples of organic non–soaps, having spherical or plate–like fine particles. Inorganic non–soaps are very fine particles having enough surface area and porosity to absorb oil; clay and silica are typical examples of inorganic non–soap. These non–soaps do not show any phase change or melting point at elevated temperatures. Therefore, these greases are preferred for high–temperature applications.

2.3.2.3 Mixed thickener

If grease contains more than one soap cations, it is referred to as *mixed–soap–grease*. Lithium–calcium (LiCa), calcium aluminum (CaAl), and calcium–sodium (CaNa), etc., are typical examples of mixed greases. The terminology of mixed grease comprises cations of both soaps whose portion is higher in the mixture is designated first, and whose portion is lower, designated at last (Ishchuk, 2005). For example– in lithium–calcium mixed grease, it indicates that the portion of lithium cations is higher than calcium cations in the mixture, so lithium comes first in the nomenclature and calcium at last. The properties of mixed greases are distinct from their parent grease. Lithium–calcium grease demonstrates better shear stability and water resistance in comparison to raw lithium grease. The 20% w/w concentration of calcium soap in lithium soap increases the dropping point and improves the antifriction (AF) and antiwear (AW) performance of mixed grease as compared to raw lithium grease (Mang and Dresel, 2007). Similarly, a minor proportion of clay thickener mixed with aluminum complex grease results in improved mechanical properties, and heat resistance characteristics achieved are better than the pure aluminum complex grease (Polishuk, 1971).

2.3.3 Additives

Chemicals, solid particles, and fillers are added to the lubricants/greases for enhancing their physicochemical, and lubrication properties are referred to as *additives*. The drain time of lubricants/greases is very important for their applications. Various factors, such as severe loading conditions, high temperature, high speed, environmental conditions, mechanical and thermal stresses, affect the life and drain time of grease. Therefore, the grease does not achieve the performance measures for which they are designed. As the grease ages, it becomes dry and brittle, so it does not exhibit lubrication performance satisfactorily. To extend the useful life and improve the lubrication performance of grease, a lot of additives and fillers are used.

The typical greases usually contain 0–10% additives, depending on their applications. Commercial greases contain a package of additives such as extreme pressure (EP) agents, oxidation inhibitors, friction modifiers (FM), AW agents, corrosion inhibitors, and tackiness. Conventional organic additives such as trixylyl phosphate (TXP) and zinc dialkyl dithiophosphate (ZDDP) are the commonly used AW/EP additives. They comprised active elements such as chlorine (Cl), sulfur (S), and phosphorus (P), and the polarity associated with these heteroatoms facilitates the strong adsorption on friction surfaces. The environmental threat arises from the use of P and S elements in additives (Boshui et al., 2015). The nonvolatility of inorganic nanomaterials is better than organic nanomaterials that make them favorable to endure for high–temperature applications.

The prime objective of additives is to enhance the physicochemical and tribological properties of the greases. The additives utilized in the lubricants (liquid) are almost the same for grease applications. The addition of additives in the grease modifies its tribological and rheological performance. Some additives destroy or alter the fibrous microstructure of the grease (Adhvaryu et al., 2005; Singh et al., 2017), which directly affects the lubrication performance. If grease is used in severe conditions, then grease is enriched with an enhanced package of additives. The examples of widely used additives are mentioned in **Table 2.3**.

Table 2.3: Common examples of various kinds of additives used in the greases (Ishchuk, 2005; Lugt, 2013; Rudnick, 2017)

Additives	Examples
Antifriction and antiwear	ZDDP, metal oxides, carbon–based materials, nanomaterials
Corrosion inhibitors	Metal sulfonates (sodium, barium, calcium, ammonium); metal naphthenates (zinc, lead, bismuth); metal carboxylates (zinc, calcium); alkenyl succinic acid esters; sarcosine derivatives; imidazoline; amides; phosphate esters etc.
Extreme pressure	Phosphate and thiophosphate esters; sulfurized fats, olefins, and esters; sulfides and disulfide; metal dialkyl dithiophosphate (zinc, antimony); graphite
Oxidation inhibitors	Hindered phenols; metal dialkyldithiophosphates; aromatic amines; metal dialkyldithiocarbamates; zinc dialkyl–dithiophosphates; diaryldisulfides; etc.
Tackiness	latex compounds; ethylene–propylene olefin copolymer (OCP); polyisobutylene; copolymer; polybutene; etc

Corrosion inhibitors are incorporated to prohibit the electrochemical oxidation of the metallic surface and their dissolution. They are classified as anodic and cathodic inhibitors. Anodic inhibitors retard the anodic reaction of metals and their dissolution, while cathodic inhibitors prevent cathodic reactions, decreasing the formation of oxygen or hydrogen ions. Oxidation inhibitors are used in grease to minimize the reaction rate of hydrocarbons with oxygen and prevent the formation of hydroxides and peroxides. AF/AW additives are used to minimize the scuffing and wear of mating surfaces, and EP additives are added to enhance the load–bearing capacity of the grease under severe loading conditions. The grease is doped with tackiness additives to improve cohesive and adhesion properties, increase the water wash–off resistance, and throw–off resistance from bearings. Tackiness additives also provide extra cushioning and reduce noise.

2.4 Role of additives

The effectiveness of nanomaterials in augmenting the tribological performance of lubricants depends on various attributes such as their size, crystal structure, concentration, morphology, composition, and compatibility with lube base stocks (Dai et al., 2016). Nanomaterials show versatile potentials to serves as FM, AW, and EP additives (Gupta and Harsha, 2017; Kumar and Harsha, 2020). The optimum concentration and size of nanomaterials furnished excellent tribological performance and beyond which tribological performance starts to deteriorate (Azman et al., 2016; Battez et al., 2008). The friction and wear preventive characteristics of greases depend on ambient and working conditions such as temperature, applied load, velocity, and surface roughness of interacting surfaces. The lubrication mechanism of greases doped with nanoadditives is crucial for understanding their active roles in improving tribological performance. Four types of lubrication mechanisms are proposed to understand the role of nanoadditives, i.e., (a) mending effect,

(b) rolling mechanism, (c) protective film, and (d) polishing mechanism. Different lubrication mechanisms of greases are schematically illustrated in **Figure 2.4.**

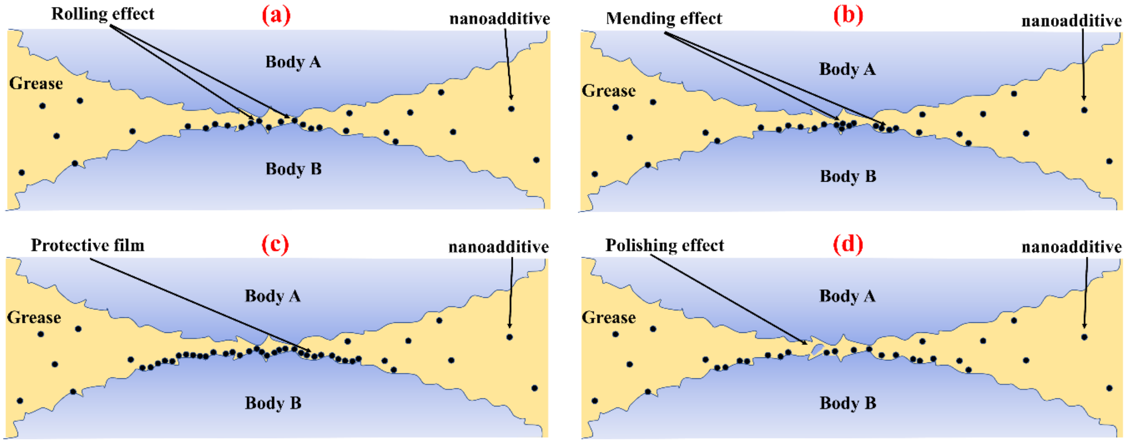


Figure 2.4: Schematic demonstration on the role of nanoadditives in grease lubrication (a) rolling effect (b) mending effect (c) protective film (d) polishing effect

Rolling mechanism, in this mechanism, the quasi–spherical and spherical nanomaterials would roll between the tribo–surfaces and impersonate as nano–bearing. It is believed that this nano–bearings transform the sliding friction into rolling friction or partially rolling friction, which leads to minimize friction and wear. This phenomenon is also called the *ball–bearing effect*. The type of loading and hardness of tribo–pair, shape, and mechanical strength of nanomaterials are the other factors determining the rolling mechanism. At stable low–load conditions, the shape, and rigidity of nanomaterials are maintained between the shearing surfaces, resulting in rolling friction. This rolling mechanism has been reported by several researchers (Asrul et al., 2013; Kashyap and Harsha, 2016).

Mending effect is a surface repairing technique by the deposition of nanomaterial in the grooves and scars of the tribo–surfaces. The deposition of nanomaterials reduces the abrasion phenomenon, results in compensating the material loss at the interacting surfaces. The nano dimension of materials furnishes the ability to patch the scars and grooves developed on the worn surfaces. Therefore, it is also referred to as a *self–repairing effect*.

A majority of investigations have affirmed the deposition of nanomaterials on the worn scars through energy–dispersive X–ray spectroscopy (Gupta and Harsha, 2017; Talib et al., 2017).

Protective film of nanomaterials is formed on the friction surfaces by the physisorption and chemisorption interactions. This protective film is also termed as *tribo–film*. The hardness and chemical reactivity of nanomaterials play a vital role in forming the tribo–film (Shafi and Charoo, 2021). The tribo–film minimizes the direct interactions of asperities, consequences excellent protection of interacting surfaces against friction and wear. The X–ray photoelectron spectroscopy and Raman spectroscopy are very informative analytical tools to verify the formation of tribo–film (Boshui et al., 2015; Gulzar et al., 2015).

Polishing mechanism is another surface improvement technique. In this phenomenon, the nanomaterials behave as three–body abrasive, resulting in reducing surface roughness. The reduction in surface roughness is ascribed to the polishing of surfaces, and it is also termed as a *smoothing effect* or *artificial smoothing*. This smoothing effect improves the tribological performance (Sajeeb and Rajendrakumar, 2020). The surface topography characterization techniques, i.e., atomic force microscopy (AFM), are beneficial to observe the effect of nanomaterials on the roughness of tribo–pairs (Rastogi et al., 2013; Thottackkad et al., 2012).

2.5 Basic process for grease formulation

The nature of the thickener primarily governs the grease formulation procedure. The various grease synthesis procedures were reported, showing a great diversity (Adhvaryu et al., 2005; Chen, 2010; Delgado et al., 2005; Ge et al., 2016; Sahoo and Biswas, 2014; L. Wang et al., 2008). Typically, the preformed soap is commercially available in the form of powder or flakes. The conventional grease synthesis procedure is the dispersion of a stoichiometric amount of preformed soap in the base stock at high temperature under defined conditions, including the continuous blending/stirring. The consistency of grease is controlled with the addition of the remainder of base oil. The blending of additives enhances the physicochemical properties. In the final phase, the grease is subjected to mechanical working to homogenize the composition. This technique is preferred only to synthesize synthetic grease due to the higher cost of preformed soap (Mang and Dresel, 2007).

The soap–based grease is formulated through the in–situ scheme; a stoichiometric amount of fatty acid and alkali is added to the base oil. The dispersion mixture is heated and continuously stirred under defined conditions. In this way, the soap is formed in–situ through the saponification reaction between fatty acid and alkali. It is necessary to evaporate the water produced during the reaction and allow the soap to be crystallized. Further, the remaining base oil is added to control the consistency and followed by the blending of additives. In the final step, the grease is milled thoroughly to obtain a homogenous finished product. Sometimes, several mixing cycles are required to achieve the desired properties of the grease.

Soap–based greases had some limitations when it was exposed to extremely hot or cold temperatures. Non–soap–based greases have an excellent lubrication performance at extreme hot and cold temperatures than conventional soap–based greases. Usually, the non–soap–based thickener is mixed with base oil at room temperature to form a thickened product like conventional greases. However, some non–soap greases (viz. polyurea and polyurea–complex) require heat and chemical reactions similar to soap–based greases. These chemical reactions are not like a saponification reaction of fatty acid and alkali. Here, amines and isocyanates react with each other to form urea. The oxidative stability of polyurea grease is exceptionally high because of the absence of acids and metals. In the synthesis of organoclay–based greases, organoclay thickener and acetone (activator) are mixed with lube base oil under the shear milling process. After completion of the process, the acetone can be evaporated. Typically, organoclay greases do not have a dropping point, so these greases are widely used at high–temperature conditions, such as in bakery ovens.

Overall, in the grease synthesis process, one of the most significant concerns is the blending of additives. Generally, soap–based greases are heated at high temperatures depending on the type of thickeners. Some additives are highly sensitive to heat and become ineffective at such high temperatures. Therefore, in conventional, the blending of additives is preferred when the greases cool down in less than 85 ^{o}C. If additives are highly resistive against temperature or remain unaffected at high temperatures, they can be blended at any time of grease formulation.

It is mandatory to control all process variables to produce perfect–finished grease containing the desired physicochemical and tribological properties. An imperfect saponification reaction increases the acidity or alkalinity of the grease, which reduces the thickening effect of the soap and shows an adverse effect on various performance characteristics. If the concentration of thickener is significantly increased, which leads to an increase in the apparent viscosity, consistency, shear stability, and lowers the oil separation from the grease under pressure.

2.6 Grease structure

The soap–based greases have a fibrous structure (**Figure 2.5)**. The interlocking between the fibers of the thickener occurs through weak van der Walls forces, ionic, dipole–dipole, or hydrogen interactions (Lugt, 2009). The interaction of fibers with each other governs the effectiveness of the forces, as mentioned earlier. These interlocking of fibers form voids in the order of 10^{-6} m (Stachowiak and Batchelor, 2013). The base oil is trapped within these voids created by the fibrous network of the grease. In other words, the grease fibrous network impersonates as a reservoir of base oil. The base oil interacts with the fibers with a combined effect of capillary and van der Walls forces (Lugt, 2009). The length of thickener fibers varies in the range between 1–100 microns, and the length to diameter ratio varies from about 10–100 (Lugt, 2009). Salomonsson et al. (2008) et al. have found that the average length and diameter of fibers of lithium grease were 1μm and 30 nm, respectively. The length of soap fibers is a crucial factor that affects the lubrication performance of the grease (Yamamoto and Gondo, 2002). Non–soap–based greases are not fibrous structures. Therefore, to obtain the same level of consistency, non–soap–based greases require a higher concentration of thickener than soap–based greases (Lansdown, 2004). The thermal aging of grease affects the structure of the fibers. Couronne et al. have observed that thermal aging showed an adverse effect on the fibrous structure of lithium and lithium complex greases while a prolific effect with di–urea and tetra–urea greases (Couronne and Vergne, 2000).

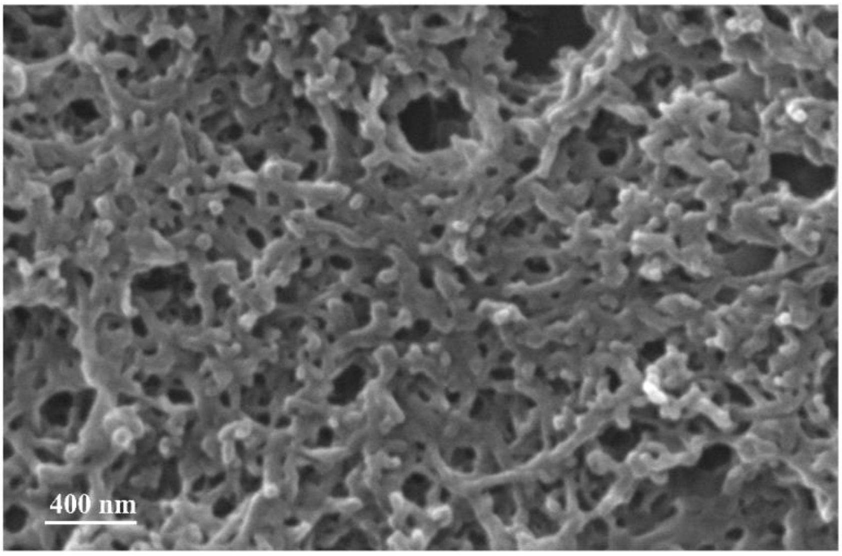


Figure 2.5: The scanning electron microscope image of 12–lithium hydroxy stearate soap network after extraction of lube base oil

2.7 Bio–greases

Typically, greases are manufactured by mineral oil, synthetic esters, and vegetable oil, and their global demand share is 90%, 9%, and 1%, respectively (Panchal et al., 2015). Environmental concern and rapid depletion of crude oil have prompted researchers to find a substitute for conventional lube base stock. The physicochemical properties of vegetable oil are already described in the previous '**Section 2.3.1.3**,' and they can be suitable candidates to substitute conventional petroleum–based oils. It is believed that bio–based grease can reduce environmental pollution due to its excellent biodegradability. The degree of biodegradability of grease is based on its ingredients. The biodegradability of different oils mineral oils, vegetable oils, and synthetic esters–based lubricants are varied in the range of 20–40%, 90–98%, and 65–100%, respectively (Florea et al., 2003).

The fatty acids of vegetable oil in the grease increase their affinity with water and deteriorate the flowing tendency at cold temperatures. The drawbacks of vegetable oils (viz. pour point and oxidation stability) have been rectified with various chemical treatments. The chemically modified vegetable oils are believed to be the most promising alternatives for mineral based oils in the development of conventional lubricating grease. It means that soap–based grease with vegetable oils can also be formulated as described in **'Section 2.4'**. Honary and Richter (2011) reported that soybean oil–based greases were commercialized in the United Nations to lubricate rail curves and flanges of locomotive wheels. Further, bio–based greases have applications in the greasing of the truck fifth wheel.

In general, the presence of unsaturation in vegetable oils made it significantly prone to oxidation. Oxidation degradation is not a significant concern if base oil is entrapped within the fibrous mesh of the thickener as long as possible. When base oil is discharged from the fibrous network of the thickener under pressure or due to degradation of the fibrous structure, oxidation degradation of base oil becomes more predominant. In this context, some investigations on soybean oil–based greases were carried out to comprehend the effect of chain length and composition on the thermo–oxidative behavior of the grease (Adhvaryu et al., 2004; Sharma et al., 2006, 2005). Suitable antioxidants in optimum concentration can provide excellent oxidation stability to the soybean oil–based grease (Sharma et al., 2005). Besides, a high soap–to–oil ratio (range 1:2 to 1:4) has improved the lubricity and oxidation stability of the grease. Adhvaryu et al. have inferred from their study that the chain length of fatty acids in lithium soap does not significantly affect the oxidation and thermal stabilities of the grease (Adhvaryu et al., 2004).

2.8 Review on tribological studies of greases

The tribological studies of lubricating greases are essential to understand the exact lubrication mechanism and performance of the greases. Tribometers assess the load–bearing capacity and capability of the greases to minimize friction and wear. Various tribometers such as four–ball tester, pin–on–disc, FZG gear tester, SRV tribometer, ball–on–disc, etc., are available to evaluate the tribological performance of the greases. The tribological performance of the grease was assessed with different types of base oils, its viscosity, type of thickener and its concentration, and the package of additives. Several research articles are available on the tribological performance of conventional greases. In the present study, the literature review of the tribo–performance of greases is classified into three categories:

- Review based on mineral oil–based greases,
- Review based on synthetic oil–based greases, and
- Review based on vegetable oil–based greases.

2.8.1 Review based on mineral oil–based greases

The tribological performance of the lubricating grease is entirely reliant on the properties of the ingredient involved in their composition. In recent years, solid nanomaterials with variable morphologies, chemical structure, mechanical strength, and inherent lubricious nature have gained increasing attention as grease additives. The carbon nanomaterials, metal oxide, sulfides, metals, rare earth compounds, transition metal dichalcogenides, nanocomposites, and so on, have been explored as additives with different lubricants (Dai et al., 2016). These nanoadditives in grease enhance the tribological performance and affect the microstructural features of grease (Adhvaryu et al., 2005). Several studies have been carried out to find the optimum concentration of nanomaterials in greases for the best tribo–performance. The lower and higher concentration to optimum dose may lead to detrimental events and compromised the tribo–performance (Azman et al., 2016).

Recently, numerous investigations have been carried out to exhibit the tribo–performance of distinct types of greases using nanostructured lamellar materials as friction and wear modifiers. Singh et al. (2016) have investigated 0.4 wt% of reduced graphene oxide (rGO) in commercial lithium grease and shown a decrease in friction by 30% in rolling and 20% in sliding–induced rolling contact. The tribo–performance of rGO was further compared with $CaCO_3$ and α–Al_2O_3 nanoparticles as additives to lithium grease and found that the rGO outperformed among all types of greases and reduced the friction by 35% (Singh et al., 2017). Fan et al. (2014) have demonstrated significant improvement in tribological properties by dispersing the graphene into the bentone grease. The tribo–performance of nanostructured graphene–blended grease was found superior to that of graphite particles–blended grease. The graphene oxide (GO), an oxidized form of graphene, as an additive to commercial lithium grease has reduced wear and friction by 50 and 60%, respectively, compared to graphite–based grease (Cheng and Qin, 2014). The GO and graphene sheets blended in the grease were adsorbed on the rubbing surfaces under the tribo–stress and formed a protective coating, which enhanced the tribo–performance by decreasing wear and friction. The graphene–doped (3 wt%) calcium grease has decreased the friction and wear scar diameter (WSD) by 61% and 45%, respectively, whereas and improved the EP property 60% compared to bare calcium grease. As confirmed by an electron microscope, graphene–based thin–film formation protected the contact interfaces against the material loss and reduced the friction (Kamel et al., 2017a). The graphene dispersed in the grease plays a crucial role in governing the rheological properties. Kamel et al., 2017b revealed that increasing the dosage of graphene gradually increased the viscosity of calcium greases and showed the non–Newtonian behavior, supported by a linear correlation between the shear rate and the shear stress.

The MoS_2 containing lithium grease has remarkably improved the AW and EP properties by forming a lubricating film. A 3% of MoS_2 could improve the EP property of lithium grease from 100 to 220 kg load (Gänsheimer and Holinski, 1972). The tribo–performance of MoS_2 nanoparticles encapsulated in lithium stearate soap is strongly influenced by the load, temperature, and concentration. The soap particles liquified at a higher temperature and contact pressure, consequently the encapsulated MoS_2 nanoparticles are released on the worn track and established a thin film on tribo–interfaces under the sheared contact and reduced the friction (Sahoo and Biswas, 2014). The nanoparticles entrapped in the grease matrix easily migrated into the contact zone for their effective tribo–performance. **Table 2.4** summarizes the tribological performance of nanoadditives blended mineral oil–based greases.

Table 2.4: Tribological performance of mineral oil–based greases with numerous nanoadditives

Reference	Base oil	Thickener	Nanoparticles	Shape	Size	Optimum concentration	Coefficient of friction (μ)	Wear scar diameter (WSD)/ Mean wear volume (MWV)/ Wear rate (WR)	Extreme pressure (EP)
Gänsheimer and Holinski, 1972	mineral oil	lithium soap	MoS$_2$	lamellar	t = 5–10 μm	3.0% w/w	—	—	EP↑ 100kg to 220kg
Kobayashi et al., 2005	mineral oil	lithium soap	carbon nanohorn (CNH) heat–treated carbon nanohorn (HT–CNH) graphite	horn–shaped tip horn–shaped rounded tip flake	d < 80–100 nm d > 80–100 nm d = 600 nm (average)	less than 1 mass% less than 1 mass% 3 or more mass%	μ↓ μ↓ μ↓	WSD↓ WSD↓ WSD↓	— — —
Wang et al., 2007	commercial lithium grease		CaF$_2$	cubic	l = 60–65 nm	1.0% w/w	μ↓ 29%	WSD↓19%	EP↑ 48%
Wang et al., 2008	paraffin oil	lithium soap	OA–CeF$_3$	hexagonal	d = 20 nm	2.0% w/w	μ↓	WSD↓	EP↑

Chen, 2010	mixture of neopentyl polyol ester, soy bean oil and commercial 650SN (4.5:2.5:1)	titanium complex soap	PTFE	—	—	2.0 wt%	μ↓34.58%	WSD↓ 4.95%	—
			$\mathrm{TiO_2}$	—	—	0.5 wt%	μ↓22.97%	WSD↓ 4.35%	—
			$\mathrm{SiO_2}$	—	—	1.5 wt%	μ↓24.47%	WSD↓ 1.80%	—
Yang et al., 2011	commercial greases (Daphne Alphagel ET) (Daphne Eponecks SR) Alvania grease S2)		CNTs	tubular	d = 150 nm, l = 10–20 μm	0.3 wt%	μ↓	WSD↓	—
Zhao et al., 2013	mineral oil	lithium soap	calcium borate	spherical	d = 70 nm	6.0 wt%	μ↓	WSW↓	EP↑
Sahoo and Biswas, 2014	mineral oil	lithium soap	$\mathrm{MoS_2}$	lamellar	l ~350 nm	0.2 wt%	μ↓	—	—
Chang et al., 2014	commercial lithium grease (LB80102)		$\mathrm{TiO_2}$	spherical	d = 40–60 nm	1.0 wt%	μ↓40%	WSD↓	—
			CuO	spherical	d = 90–110 nm	2.0wt%	μ↓	WSD↓60%	—
Cheng and Qin, 2014	commercial lithium grease		graphene oxide	flake	d = 185 to 210 nm	0.075% w/w	μ↓ 40–60%	WSD↓ 50%	—
Ge et al., 2015	naphthenic oil	PTFE	$\mathrm{TiO_2}$	spherical	d = 35 nm	0.1 wt%	μ↓	WSD↓	—
			$\mathrm{SiO_2}$	spherical	d = 30 nm	0.1wt%	μ↓	WSD↓	—

Peña–Parás et al. 2015	commercial grease (Mobilgrease 28 and Uniflor 8623B)		TiO_2 Al_2O_3 CuO MWNTs	spherical spherical tubular tubular	d < 21 nm d < 50 nm d < 50 nm d = 6–9 nm, l = 5 μm	0.1 wt% 0.1 wt% 0.1 wt% 0.01 wt%	μ↓30% μ↓7.5% μ↓36% μ↓16%	WSD↓20% WSD↑11% WSD↓14% WSD↓4%	— — — —
Mohamed et al., 2015	commercial lithium grease		CNTs	tubular	d = 10 nm, l = 5 μm	1.0 wt%	μ↓81.5%	WSD↓63%	EP↑52%
Chang et al., 2015	commercial lithium grease		Sn1 Sn2 Sn3	spherical	d = 60 nm d = 80 nm d = 120 nm	1.0 wt%	μ↓63.5%	WSD↓ 58.9%	—
Akhtar et al., 2016	commercial lithium grease		rice husk ash	flake	—	0.5 wt%	μ↓	WSD↓	EP↑
Shen et al., 2016	mixed oil (350SN and 650 SN) (1:1 weight ratio)	titanium complex soap	CeO_2	spherical	d = 10 nm	3.0 wt%	μ↓	WSD↓	EP↑
Kamel et al., 2016	commercial calcium grease (MERKAN 23)		MWCNTs	tubular	d = 10–12 nm, l = 1–20 μm	3.0 wt%	μ↓50%	WSD↓32%	EP↑38%
Singh et al., 2016	commercial lithium grease		rGO	lamellar	—	0.4 wt%	μ↓30%	—	—
Qiang et al., 2017	commercial lithium grease		Cu	spherical	d = 10 nm	0.25 wt%	μ↓	WSD↓	—
Jing et al., 2017	commercial oil (MVI500)	lithium soap	graphene	lamellar	—	0.5 wt%	μ↓18.9%	WSD↓ 10.4%	—

Kamel et al., 2017a	commercial calcium grease (MERKAN 23)	graphene	lamellar	t = 1.3 nm, l = 2 μm	3.0 wt%	μ↓61%	WSD↓45%	EP↑60%
Singh et al., 2017	commercial lithium grease	rGO $CaCO_3$ Al_2O_3	lamellar cubic random	l = 500 nm l = 50 nm l = 40 nm	0.4 wt% 5.0 wt% 0.8 wt%	μ↓ 35% μ↓ 27% μ↓ 10%	— — —	— — —
Singh et al., 2018	commercial lithium grease	rGO $CaCO_3$ Al_2O_3	lamellar cubic random	l = 500 nm l = 50 nm l = 40 nm	0.4 wt% 5.0 wt% 0.8 wt%	— — —	— — —	EP↑45% EP↑25% no change
Wu et al., 2018	commercial grease	zinc borate & MoS_2 (nanocomposite)	—	—	0.06 wt%	μ↓28.2%	WSD↓ 23.1%	EP↑23.1%
He et al., 2018	commercial lithium grease	CeO_2	random	l < 500 nm	0.6 wt%	μ↓28%	WSD↓13%	—

Note: d – diameter; l – length; t – thickness; ↓ – decrease; ↑ – increase

2.8.2 Review based on synthetic oil–based greases

Synthetic oils are prepared by chemical processing to enhance the desired properties of the mineral oils. Synthetic oil–based greases are formulated where mineral oil–based greases are unable to fulfill the service requirements. Generally, synthetic base oils are not companionable with conventional thickening agents. Clay, polyurea, fumed silica, Teflon, etc., are commonly preferable thickening agents in the formulation of grease lubricants.

Gonçalves et al. (2017) have explored the effect of base oil and thickener on the coefficient of friction (COF) and the film thickness, and found that synthetic oil–based greases achieved low friction. Further, it was found that the film thickness depends on operating parameters, formulation of greases, and mostly on thickener type. Schultheiss et al. (2016) have investigated the wear behavior of grease–lubricated gears under boundary lubrication conditions. The result revealed that the thickener type, especially the additive type, significantly influenced the wear behavior of gears lubricated with grease and running at slow speeds. Further, it was found that PAO oil–based greases have improved the AW characteristics than mineral oil–based greases. Shu et al. (2018) have examined the lubricating performance of polyalphaolefin (PAO10) oil thickened via polypropylene and lithium complex thickeners with 2 wt% of ZDDP or MoDTC, or a mixture of ZDDP and MoDTC additives. The additives mixture of ZDDP and MoDTC showed excellent tribological performance in both grease samples compared to individual additives in greases and bare greases. Moreover, the polypropylene formulated grease added with a combination of ZDDP and MoDTC additives showed superior lubrication performance compared to lithium complex greases. The summary of some critical works on the effect of additives on the tribological performance of synthetic oil–based greases is presented in **Table 2.5**.

Table 2.5: Tribological performance of synthetic oil–based greases with numerous nanoadditives

Reference	**Base oil**	**Thickener**	**Nanoparticles**	**Shape**	**Size**	**Optimum concentration**	**Coefficient of friction (μ)**	**Wear scar diameter (WSD)/ Mean wear volume (MWV)/ Wear rate (WR)**	**Extreme pressure (EP)**
Z. Wang et al., 2010	PAO–100	polyurea	MoS_2 KB_3O_5 PS PN	— — — —	— — — —	— — — —	μ↓ μ↓ μ↓ μ↓	WR↓ WR↑ WR↓ WR↓	— — — —
Ji et al., 2011	PAO	lithium soap	$CaCO_3$	cubic	l = 45 nm	5.0 wt%	μ↓	WSD↓	EP↑
Hongtao et al., 2014	PAO (DURASYN–166)	calcium–sodium soap	CNTs	tubular	d = 1.4 nm, l = 0.5–40 μm	—	μ↓	wear ratio↓	—
Chen et al., 2014	PAO–40	attapulgite/bentonite clay	PTFE MoS_2 $CaCO_3$ graphite	— — — —	— — — —	3.0 wt%	μ↓ μ↓ μ↑ μ↓	MWV↑ MWV↓ MWV↑ MWV↑	—
Fan et al., 2014	PAO–40	bentone soap	graphene	lamellar	t = 1.3 nm	0.1 wt%	μ↓10.4%	MWV↓ 25–50%	—

Ge et al., 2016	PAG	PTFE	CB	spherical	d = 35 nm	1.0 wt%	μ↓	MWV↓	—
			MWCNTs	tubular	d = 50 nm	1.0 wt%	μ↓	MWV↓	—
			CMWCNTs	tubular	d = 50 nm	1.0 wt%	μ↓	MWV↓	—
			SWCNTs	tubular	d = 1–2 nm	1.0 wt%	μ↓	MWV↓	—
Schultheiss et al., 2016	PAO mineral oil	lithium soap aluminum complex soap	RC9505	—	—	4.0 wt%	—	wear↓	—
			graphite			4.0 wt%	—	wear↑	
			MoS_2			4.0 wt%	—	wear↑	
Dai et al., 2017	POA–8	calcium soap	zirconium phosphate	—	—	3.0 wt%	μ↓	WSD↓	EP↑
Shu et al., 2018	PAO–10	polypropylene lithium complex soap	ZDDP	—	—	2.0 wt%	μ↓	WSD↓	—
			MoDTC	—	—	2.0 wt%	μ↓	WSD ↓	—
			ZDDP+MoDTC	—	—	1.0 + 1.0 wt%	μ↓	WSD ↓	—

Note: d – diameter; l – length; t – thickness; ↓ – decrease; ↑ – increase

2.8.3 Review based on vegetable oil–based greases

According to the current scenario, the biodegradability of lubricant is a crucial facet, and the biodegradability of vegetable oil–based greases is superior to conventional greases. Florea et al. (2003) have developed biodegradable greases using soybean oil, rapeseed oil, and castor oil as base oils and lithium soap as a thickener. Another type of biodegradable grease was formulated with the synthetic ester (dioctyl adipate and dioctyl sebacate) as a base oil and organo–clay as a gelling agent. The biodegradability test (CEC–L–33–A–94 method) results showed that the biodegradability of vegetable oil and diester–based greases are over 85% and 80%, respectively. Further, α–tocoferol was used as an antioxidant additive in biodegradable grease to improve oxidation stability. These results indicate that vegetable oil–based greases have superior biodegradability than synthetic esters–based greases. The chain length of fatty acids and the degree of unsaturation has greatly influenced the lubrication performance of bio–greases. Sharma et al. (2005) have studied the tribological and thermo–oxidation behavior of grease made by soybean oil thickened with a lithium soap. The variable composition of thickener was used to understand the effect of fatty acids chain length and degree of unsaturation on the lubrication performance of the soy–grease. The results revealed that the lubricity and oxidation stability of the grease increased with decreasing of unsaturation in fatty acids.

Barriga et al. (2005) have investigated sunflower oil–based grease thickened with polymer for heavy–duty applications. It showed superior tribological performance in a gear simulation test rig compared with mineral grease and relatively identical performance with slightly higher wear on a four–ball tester. Similarly, epoxy soy oil–based lithium grease exhibited excellent oxidation stability and tribological behavior compared to commercially available mineral oil–based greases (Sharma et al., 2006). Refined bleach deodorized palm oil (RBDPO) and epoxy RBDPO were thickened with lithium and calcium soaps to develop additive–free palm grease, and it showed better tribological performance than mineral (HVI 160S) grease (Sukirno et al., 2010, 2009). Panchal et al. (2015) have formulated bio–based grease with trans–esterified Karanja oil and lithium soap, which exhibited similar tribological behavior as mineral greases. The jatropha vegetable oil–based lithium grease with multifunctional additive showed excellent tribological performance compared to commercial grease (Nagendramma and Kumar, 2015). The tribological results of additive–free vegetable oil thickened with metallic soap bio–greases demonstrated superior AW and AF characteristics compared to conventional greases.

The lubrication engineers are endeavoring their efforts to replace the traditional thickeners with environmentally friendly thickening agents. The biopolymers are gaining more attention due to its eco–friendly nature and high biodegradability. Therefore, bio–polymers (viz. methylcellulose, ethylcellulose, Kraft cellulose pulp, and chitosan) were investigated to substitute for traditional thickening agents (García–Zapateiro et al., 2014; Martín–Alfonso et al., 2011; Sánchez et al., 2009). Gallego et al. (2016) have developed a biodegradable grease with castor oil and chemically modified biopolymers (cellulosic pulp, chitin, and methylcellulose). They evaluated then for tribological performance against conventional calcium and lithium–based greases. The methylcellulose–based grease has established minimum COF with time as compared with other types of greases. From the aforementioned studies, vegetable oil thickened with biopolymers showed its significant potential to protect the tribo–pairs against friction and wear. The efforts of researchers suggest that vegetable oil–based greases are biodegradable, having excellent tribological performance, and will be a suitable substitution for conventional greases. A summary of some critical works on the tribological performance of the vegetable oil–based greases is presented in **Table 2.6**.

Table 2.6: Tribological performance of vegetable oil–based greases

Reference	Base oil	Thickener	Nanoparticles	Shape	Size	Optimum concentration	Coefficient of friction (μ)	Wear scar diameter (WSD)/ Mean wear volume (MWV)	Extreme pressure (EP)/ Load wear index (LWI)
Barriga et al., 2005	sunflower	polymer	—	—	—	—	—	WSD↓	no change
Sharma et al., 2005	soybean	lithium soap	—	—	—	—	μ↓	—	—
Sukirno et al., 2009	refined bleach deodorized palm oil (RBDPO)	lithium soap	—	—	—	—	—	MWV↓	—
Sukirno et al., 2010	refined bleach deodorized palm oil (RBDPO)	lithium soap	—	—	—	—	—	MWV↓	—
Fiedler et al., 2011	high oleic sunflower oil (HOSO) octyldodecyl isostearate (OCT) trimethylolpro–pane trioleate (TMPO) PAO	highly dispersed silica (HDS) lithium soap calcium soap	—	—	—	—	μ↓	Wear↓	—
Panchal et al., 2015	karanja oil	lithium 12–hydroxystearate	—	—	—	—	μ↓	WSD↓	EP↑

Nagendramma and Kumar, 2015	jatropha	lithium soap	ZDDP	—	—	5 wt%	—	WSD↓	EP↑
Buczek and Zajezierska, 2015	rapeseed	calcium 12–hydroxystearate lithium 12–hydroxystearate	zinc dioctyldithiophosphate	—	—	0.5 % mass 1.0 % mass	— —	— —	35.6 (LWI) 36.1 (LWI)
Padgurskas et al., 2015	rapeseed lard	sodium soap lithium soap	biological anti–wear additive LZ	—	—	1.0 wt%	—	WSD↓ (rapeseed) WSD↑ (lard)	—

Note: d – diameter; l – length; t – thickness; ↓ – decrease; ↑ – increase;

2.9 Problem formulation

The detailed, in–depth literature review has specified that the following gaps are shown in the research area of vegetable oil–based greases.

- Though the tribo–performance of vegetable oil–based greases with conventional additives are explored in very few investigations, no systematic efforts are made to explore tribo–performance of vegetable oil–based greases, especially with various nanoadditives.
- The comparative study of conventional and vegetable oil–based greases has not been explored with various nanoadditives.
- Hardly any study was carried out to provide an insight into the effect of nanoadditives morphology and concentration on tribo–performance of vegetable oil–based greases.
- The effect of fatty acid compositions of the vegetable oil on the tribological performance of vegetable oil–based greases has not been explored extensively.
- Coconut oil is the most saturated among all vegetable oils and has not been explored for tribo–performance of vegetable oil–based greases with or without nanoadditives.

2.9.1 Motivation

The crude based–oil is the preferred lube base stock in conventional lubricating greases. Crude oil–based greases are toxic, non–renewable, and their biodegradability is very poor. The disposal of drained out lubricants/greases is a very challenging task. Inappropriate disposal causes groundwater contamination, hazardousness to aquatic life, and adverse effects on our ecosystem. Non–sustainability, continuous depletion, and rising prices of petroleum products are the primary concerns. With the growing awareness about the environment, it is imperative to find an alternative base stock for lubricants.

2.9.2 Problem definition

In the last two decades, nanomaterials were used as additives in grease lubrication, and their performance has attracted immense attention from lubrication engineers. The effectiveness of nanomaterials depends on the morphology, size, concentration, and compatibility with base stock. They quickly enter the tribo–pairs due to their nanosize and prevent direct asperities contact. The nanomaterials have different morphologies, viz. nanosheets, nanotubes, nanosphere, nanohorn, etc., which significantly influence the tribological performance of the grease. The non–toxicity, biodegradability, renewability, and eco–friendly nature of vegetable oils enfold the attention for replacing the conventional base stock. Several tribological investigations were conducted on various types of vegetable oil–based greases to evaluate their lubrication potential in the last few years. The results revealed that vegetable oil–based greases have excellent tribo–performance than conventional greases. Given the past known state–of–art, very few researches are reported on the tribo–performance of vegetable oil–based greases with nanoadditives. Therefore, the following queries arise:

- Are conventional greases and vegetable oil–based greases having identical affinities with different nanoadditives?
- Is there any significant effect of nanoadditives morphology and their concentration on physicochemical and tribo–performance of vegetable oil–based greases?
- Is the addition of nanoadditives in the vegetable oil–based greases improve or deteriorate its tribo–performance than conventional greases?

- Whether all nanoadditives exhibit good compatibility with each type of grease to enhance tribological properties?

The present study attempts to explore all these queries through systematic and detailed experimental assessment. Hence, the objectives of the present study are outlined accordingly.

2.10 Objective of work

The objectives of the present work are as follows:

- To explore mineral (i.e., paraffin) and vegetable oils (i.e., castor and coconut) as a base stock and lithium soap as a thickener for the formulation of greases and investigate them for physicochemical and tribological performance.
- To understand the role of the fatty acid composition of castor and coconut oil on the tribological performance of greases.
- To synthesis various nanoadditives and ensure the formulation of nanoadditives using numerous characterization techniques.
- To investigate the physicochemical and tribological properties of greases having different types of nanoadditives under the boundary lubrication regime. The details of nanoadditives investigated are as follows:
    - Molybdenum disulfide (MoS_2) nanosheets in variable concentrations (0.01–0.05% w/w),
    - Chemically functionalized molybdenum disulfide with long–chain octadecanethiol (MoS_2–ODT) nanosheets in variable concentrations (0.01–0.05% w/w),
    - Graphene oxide (GO) nanosheets in variable concentrations (0.01–0.05% w/w),

    - Reduced graphene oxide (rGO) nanosheets in variable concentrations (0.01–0.05% w/w), and
    - Chemically functionalized graphene oxide with long–chain octadecylamine (GO–ODA) nanosheets in variable concentrations (0.01–0.05% w/w).
- To explore the synergistic effect of different morphologies of nanoadditives on the physicochemical and tribological performance of vegetable oil–based greases.
- To optimize the nanoadditives concentration in greases and evolve the lubrication mechanism by emphasizing the role of nanoadditives by conducting detailed studies of worn surfaces.

Justification for selection of base oil, thickener, and nanoadditives

The paraffin oil having saturated long hydrocarbon chains furnishes excellent oxidation stability. Therefore, it has been opted as a base stock for the synthesis of mineral oil–based greases. The vegetable oils show immense interest as a green and clean alternative to mineral oil–based lubricants because of their inherently high lubrication properties, excellent biodegradability, large VI, good affinity towards metal surfaces, and low volatility (Fox and Stachowiak, 2007; Gulzar et al., 2015; Gupta et al., 2018). Castor oil is non–edible vegetable oil and widely grown in India. The castor oil contains ricinoleic acid (12–hydroxy oleic acid) as a major fraction in the range between 85 to 95% (Honary and Richter, 2011). Due to the presence of hydroxyl groups, it has a high viscosity and can be used as viscosity modifiers (Singh, 2011). Coconut oil is used as an edible oil in the southern states of India, and it contains a higher degree of saturated fatty acid esters (> 90%) with a major fraction of lauric acid. Thus, it has a high pour point (~21 °C) and low iodine value (6–8) (Honary and Richter, 2011; Jayadas and Nair, 2006; Koshy et al., 2015). The thickener primarily governs the dropping point and textural features of grease. The lithium 12–hydroxystearate metallic soap offers a good dropping point (177–204 °C) and water resistance property (Ehrlich, 1984). Thus, it has been chosen as a thickening agent for the present work.

The solid nanomaterials with variable morphologies, chemical structure, mechanical strength, and inherent lubricious nature are gaining increasing attention as grease additive. The nano–sized particles as an additive in lubricating oils furnished better tribological properties than bulkier particles. The size, morphology, crystal structure, and compatibility with lubricating base oil govern the effectiveness of nanomaterials for their tribo–performance. The MoS_2 nanoslices easily enter into the contact interfaces of tribo–pair and provide better lubrication than nanoballs (Hu et al., 2010). Graphene, a two–dimensional honeycomb lattice structure of sp^2–hybridized carbon, has been considered the most emergent material of the decade. The excellent mechanical strength, high conductivity, low–shearing property because of the weak van der Waals interaction between adjacent atomic–thick lamellae, and large surface area promises the potential of graphene–based materials as lubricant additives and lubricious thin films for enhancement of tribological properties (Georgakilas et al., 2016).

2.11 Research plan methodology

Given these objectives mentioned above, the research plan methodology is shown in **Figure 2.6**. The proposed work is segmented into three types of lubricating greases (a) mineral oil–based greases, (b) vegetable oil–based greases, and (c) hybrid greases. The selection of base oil, thickener, and nanoadditives are crucial factors. In the first step, the nanoadditives will be prepared with their respective methods. Further, the nanoadditives will be characterized via various analytical tools to evaluate the morphological, crystalline, and chemical features. Subsequently, all three kinds of grease samples will be formulated with and without nanoadditives. All grease samples will be evaluated for physiochemical and tribological performances. Various characterization tools will be used for probing the worn surfaces lubricated with different types of grease samples to understand the lubrication behavior and the role of nanoadditives. In the final step, the results will be concluded through technical discussion.

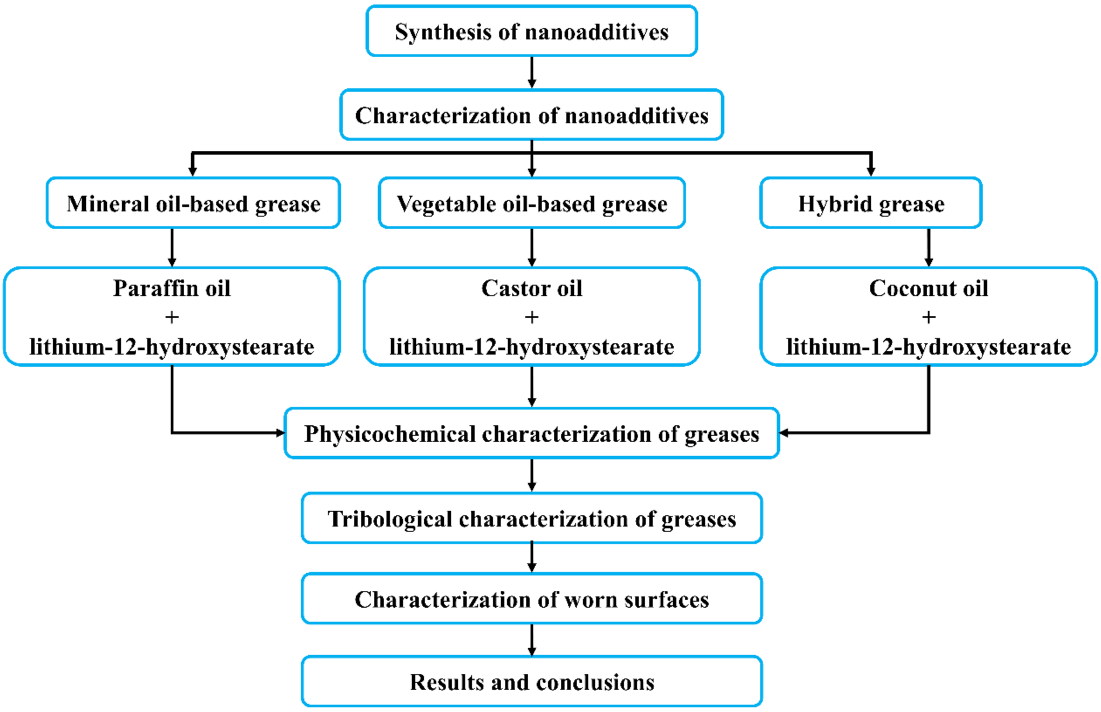


Figure 2.6: Research plan methodology of the present study

2.12 Summary of the chapter

This chapter provides an in–depth sight of greases, their composition, synthesis process, and lubrication behavior. The effects of nanoadditives on the tribological performance of greases are explained. Furthermore, the chapter presents a critical review of the previous studies about the tribological performance of various types of greases blended with nanoadditives. The gaps in the research area of vegetable oil–based greases are identified, and thus the objectives of the present work are outlined accordingly. At last, this chapter presents the research plan methodology of thesis work.