

Chapter-2

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2. Literature review

This chapter highlights previous studies carried out on lubrication by various researchers. It comprises a brief insight into polyalphaolefins (PAOs), their synthesis process, physical properties, comparison with petroleum-based lubricants, advantages and disadvantages, and their applications. The evolution of the lubricant additive provides insight into the transformation from SAPS (sulphated ash, phosphorus, and Sulphur) containing additive (hazardous) to nanoparticles (non-hazardous), taking into account of environmental concerns. In addition, the role of several types of additives and possible lubrication mechanisms to improve tribo-performance provides a comprehensive foundation for the work. This chapter concludes with the final objective of the thesis work.

2.1. Background

The global expansion of industry and motorization has increased the demand for petroleum products. Due to the progressive diminution of petroleum-based resources and the inability to solve the specific performance characteristic problem by mineral-based lubricants, the need for high-performance lubricants is increased rapidly. Therefore, most industries are switching to synthetic lubricants due to their better lubrication properties than petroleum-based lubricating oils. The use of synthetic lubricants in the modern age is becoming essential. They would conserve scarce petroleum products and increase the life and performance of equipment, i.e., reduced maintenance and waste, lower emissions and pollution, higher reliability and efficiency, etc. [17]. Polyalphaolefins (PAOs) are one of the most popular high-performance synthetic base oils. Among the synthetic base oil, polyalphaolefins (PAOs) have gained more attention because of their intrinsic attributes such as high viscosity indices, wide operating temperature range, better oxidation and thermal stability, and lower volatility, etc. According to consumer reports, PAOs are

becoming the new standard as a lubricant, with approximately 70% of new vehicles in 2019 having either PAO or PAO-based blended oils [18]. Among the presently used synthetic base oils for lubrication, PAOs are in their closest challenger, such as organic esters and PAGs. As per the report of MarketsandMarkets™ 2019, the market size of synthetic lubricants is considered to be USD 32.2 billion in 2018 and is expected to achieve USD 37.3 billion by 2023. PAO is predicted to dominate the synthetic lubricants market at a compound annual growth rate (CAGR) of 3.0 percent between 2018 and 2023 [19].

2.2. Polyalphaolefins (PAOs)

The term “polyalphaolefins” (PAOs) is derived from the lubricant base stock, i.e., saturated α -olefin oligomers. PAOs are hydrogenated olefin polymers that are produced by catalytic oligomerization of linear- α -olefin. An α -olefin is a member of an olefin family containing a carbon-carbon double bond at the first and second carbon of the molecular chain. Therefore, since the oligomers are saturated, PAOs, usually termed synthetic hydrocarbons, are the primary class of synthetic base oils. The American Petroleum Institute (API) has categorized the character of PAOs into group IV (**Table 2.1**) and classified them as high-performance lubricants. Currently, PAOs products are engineered with a broad viscosity range from 2 to 100 cSt at 100 °C and traded commercially [20]. PAO having viscosities 2, 4, and 6 cSt at 100°C referred to as low viscosity PAOs, and 8, 10, 40, 100 cSt are considered medium to high viscosity PAOs.

Table 2.1: American Petroleum Institute (API) classification of base stock [21]

Group	Sulphur (wt.%)	Saturates (wt. %)	Viscosity Index
Group I	> 0.03	< 90	80-119
Group II	< 0.03	> 90	80-119
Group III	< 0.03	> 90	>120
Group IV	Polyalphaolefin (PAO)		
Group V	All other base stocks not comprised in Group I-IV		

2.2.1. The synthesis process of PAOs

A two-step reaction process produces PAOs from linear α -olefin (1-decene), which is the basic olefin (or fundamental building block) for the production of PAOs. The linear α -olefin is derived from ethylene. In the first step, the ethylene is polymerized to 1-decene. The linear 1-decene is further oligomerized in the presence of a catalyst, yielding low molecular weight unsaturated oligomers, such as a dimer, trimer, tetramer, and some higher oligomers [22]. To develop low viscosity PAOs (i.e., 2 cSt to 10 cSt at 100°C), Lewis's acid catalysts such as boron trifluoride and alcohol or water as co-catalysts are used. In contrast, Ziegler–Natta catalysts such as trialkylaluminium or alkylaluminium halide with second moiety, namely a halogen or halide source, are preferred to produce high viscosity PAOs (40 cSt and 100 cSt) [23].

In the final step of the synthesis process, these unsaturated oligomers are hydrogenated by using a metal catalyst as palladium or nickel to develop a fully saturated hydrocarbon mixture. These saturated hydrocarbon mixtures are fractionated through the distillation to obtain desired viscosity of PAOs. The hydrogenation may be performed before or after distillation. The molecular structures of dimers, trimers, and tetramers of 1-decene are displayed in **Figure 2.1**. All these unsaturated oligomers exhibit various isomeric forms. The word “PAO” is only adopted when the fluid is saturated in downstream chemical

hydrogenation. A graphical representation of the manufacturing process for PAO products is depicted in **Figure 2.2**. The physical properties of final products (PAOs) are greatly influenced by the various process parameters (reaction parameters), i.e., the physical properties of PAO products required for the end-use application can be tailored by controlling the process parameters [24]. Some critical reaction parameters are as follows:

1. Catalysts and their concentration
2. Co-catalysts
3. The chain length of olefin feedstock
4. Temperature
5. Time
6. Pressure
7. Catalysts for hydrogenation
8. Distillation

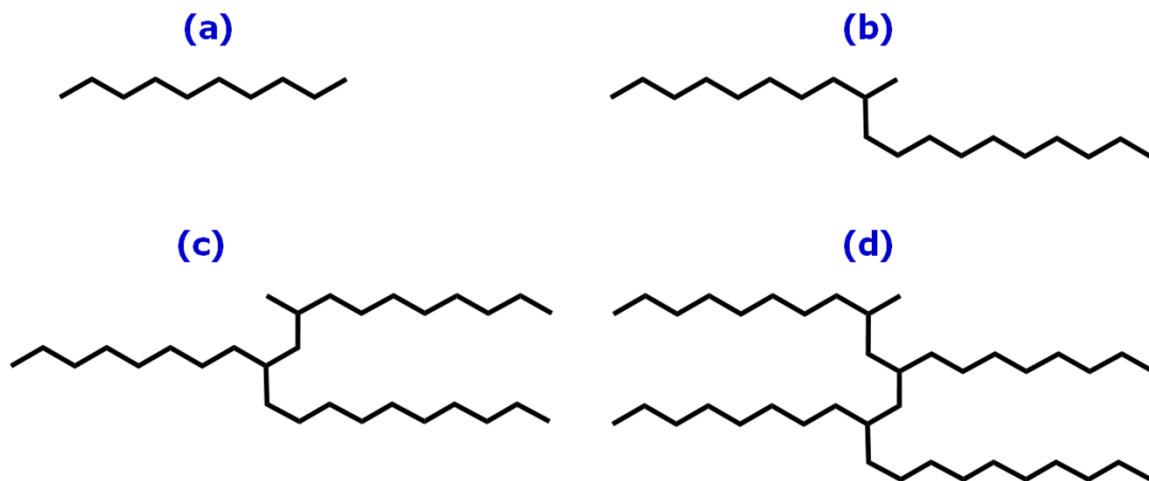


Figure 2.1: Molecular structure of 1-decene (PAO) components (a) monomer (b) dimer (c) trimer, and (d) tetramer

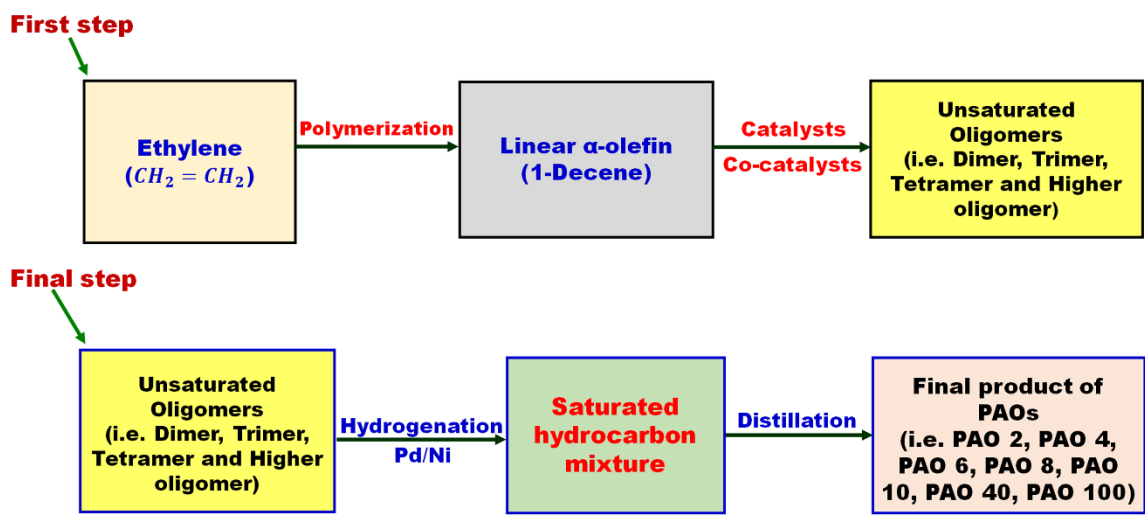


Figure 2.2: Manufacturing process of PAOs

2.2.2. Physical properties of PAOs

The typical physical characteristics of some commercially available 1-decene-based PAOs are listed in **Table 2.2**. The most common convention for designating the different grades is to use the kinematic viscosity in cSt (mm²/s) at 100 °C. Therefore, a PAO oil having kinematic viscosity 2 cSt can be denoted as PAO 2. For PAO 2, the viscosity index is not mentioned in **Table 2.2**. Since the viscosity index for any base oil acquiring a kinematic viscosity less than 2 cSt at 100 °C is undefined [24].

2.2.3. Comparison of PAOs with petroleum-based mineral oils

PAOs show a distinct chemical composition as compared to conventional mineral base oils. A blob of synthetic oil under a microscope reveals countless molecules having approximately the same size and shape. Conversely, a blob of traditional oil under a microscope features myriad molecules in diverse sizes, shapes, and structures. Today, most vehicles are suitable for employing either PAO-based oils or natural mineral oils that meet the American Petroleum Institute (API) and the International Lubricant Standardization and Advisory Committee (ILSAC) requirements. A particular PAO oil may acquire certain advantages, but no individual lubricant is superior in all respects. However, PAOs are often

offered excellent performance as compared to petroleum-based oil. This higher performance may only be linked to specific attributes. It may be possible that some traditional mineral oil-based formulations may demonstrate superior performance on specific properties.

Table 2.2: Physical properties of different grades of PAOs [24]

Property	ASTM standard	PAO 2	PAO 4	PAO 6	PAO 8	PAO 10	PAO 40	PAO 100
Kinematic viscosity (cSt @100°C)	D445	1.8	4.1	5.93	7.74	9.87	39	100
Kinematic viscosity (cSt @40°C)	D445	5.5	19	31	46.3	64.5	396	1150
Viscosity index	D2270	-	126	138	136	137	147	179
Density (g/ml)	D1298	0.798	0.821	0.827	0.833	0.835	0.850	0.853
Pour point (°C)	D97	-66	-66	-63	-57	-53	-36	-30
Flash point (°C)	D92	165	220	246	252	264	281	300
Noack volatility (wt.%)	D5800	99	14	6.8	3	2	0.7	0.6

Based on the test results conducted on various physical, chemical, and performance properties such as low-temperature pumpability, shear stability, oxidation resistance, deposit formation, volatility, and rheological (viscosity) change caused by oxidation, etc. American Automation Association (AAA) illustrated that PAOs outperformed mineral oils

by approximately 47% [18]. Nevertheless, in the past few years, PAOs have faced tough competition in the market comparably from low-cost group III lubricants. Although, with the increasingly growing demand for engine efficiency and strict emission standards, the market for PAOs will continue to be high in the following years.

The comparisons of typical features of PAOs, such as viscosity range, oxidation stability, thermal stability, corrosion stability, etc., of mineral oil and other synthetic oils are presented in **Table 2.3**.

2.2.4. Advantages of PAOs

- ***Higher viscosity index:*** - This implies that the viscosity varies less (more stable) as temperature alters during the normal engine's start-up and working conditions. Viscosity is an essential characteristic of lubricants, producing fluid film or clearance between sliding or rotating metal surfaces. Intense friction and wear will take place without this fluid film.
- ***Better oxidative stability:*** - Conventional petroleum-based mineral oils are more likely to be chemically degraded (oxidation) than PAOs when it is subjected to certain conditions such as combustion of by-products, fuel dirtiness, acids, pro-oxidants, water adulteration, metal particles, and extreme heat (i.e., from combustion). Such conditions are generally occurring in engines. Oil decay can lead to sludge formation, corrosion, varnish or deposits, change in viscosity, and decrease in engine efficiency.
- ***Lower temperature fluidity:*** - Mineral oils (in comparison with PAOs) can become so thicker (highly viscous) at extremely low temperatures that the oil is not pumpable or cannot flow adequately in the engine. The scarcity of oil flow can lead to lubricant starvation conditions and malfunctioning of engine operations.

Table 2.3: Comparison of typical properties of PAOs with mineral and other synthetic oils [25]

Properties	Polyalphaolefins (PAOs)	Mineral oil	Diester	Polyol ester	Phosphate ester	Polyalkylene glycol	Silicon oil	Perfluoropolyether
Cost	M	L	M	M	VH	M	H	VH
Viscosity range	VW	W	L	L	L	V	W	W
Viscosity temperature	VG	F	G	G	P	E	E	NA
Temperature range	VG	BA	G	V	G	G	E	E
Oxidative stability	VG	BA	G	VG	VG	VG	E	E
Thermal stability	G	F	G	G	F	F	G	NA
Low volatility	E	F	E	E	G	G	G	NA
Corrosion stability	E	E	BA	BA	VG	G	G	BA
Hydrolytic stability	E	E	F	F	F	VG	G	NA
Compatibility with mineral oil	E	E	G	G	BA	BA	BA	BA
Pour point	L	G	L	L	VG	M	VL	L
Flash point	VG	M	G	VG	E	G	E	E
Additive solubility	G	E	VG	VG	G	F	P	NA
Seal compatibility	VG	VG	BA	BA	BA	G	VG	VG
<p>Where: L = Low, VL = Very low, M = Medium, H = High, W = Wide, VW = Very wide, H = High, VH= Very high, F = Fair, G = Good, VG = Very good, E = Excellent, P = Poor, BA = Below average or less than ideal, NA = Not available</p>								

- **Lower volatility:** - PAOs-based engine oils usually exhibit low volatility compared to mineral oils. This indicates that the oil is less wasted through the exhaust flux of the engine and less harmful to the environment. Consequently, the necessity of makeup oil is reduced between oil change intervals.
- **Greater thermal stability:** - PAOs withstand higher temperatures with minimum decomposition than conventional mineral oils.
- **Longer life span:** - The most significant advantage of PAO oils is that they have a longer service life than traditional petroleum-based mineral oils. For PAO oils, the suggested change period is about every 5,000-7,000 miles, whereas, for some brands, the change interval is approximately 15,000-25,000 miles. In addition, PAO oils offer a longer lifetime and require less oil changes, leading to decreased environmental impacts per distance covered. This can lead to environmental benefits from a life cycle perspective.
- PAO oils also possess other vital features over mineral oils and are as follows:
 - ❖ Low toxicity
 - ❖ Hydrolytically stable
 - ❖ Compatible with mineral oils, esters, and alkylated naphthalene
 - ❖ Lower traction force
 - ❖ Low corrosion

2.2.5. Disadvantages of PAOs

PAO base oils do have some negative effects, and these are as follows

- **High cost:** - The cost is the most noticeable drawback of PAOs. The value of PAOs is around two to four times higher than that of mineral oils.

- **Limited additive stability:** - Due to composition purity and very low polarity, PAOs provide insufficient solvency for common additives essential for fully formulated lubricants. Also, additive stability in PAOs under cold temperature conditions for a long period may be a significant challenge.
- **Seal shrinkage risk:** - The highly non-polar characteristics of PAOs may affect the seal performance in some situations. Therefore, PAO-based lubricants are generally mixed with ester oil to counteract the shrinking effect of PAO molecules.

2.2.6. Recent developments

After the successful acceptability of PAOs in various applications, ExxonMobil Chemical Co. launched a new class of PAOs, i.e., SpectraSyn Ultra™ PAO. The SpectraSyn Ultra™ PAOs are manufactured from 1-decene, the same basic stock used to produce traditional PAO. The physical attributes of commercial SpectraSyn Ultra™ PAOs are summarized in **Table 2.4**. The SpectraSyn Ultra™ PAOs exhibit higher VI, lower pour point, and higher viscosity than conventional PAOs. These novel lubricants can be employed in automotive engine oil and industrial oil formulations to offer benefits in terms of viscosity characteristics, shear stability, and augmented film thickness of lubricants.

2.2.7. Applications of PAOs

PAOs are acquiring rapid admissibility in many niche applications because of their inherent and attractive characteristics. The application areas of PAO base oils based on their viscosity grades are shown in **Table 2.5**.

Table 2.4: Physical attributes of a new class of PAO, i.e., SpectraSyn Ultra™

Property	ASTM standard	SpectraSyn Ultra™		
		PAO 150	PAO 300	PAO 1000
Kinematic viscosity (cSt @100°C)	D445	150	300	1000
Kinematic viscosity (cSt @40°C)	D445	1500	3100	10000
Viscosity index	D2270	218	241	307
Density (g/ml)	D1298	0.850	0.852	0.855
Pour point (°C)	D97	-33	-27	-18
Flash point (°C)	D92	>265	>265	>265

2.3. Lubricant Additives

There are various critical tribological contact conditions in modern types of machinery, and mechanical components undergo extreme pressure conditions during start-up or shutdown stages. Under such circumstances, mineral base oils, even synthetic lubricants, cannot form a stable lubricating film at the friction pairs. Consequently, boundary lubrication or mixed lubrication occurs and results in severe friction and wear. Lubricant additives are one of the most effective ways to reduce friction and wear under boundary lubrication. Lubricant additives are chemicals nearly organic or organometallic incorporated into base oil in tiny weight percentage to enhance the lubricating performance and durability of the base oils. In general, lubricants additives serve three primary functions as follows:

- Enhance existing base oil properties
- Suppress undesirable base oil properties
- Impart new properties to base oils

It is crucial to select the correct lubricant additives based on the final application. It is feasible to opt for the additives based on the tribological system.

Table 2.5: Application of different grades of PAOs in various areas [26]

Applications	Conventional PAOs							SpectraSyn Ultra™		
	PAO 2	PAO 4	PAO 6	PAO 8	PAO 10	PAO 40	PAO 100	PAO 150	PAO 300	PAO 1000
Gasoline & Diesel engines	-	XX	XX	XX	-	XX	-	XX	XX	-
Automatic transmissions	XX	XX	-	-	-	-	-	XX	-	-
Industrial/ automotive gear and transmissions	X	XX	XX	X	X	XX	XX	XX	-	-
Hydraulic systems	XX	XX	XX	X	X	XX	XX	XX	-	-
Industrial bearings	-	-	XX	X	X	XX	XX	XX	XX	-
Rotary air and gas compressor	-	X	XX	XX	XX	XX	XX	-	-	-
Hydrocarbon refrigeration compressor	X	X	X	X	X	X	-	-	-	-
Greases	X	X	XX	X	X	XX	XX	XX	XX	XX
Turbines	-	XX	XX	X	X	XX	XX	-	-	-
Heat transfer fluids	XX	X	-	-	-	-	-	-	-	-
Automotive hydraulic fluids	XX	-	-	-	-	-	-	-	-	-
Mist lubricants	-	XX	XX	X	X	X	X	XX	-	-
Where: - XX- Most commonly used applications, X- Less commonly used applications										

2.3.1. Evolution of lubricant additive

It was stated that the development of modern engines and transmission technologies would be impossible without lubricant additives. From its conception in the early 1900s, Vehicle design advancements are the starting point for the demand for high-performance requirements, which stimulate the development of new lubricant and additives technologies. There is a growing need for lubricant additives to play a significant role in more complex components such as engine and transmission systems. Since the discovery of antioxidant and anti-wear chemistry, the performance of a liquid lubricant has been enhanced in multiple ways by adding a combination of additives such as anti-wear (AW) and extreme pressure (EP) agent, corrosion, rust inhibitor, detergent, dispersant, and friction modifiers (FM). Such additives include organo-molybdenum compounds and organo-zinc phosphate compounds. Among these additives, friction reducers and AW additives have evolved rapidly and attracted significant attention in recent years due to the increasing demand for improvement in fuel economy and emission reduction. Conventionally, the prominent agents used as friction-reducing and anti-wear additives in PAO base oils are zinc dialkyldithiophosphate (ZDDP) and molybdenum dithiocarbamate (MoDTC). Despite their impressive tribological performance and good dispersion stability, they may have one or more drawbacks such as toxicity, copper and/or lead corrosion, increased levels of sulphur and/or phosphorus in the finished lubricant, releasing sulphated ash, phosphorous, and sulphur (SAPS) which pollutes the environment. Further, rapid thermal degradation of these additives results in a lack of lubrication performance during their applications.

In view of the above, there is a need for lubricant additives that can improve the overall performance of the lubricant and are environment-friendly, which can comply with the pollution control standards used for automotive engines and lead to the exploring new kinds

of additives. In this prospect, nanomaterials-based additives (nanoparticles) are the most effective lubricant additives to meet these demands. Different kinds of nanomaterials were used as an additive in various lubricating oils and are currently being examined. Nanoparticles are comparably a new category of lubricant additives in the history of lubricant additives [27], shown in **Figure 2.3**.

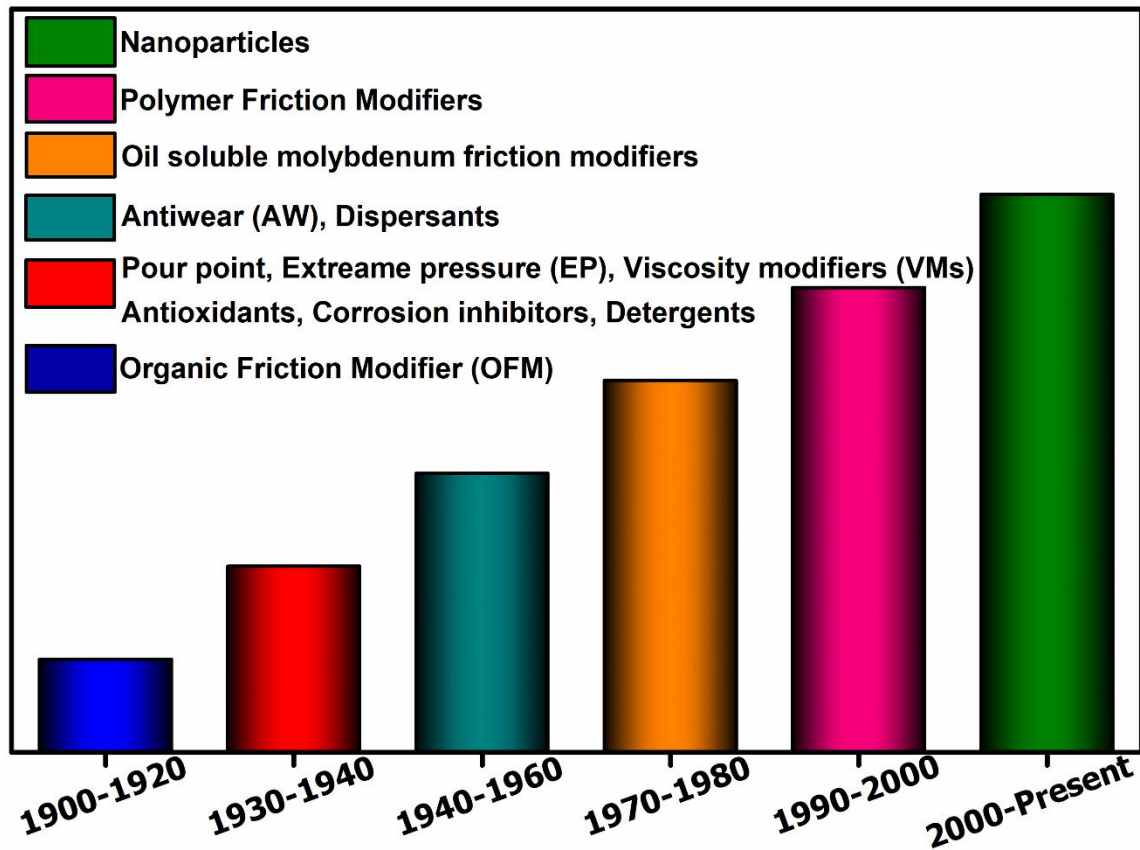


Figure 2.3: The chronology of the evolution of lubricant additives [27]

2.3.2. Nanoparticles as lubricant additive

With the development of nanotechnology, nanomaterial-based nanoparticles have become one of the most attractive fields in physics, chemistry, and materials science. Due to the tiny nano-size, it is easy for nanoparticles to infiltrate in the grooves of rubbing surfaces and form a protective tribo-film, preventing friction and surface from being worn. Furthermore, nanoparticles have high surface activity, which can improve the film-forming stability of tribo-film through physical and/or chemical adsorption. Many researchers have

reported that a single type of nanoparticle has served multiple purposes as an anti-wear (AW), extreme pressure (EP) additive, and friction modifier (FM). Nanoparticles as lubricant additives have many potential advantages over traditional lubricant additives as follows [28]:

1. Insolubleness in non-polar base oils
2. Low reactivity with other additives in the lubricant
3. Higher probability in forming a lubricant film at mating surfaces
4. Great sustainability
5. Very low volatility to withstand high temperatures

However, the performance of nanoparticles in the base oil is strongly influenced by several factors such as size, shape, and concentration of nanoparticles.

2.3.3. Classification of nanoparticles

The nanoparticles can be classified into various categories according to their physical and chemical properties, size, morphology, and applications. **Figure 2.4** demonstrates the three fundamental types of nanoparticles but designed (synthesized) nanoparticles gained more attention in the field of lubrication due to their unique shape, structure, and characteristic chemical elements. The designed nanoparticles have been further classified into seven major categories based on their extensive use in lubricants. Thus, In this thesis work, the nanoparticles have been categorized based on tribological applications.

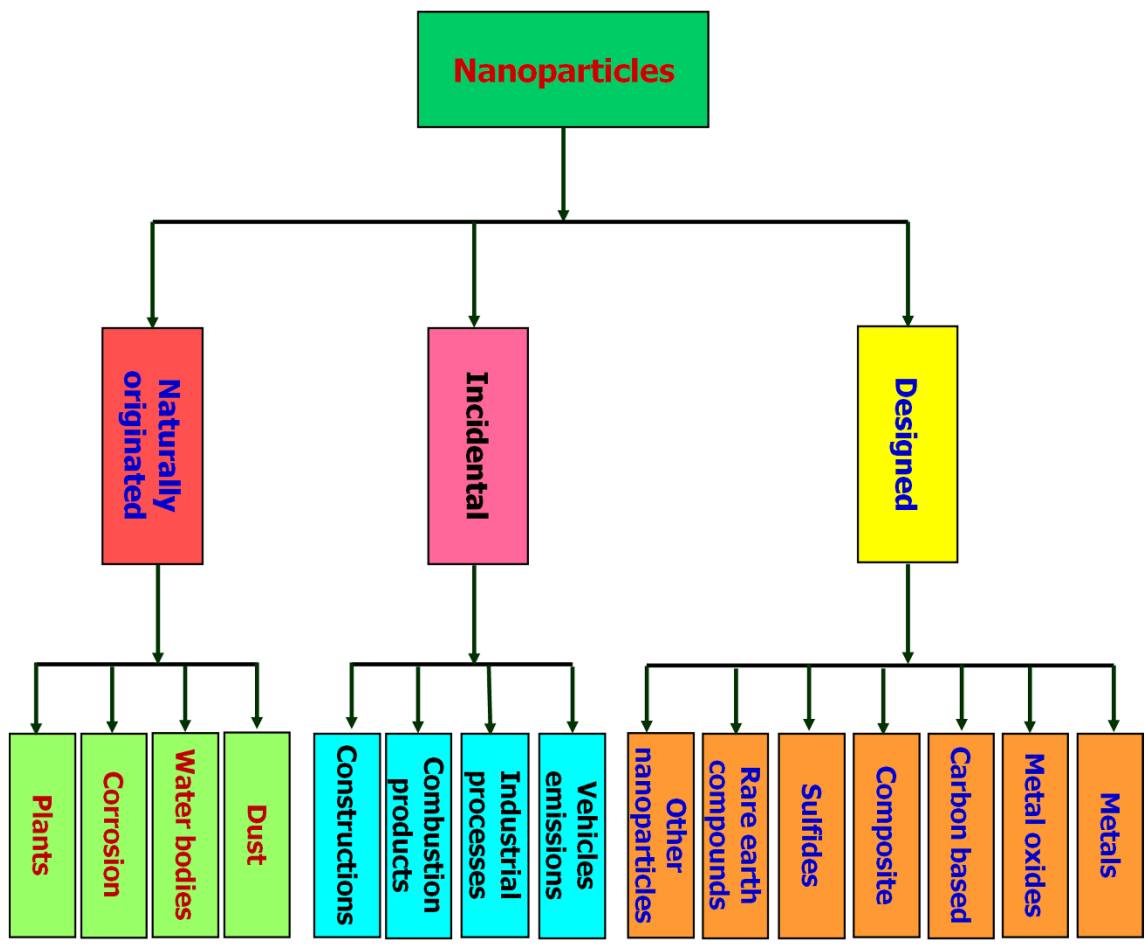


Figure 2.4: Classification of nanoparticles based on their origin

2.3.3.1. Metals-based nanoparticles

Metal-based nanoparticles offer excellent chemical and physical properties, such as unique thermal, electrical, magnetic, optical, chemical, and catalytic properties [29]. Several researchers have investigated various metallic nanoparticles as an additive in different base oils and reported the distinct outcome of nanolubricant formulations (**Table 2.6**). The results revealed that the inclusion of these nanoparticles into lubricating oils reduced the friction and improved the anti-wear and extreme pressure performance.

2.3.3.2. Metal oxides nanoparticles

Several metal oxides nanoparticles were also employed in various base oils as lubricant additives to explore tribo-performance across multiple contact configurations. Metal oxides nanoparticles include zirconium, titanium, zinc, copper, cerium, aluminium, and iron oxides. Metal oxides nanoparticles exhibit similar lubrication mechanisms to metals-based nanomaterials, such as tribo-films or adsorption film formation, rolling action, and sintering or repair effect [30]. A summary of some key literature on oxide-based nanolubricants and tribological performance has been listed in **Table 2.7**. In addition, for the formulation of nanolubricants, it may be interesting questions about how the same nanoparticles with different morphologies react in the same base oil. Gao et al. (2013) [31] observed the morphology effect (hexagonal, octahedral, and irregular shape) of Fe_3O_4 nanoparticles in engine oil. They reported that the hexagonal shape of the nanoparticles has superior antifriction as well as anti-wear properties.

Table 2.6: Summary of tribological performance of metals-based nanolubricants

Nano particles	lubricant	Additive source	APS (nm)	Morphology of additive	Concentration	Test Configuration	Outcomes	References
Cu	Raw oil	Commercial	25, 60	Spherical	0.1 vol.%	Disc-on- disc	COF ↓ by 51% for 25 nm COF ↓ by 69% for 69 nm at 2200 N	Choi et al. (2009) [32]
	SAE 10	Commercial	–	Nearly Spherical	0.5 wt.%	Four-ball	COF ↓ by 49% WSD ↓ by 47%	Padgurskas et al. (2013) [33]
	SAE 40	Synthesized	50, 130	Spherical	0.005, 0.01 and 0.02 wt.%	Ball-on-disc	COF ↓ by 18% and WR ↓ by 50% with 130 nm while no effect with 50 nm (optimum concentration=0.01%)	Zin et al. (2015) [34]
	Liquid paraffin	Synthesized	3.5	Sphere like	0.2-1.0 wt.%	Four-ball	AF, AW, and EP ↑ (0.4 wt.% exhibited best AF performance 1.0 wt.% exhibited best AW and EP performance)	Zhang et al. (2015) [35]

Ni	500SN (Mineral oil)	Synthesized	10	Spherical	0.2-3 wt.%	Four-ball	WL ↑ by 67 %. AW ↑ by 33% COF ↓ by 26 %	Qui et al. (2001) [36]
	PAO 6	Commercial	20	Nearly Spherical	0.5, 1, and 2 wt.%	Block-on- ring	COF ↓ by 30% and WR ↓ by 54% (Optimum concentration=0.5 wt.%)	Chou et al. (2010) [37]
Al	Liquid paraffin	Commercial	65	Spherical	0.025-1.0 wt.%	Ball-on- ring	COF and WSD ↓ (Optimum concentration=0.5 wt.%)	Peng et al. (2010) [38]
	Glycerol	Commercial	50	Spherical	0.25-1.0 wt.%	Thrust-collar	COF and WR ↓ (Optimum concentration=0.6667 wt.%)	Le et al. (2017) [39]
Pd	Liquid paraffin	Synthesized	2.2	Spherical	5.0 wt.%	Pin-on-disc	COF ↓ The electrical resistance of contact ↓ by 97%	Kolodziejczyk et al. (2007) [40]
	TBA	Synthesized	2	Spherical	1-10 wt.%	Ball-on- disc	COF ↓ AW and EP ↑ (Optimum concentration =2 wt.%)	Abad et al. (2013) [41]

Fe	SAE 10	Commercial	–	Nearly Spherical	0.5 wt.%	Four-ball	COF↓ by 39% WSD ↓ by 23%	Padgurskas et al. (2013) [33]
	SAE 10 (mineral) and rapeseed oils	Synthesized	50-340	Nearly spherical	0.1 wt.%	Four-ball	Slight improvement in AF but significant enhancement in AW performance of both base oils (Optimum size = 50-140 nm)	Maliar et al. (2015) [42]
<p>APS: Average particle size, AF: Antifriction, AW: Anti-wear, EP: Extreme pressure, COF: Coefficient of friction, WSD: Wear scar diameter, WR: Wear rate, MWV: Mean-wear volume, ↓: Decrease, ↑: Increase/ improvement</p>								

Table 2.7: Summary of tribological performance of nanolubricants with metal oxides nanoparticles

Nano particles	lubricant	Additive source	APS (nm)	Morphology of additive	Concentration	Test Configuration	Outcomes	References
CuO	API SF oil, Base oil	Synthesized	5	Sphere like	1.0 wt.%	Ball-on-flat (Reciprocating test rig)	In the case of API SF oil, COF, and WSD ↓ by 18.4% and 16.7%, respectively Whereas for base oil, COF, and WSD ↓ by 5.8% and 78.8%, respectively.	Wu et al. (2007) [43]
	Coconut oil	Commercial	20-150	Spherical	0.1-0.4 wt.%	Pin-on-disc	AF and AW ↑ (Optimum concentration=0.34 wt.%)	Thottackkad et al. (2012)[44]
	Liquid paraffin	Commercial	50	Nearly Spherical	0.2, 0.25, 2 and 3 wt.%	Four-ball	AF and AW ↑ (0.2 wt.% exhibited best AF performance 3.0 wt.% exhibited best AW performance)	Arsul et al. (2013) [45]
	Mineral oil PAO oil, Vegetable oil	Synthesized	4.35	Nearly Spherical	0.5 wt.%	Ball-on-disc (High-frequency reciprocating test rig)	AF and AW ↑ (Vegetable oils exhibited superior AF and AW performance than mineral and PAO oil)	Alves et al. (2013) [46]

	Modified palm oil	Synthesized	50-300	Sphere like	0.25-1.5 wt.%	Four- ball	AW/EP↑ by 1.5 times (Optimum concentration= 1.0 wt.%)	Gulzar et al. (2015) [47]
	Fully formulated oil (GL-4), PAO 8	Commercial	50	Spherical	0.5, 1.0 and 2.0 wt.%	Ball-on disc, Four-ball	For PAO 8, COF, WSD↓, and EP ↑ by 18%, 14%, and 273%, respectively, In the case of GL-4, EP↑ by 14% as well as COF and WSD↓ (Optimum concentration=2.0 wt.%)	Pena-Paras et al. (2015) [48]
	Multi grade engine oil	Commercial	40	Spherical	0.5-1.5 wt.%	Pin-on-disc	AF and AW ↑ (Optimum concentration=1.0 wt.%)	Jatti and Singh (2015) [49]
ZnO	PAO 6	Commercial	20	Nearly Spherical	0.3, 1.0 and 3.0 wt. % (Dispersing agent=1, 1.5 and 3.0 wt.%)	Four-ball	WSD↓ and EP↑ (Optimum concentration=0.3 wt.% ZnO +3 wt.% dispersing agent)	Hernandez et al. (2006) [50]
	60 SN (mineral oil)	Commercial	10-30	Spherical	0.2, 0.5, 0.8 and 1.0 wt. % (Oleic acid=8 wt.%)	Four-ball	COF and WSD ↓ (Optimum concentration=0.5 wt.%)	Ran et al. (2016) [51]

TiO₂	Chemically modified rapeseed oil	Commercial	20 nm, 40µm	Spherical	0.05 wt.%	Pin-on-disc	COF↓ by 15.2% and AW↑ by 11% with 20 nm TiO ₂ COF↓ by 6.9% and AW↑ by 6.1% with 40 µm TiO ₂	Arumugam et al. (2013) [52]
	Servo 4T synth 10W-30	Commercial	10-25	Sphere like	0.3, 0.4 and 0.5 wt.%	Pin-on-disc	COF ↓ by 86% at 4 kgf load, AW ↑ (Optimum concentration= 0.3 wt.%)	Laad and Jatti (2018) [53]
Fe₃O₄	Engine oil	Synthesized	a: 45.8, b: 49.2, c: 50.1	a: Hexagonal, b: Octahedral, c: Irregular	0.5, 1.0, 1.5 and 2.0 wt.%	Four-ball	COF ↓ by 58.16, 47.96, and 34.69 %, and the WSD ↓ by 13.87, 11.17, and 10.18 % for hexagonal, octahedral, and irregular morphologies of Fe ₃ O ₄ , respectively. (Optimum concentration= 1.5 wt.%)	Gao et al. (2013) [31]
Al₂O₃	Lubricating oil	Synthesized	78	Spherical	0.05, 0.1, 0.5, and 1 wt%	Four-ball and thrust-ring	AF↑ by 23.92 and AW↑by 41.75% (optimum concentration= 0.1 wt.%)	Luo et al. (2014) [54]

ZrO₂	20# Machine oil	Synthesized	<100	Amorphous	0.5, 0.1 and 1.0 wt.%	Four-ball and thrust-ring	COF↓ by 5.36% and WSD↓ by 3.98% on four-ball tribometer, whereas COF ↓ by 27.34% on the thrust-ring test rig. (Optimum concentration=0.5 wt.%)	Ma et al. (2010) [55]
SiO₂	Water	Commercial	30	Amorphous	0.1, 0.2, 0.3, 0.4 and 0.5 wt.%	Four-ball	AF↑ and AW↓ (optimum concentration= 0.3 wt.%)	Bao et al. (2017) [56]
	Paraffin grease	Synthesized	70	Nearly spherical	0.01, 0.02, 0.03, 0.04 and 0.05 wt.%	Four-ball	COF ↓ by 20%, MWV ↓by 40% (Optimum concentration=0.03 wt.% for COF and 0.05 wt.% for MWV	Rawat et al. (2019) [57]
<p>APS: Average particle size, AF: Antifriction, AW: Anti-wear, EP: Extreme pressure, COF: Coefficient of friction, WSD: Wear scar diameter, WR: Wear rate, MWV: Mean-wear volume, ↓: Decrease, ↑: Increase/ improvement</p>								

2.3.3.3. Carbon-based nanoparticles

Carbon and its derivatives-based nanoparticles are a recent trend to use as a lubricant additive. The carbon-based nanomaterial includes fullerene, nano carbon onions, carbon nanotubes (i.e., single-walled carbon nanotubes (SWCNTs), and multi-walled carbon nanotubes (MWCNTs), graphene, graphene oxide (GO), reduced graphene oxide (rGO), nano-diamond (ND), and graphite, etc. Their superior mechanical properties and chemical stability offer excellent tribological properties and environment-friendly performances for a sustainable future [58]. Furthermore, carbon-based nanomaterials can be divided into four primary allotropes, which are: zero-dimensional (i.e., fullerene, quantum dot), one-dimensional (i.e., CNTs), two-dimensional (graphene), and three-dimensional (graphite and nano-diamond). Liu et al. (2011) examined the stearic acid (SA) functionalized MWCNTs dispersed in paraffin oil and revealed that at an optimum dose of 0.025 wt.%, the COF and wear scar diameters were decreased by 80% and 50%, respectively, which was credited to the bearing structure of MWCNTs and isolating effect [59]. Song et al. (2016) studied two forms of carbon allotropes, i.e., carbon sphere (CS) and flaky graphene oxide (GO), as an additive in sunflower oil to correlate suspension stability and tribo-performance [60]. They found flaky structure exhibits good suspension, thus better tribological results. **Table 2.8** summarizes the tribo-performance of nanolubricants incorporating various carbon-based nanoparticles.

Table 2.8: Summary of tribological performance of different base oils with carbon-based nanoparticles as an additive

Nanoparticles	Lubricant	Additive source	APS (nm)	Morphology of additive	Concentration	Test Configuration	Outcomes	References
Ni/Y-SWCNTs	PAO oil	Synthesized	10	Tubular	0.1 wt.%	Pin-on-flat	Significant AW↑ Mild AF↑	Jolly Pottuz et al. (2008) [61]
F-MWCNTs	Paraffin oil	Synthesized	10 μm	Tubular	0.01, 0.025, 0.05, 0.1 and 0.25 wt.%	Ball-on-plate (Wear and friction testing machine)	AF and AW ↑ (Optimum concentration=0.025 wt.%)	Liu et al. (2011) [59]
SA-MWCNTs	Water	Synthesized	10-20	Tubular	0.05, 0.1, 0.15 and 0.2 wt.%	Four-ball	COF and WSD↓, EP ↑ by 151% (Optimum concentration=0.2 wt.%)	Peng et al. (2013) [62]
Carbon nano capsules	Mineral oil	Synthesized	40-80	Onion like	0.01, 0.03, 0.05, 0.07 and 0.1 wt.%	Block-on-ring	COF and MWV ↓ (optimum concentration=0.05 wt.%)	Jeng et al. (2014) [63]
a: Graphene, b: MWCNTs	Ionic liquid	Synthesized	25-40	a: sheet-like, b: tubular	0.075 wt./vol.%	Ball-on-disc	COF and WR ↓ (MWCNTs are more effective at a low applied load, whereas graphene nanosheets are better at a high load.)	Zhang et al. (2014) [64]

F-SWCNTs, F-MWCNTs	Oil, Water	Synthesized	12-85	Tubular	0.01 and 0.05 wt.%	Disc-on-disc (twin-disc machine)	AF and AW ↑ (0.05 wt.% of SWCNTs in water and 0.01 wt.% of MWCNTs in oil exhibited best results	Corneli et al. (2016) [65]
IL-MWCNTs	Water	Synthesized	20-40	Tubular	0.01, 0.015 and 0.02 wt.%	Four-ball	COF and MWV ↓ by 42% and 72%, respectively (optimum concentration= 0.015 wt.%)	Wang et al. (2017) [66]
MWCNTs	LB2000 vegetable -based oil	Commercial	a: 10- 20, b: 60- 100	Tubular	0.05 and 0.25 wt.%	Pin-on-disc	AF and AW↑ (optimum concentration=0.05 wt.%) MWCNTs of size “a” exhibited best tribological performance than “b”.	Su et al. (2018) [67]
a: Graphene, b: MWCNTs, c: fullerene (C₇₀)	Fomblin- Y (LVAC 06/6)	Commercial	a: 5-10 µm, b: 1- 10 µm, c: 10- 13 nm	-	1.0 wt.%	Ball-on-disc	AF and AW ↑ (a+c combination exhibited the best tribological characteristics)	Upadhyay et al. (2019) [68]

a: GO b: rGO c: GO-ODA	Paraffin grease	Synthesized	-	Sheet like	0.01, 0.02, 0.03, 0.04 and 0.05 wt.%	Four-ball	For a, b and c, COF by 34.3, 50.3, and 34.3%, and MWV by 86.6, 85.4, and 80.9%, respectively (optimized dose of GO (0.01 wt.%), rGO (0.01 wt.%), and GO-ODA (0.05 wt.%))	Rawat et al. (2020) [69]
APS: Average particle size, AF: Antifriction, AW: Anti-wear, EP: Extreme pressure, COF: Coefficient of friction, WSD: Wear scar diameter, WR: Wear rate, MWV: Mean-wear volume, ↓: Decrease, ↑: Increase/ improvement								

2.3.3.4. Composite nanoparticles

Recent studies have demonstrated the significance of adopting composite nanoparticles. Composite nanoparticles showed the superior tribological performance to single-component nanoparticles due to the synergetic effects of more than one type of nanoparticles. Luo et al. [70] investigated the performance of $\text{Al}_2\text{O}_3/\text{TiO}_2$ nanocomposites as a lubricant additive and concluded that the antifriction and anti-wear performance of base oil improved significantly. Furthermore, $\text{Al}_2\text{O}_3/\text{TiO}_2$ nanoparticles exhibited superior tribological properties than individual Al_2O_3 and TiO_2 nanoparticles. **Table 2.9** summarizes tribological results obtained with several composite nanoparticles based nanolubricants.

2.3.3.5. Rare earth compound-based nanoparticles

Extensive research has been conducted on the tribological behaviour of rare-earth compounds in lubrication. Due to the hexagonal crystal layer structure, they feature excellent friction reduction and anti-wear properties. Among various rare-earth compounds, lanthanum (La) and cerium (Ce) elements containing rare earth compounds are most popular in lubrication. They could be used as lubricant additives or doped into other nanoparticles. Their lubricating mechanisms primarily include the development of tribo-film or adsorption film [30]. Some key literature on rare-earth compound-based nanoparticles as lubricants additives have been listed in **Table 2.9**.

2.3.3.6. Sulphides-based nanoparticles

For decades, metal sulphides, mainly molybdenum disulphide (MoS_2) and tungsten disulphide (WS_2) have been employed as solid and liquid lubricant additives in the lubrication. Besides their shape, sulphur played a vital role in particle and lubricant molecule interactions. MoS_2 and WS_2 can chemically interact with friction pairs to form a stable adsorption layer on rubbing surfaces, effectively promoting lubricant tribological

properties under extreme pressure conditions [58]. Yi and Zhang [71] recently observed that the tribological properties of MoS₂ with lamellar morphology were significantly superior to those of petal structure, suggesting that MoS₂ with lamellar structure exhibited high chemical activity and smooth interlayer sliding phenomenon. Furthermore, the tribological performance of sulphides-based nanoparticles used as lubricant additives is summarized in **Table 2.9**.

2.3.3.7. Other nanoparticles

Additionally, other nanoparticles such as hexagonal boron nitrate (h-BN), calcium carbonate (CaCO₃), zinc aluminate (ZnAl₂O₄), polytetrafluoroethylene (PTFE), etc., have been investigated as lubricants additives by various researchers to evaluate the tribo-performance of the base oil. As a result, significant improvements in wear resistance and antifriction properties of several lubricants have been achieved, as shown in **Table 2.9**. Baş and Karabacak (2014) have investigated the effect of boron compounds (hexagonal boron nitride (h-BN) and boric acid (BA) in lubricating oil and concluded that boron compound additives reduce the friction in engine oils by forming a boundary or mixed lubrication regimes [72].

Table 2.9: Summary of tribological performance of various types of nanoparticles as lubricant additives

Type	Nanoparticles	Lubricant	Additive Source	APS (nm)	Morphology of additive	Concentration	Test Configuration	Outcomes	References
Composite nanoparticles	$\text{Al}_2\text{O}_3/\text{SiO}_2$	Mineral oil	Synthesized	70	Elliptical	0.05, 0.1, 0.5 and 1.0 wt. %	Four-ball and thrust-ring	In four-ball testing, COF↓ by 20 %, AW↑ by 22 %, whereas in thrust-ring testing COF↓ by 50% (Optimum concentration=0.5 wt.%)	Jiao et al. (2011) [73]
	$\text{ZrO}_2/\text{SiO}_2$	20# mineral machine oil	Synthesized	50-80	Nearly Spherical	0.05, 0.1, 0.3, 0.5, 0.75, and 1.0 wt%	Four-ball and thrust-ring	COF↓ by 16.3%, WSD↓ by 14.6%, (Optimum concentration=0.1 wt.%)	Li et al. (2011) [74]
	Cu/SiO_2	Water	Synthesized	Cu having 20 nm embedded in 2 nm	Spherical Cu encapsulated by silica layer	0.5, 1.0, 1.5 and 2.0 wt. %	Four-ball	AF, AW and EP ↑ (Optimum concentration=1.0 wt.%)	Zhang et al. (2012) [75]

				SiO ₂ layer					
	Cu/GO (Graphene oxide)	Liquid paraffin	Synthesized	Cu=5–10 nm	Spherical Cu anchored onto the surfaces of GO nanosheets	0.025, 0.05, 0.075 and 0.1 wt.%	Four-ball	COF ↓ by 27% and WSD ↓ by 52.7% (Optimum concentration=0.05 wt.%)	Meng et al. (2015) [76]
	La (OH)₃/rGO	Diesel engine oil	Synthesized	-	Lamellar	0.05 and 0.1 wt.%	Ball-on- disc (High-frequency reciprocating rig)	AW ↑ by 40% (Optimum concentration=0.1 wt.%)	Wu Bo et al. (2020) [77]
Rare earth compound-based	LaF₃ (a: LaDTP-10, b: LaDTP-20)	Water	Synthesized	a:19.6, b: 8.5	Sphere like	0.25, 0.5,0.75 and 1.0 wt.%	Four-ball	COF↓, WSD↓ and EP↑ (LaDTP-20 exhibited better results than LaDTP-10)	Zhang et al. (2013) [78]
	LaF₃	Fluoro silicone oil	Synthesized	10-30	Nearly Spherical	0.02, 0.04, 0.06, 0.08 and 0.1 wt.%	Four-ball	AF ↑, EP↑, and WSD ↓ by 17%, 43%, and 42% at 500 N, 600 N, and 700 N, respectively (Optimum concentration=0.08 wt.%)	Hou et al. (2014) [79]

	CeO₂	Castor oil	Commercial	90	Spherical	0.1, 0.25, 0.5 and 1.0 wt./vol.%	Four-ball	AF↑, EP↑ and WSD↓ by 37.4% (Optimum concentration=0.025 wt./vol.%)	Gupta et al. (2018) [80]
Sulphides-based nanoparticles	IF-WS₂	Paraffin oil	Synthesized	100	-	5.0 wt.%	Pin-on-disc	COF↓, WR↓, Roughness ↑	Rapoport et al. (2003) [81]
	a: IF-MoS₂, b: IF-WS₂	PAO 6	Synthesized	a: 100, b: 120	a: rectangular, b: polyhedral	-	Ball-on-disc	COF↓ by 40%, WSD↓, (IF-MoS ₂ exhibited better tribological performance compared to IF-WS ₂)	Yadgarov et al. (2013) [82]
	MoS₂	Coconut oil, Paraffin oil	Commercial	90	Layered lamellar	0.25, 0.5, 0.75 and 1.0 wt.%	Four-ball	AF and AW↑, (Optimum concentration= 0.53 wt.% for coconut oil and 0.58 wt.% for paraffin oil)	Koshy et al. (2015) [83]
	MoS₂	Commercial oil (20W-40)	Commercial	150	-	0.25, 0.5, 0.75 and 1.0 wt.%	Four-ball	LWI↑, WL↑ COF and WSD↓	Srinivas et al. (2017) [84]

								(Optimum concentration=0.25-0.5 wt.%)	
	a: MoS₂, b: MoS₂-ODT	Paraffin grease	Synthesized	-	hair-like thin sheets	0.01, 0.02, 0.03, 0.04 and 0.05 wt.%	Four- ball	a: For MoS ₂ nanosheets, COF↓ by 42%, MWV↓ by 55% at 0.04 wt.%. b: for MoS ₂ -ODT, COF ↓ by 42% at 0.01 wt.%, and MWV↓ by 61% at 0.04 wt.%	Rawat et al. (2019) [85]
Other nanoparticles	CaCO₃	PAO 10	Synthesized	40	hexagonal aragonite form	1 wt.%	Ball-on-block (Optimol-SRV4 oscillating test rig)	AF, AW and LCC↑ under higher applied load, moderate frequency, longer duration time, and lower temperatures	Zhang et al. (2009) [86]
	ZnAl₂O₄	Lubricant oil	Synthesized	95	Similarly spherical	0.05, 0.1, 0.5, and 1.0 wt.%	Four-ball and thrust-ring	COF ↓ by 33% and WSD ↓ by 31% (Optimum concentration=0.1 wt.%)	Song et al. (2012) [87]

	h-BN	SAE 20W 50	Commercial	50	Lamellar	1.0, 2.0 and 3.0 wt.%	Four-ball and piston ring- cylinder liner	In four-ball test, WSD ↓ by 20 % at 1.0 wt.%, whereas, in piston ring- cylinder liner test, wear loss ↓ by 30- 70%	Charoo et al. (2017) [88]
	PTFE	API group I-II and group IV (PAO) base oils	Commercial	230	Nearly spherical	3.0 wt.%	Four-ball and ball-on-disc (optimol SRV III)	AF, AW and EP↑ (Group I based - nanolubricants offered the best EP performance while group IV based- nanolubricant exhibited the worst EP characteristics)	Saini et al. (2020) [89]
<p>APS: Average particle size, AF: Antifriction, AW: Anti-wear, EP: Extreme pressure, COF: Coefficient of friction, WSD: Wear scar diameter, WR: Wear rate, MWV: Mean-wear volume, ↓: Decrease, ↑: Increase/ improvement, LWI: Load wear index, WL: Weld load, LCC: Load-carrying capacity</p>									

2.4. Tribological performance of PAOs-based nanolubricants

Incorporating nanoadditives in PAOs oils would improve friction, wear resistance, load-carrying capacity, and rheological and thermal properties. Multiple nanoparticles have been adopted as an additive in PAOs base oils in the past few years to enhance their tribological properties. Many research studies highlighted the enhancement in tribological performances of PAOs-based nanolubricants. Moreover, it was also demonstrated that the improvement in tribological characteristics is governed by several parameters such as type of nanoparticles, the concentration of nanoparticles, formulation approach, temperature, type of base oil, the stability of additive in the base oil, etc. **Table 2.10** shows the effect of various nanoparticles on the tribological performance of different grades of PAO oils.

Industrial lubricants work under extreme conditions and stress that severely affect their structure, behaviour, and performance. Therefore, the rheological behaviour of lubricants also plays a vital role in selecting the appropriate lubricant for tribological applications. Rheology is the study of the flow of matter under different operating conditions, primarily liquids and semi-solids or solids that flow rather than deform elastically. Various investigations were carried out on the rheological characterization of different lubricating oil, but only a few reported on PAO base oils. It was also reported that the inclusion of a significant dose of nanoparticles in lubricating oil might affect the rheological performance of lubricating oils. Wu et al. (2018) reported that the addition of 1 wt.% MoS₂-NOH (n-octadecyl mercaptan) showed little effect on the viscosity of PAO 10 at 0 °C. In contrast, nanolubricant exhibited a transition from solid-like to liquid-like behaviour in the linear viscoelastic (LVE) regime [15].

Table 2.10: Summary of tribological performance of different grades of PAOs with various nanoparticles as an additive

Nanoparticle	lubricant	Additive source	APS (nm)	Morphology of additive	Concentration	Geometric Configuration	Findings	References
a: CuO, b: ZnO, c: ZrO₂	PAO 6	Commercial	a:30-50, b:20, c:20-30	Spherical	0.5, 1.0 and 2.0 wt.%	Four-ball	EP ↑ (Optimum concentration= a:0.5wt.%, b:2.0 wt.%, c:1.0 wt.%)	Hernández Battez et al. (2007) [90]
CaCO₃	PAO 10	Synthesized	40	hexagonal aragonite form	1 wt.%	Ball-on-block (Optimol-SRV4 oscillating test rig)	COF↓, WV↓ by 83.3%, and EP ↑ from 200 N to 600 N	Zhang et al. (2009) [86]
Ni	PAO 6	Commercial	20	Spherical	0.5, 1.0 and 2.0 wt.%	Four-ball and block-on-ring	COF ↓ by 30%, WV↓by 54 %, EP ↑, LWI ↑ from 201.81 N to 257.59 N (optimum concentration=0.5 wt.%)	Chou et al. (2010) [37]
a: Cu₂S, b: Cu₂S	PAO 6	Commercial	25	Nearly spherical	0.5 and 2.0 wt.%	Four-ball and block-on-ring	a: WV↓ by 31%, EP ↑ by 21.2%, b: WV↓ by 50%, EP ↑ by 8.8 % (Optimum concentration= 0.5 wt.%)	Versca et al. (2011) [91]

a:BN, b: MoS₂	PAO 10	Commercial	a:70, b:50	Spherical	3 wt.% +1 wt.% Benzethonium Chloride	Piston skirt- cylinder liner	COF ↓ (MoS ₂ exhibited best AF performance than BN), WV↓	Demas et al. (2012) [92]
Triazine derivati ve (a: NNBO, b: NN)	PAO	Synthesized	-	Sticky liquid	0.1, 0.3, 0.5, 0.7, 0.9 and 1.2 wt.%	Four-ball	COF ↓, WSD ↓ by 41% with NNBO and 36% with NN, EP ↑ (for NNBO- LCC ↑ from 380 N to 550 N, and for NN- LCC ↑ from 380N to 520N. (Optimum concentration=1.2 wt. % for COF,0.5 and 0.1 wt.% for WSD)	Yang et al. (2013) [93]
LaF₃	PAO 2	Synthesized	10	Nearly Spherical	0.5 wt.%	Ball-on-block (Optimol SRV- 4)	COF ↓, WV↓, and EP ↑ from 100 N to 600 N	Zhang et al. (2013) [94]

a: NGP, b: SWCN Ts, c: MWCN T, d: OLC-L, e: OLC-S, f: DND	PAO 6	Commercial	a:10-20, b:1-2, c:10-20, d:200, e:40, f:4-5	a: Platelets, b & c: tubular, d & e: onion like, f: nearly spherical	0.01-0.015 wt.% for DND and 0.5 wt.% for remaining	Block-on-ring	COF ↓ and WV↓ DND showed the best AF performance, while MWCNTs exhibited the best AW performance (Optimum concentration=0.015 wt.%+0.15 MoDDP for DND)	Nunn et al. (2015) [95]
Bifuncti onal hairy silica nanopa rticles (BHSNs)	PAO 100	Synthesized	100	Spherical	0.5, 1.0, 2.0 and 4.0 wt.%	Four-ball	COF ↓ by 40% and WSD ↓ by 60% (optimum concentration =1.0 wt.%)	Sui et al. (2016) [96]
Graphe ne nanopla telets (GNPs)	PAO 10 based ester blend (95% PAO 10	Commercial	100	Lamellar	0.01, 0.03, 0.05, 0.1, 0.2, 0.5, 1.0 and 3.0 wt.%	Four-ball	COF ↓ by 5% and WSD↓ by 15% (Optimum concentration=0.05 wt.%)	Azman et al. (2016) [97]

	+5 % TMP)							
Mo/B oleic diethan olamide derivati ves i.e. a: YXM, b: YXB	PAO 6	Synthesized	-	-	0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 wt.%	Four-ball	COF ↓ (YXB>YXM), WSD↓ (YXM>YXB), EP ↑ (YXM>YXB) (Optimum concentration=1 wt.% for COF, 2.5 wt.% YXM, 0.5 wt.% YXB for WSD and 3wt.% for EP)	Huang et al. (2017) [98]
Lipophi lic magneti te nanopa rticles (MagN P)	PAO 8	Synthesized	5-10	Nearly spherical	6.7 wt.%	Ball-on-disc (Optimol SRV- 4)	COF ↓ and WV ↓ by 68%	Zuin et al. (2017) [99]
a: Pd, b: Ag	PAO 4	Synthesized	a:2-4, b:3-6	Nearly spherical	0.5 and 1.0 wt.%	Ball-on-flat (reciprocating test rig)	COF ↓, WV↓ Pd nanoparticles outperformed the Ag nanoparticles (Optimum dose=1.0 wt.%)	Kumara et al. (2018) [100]

rGO	PAO 40	Synthesized	60	Lamellar	0.05, 0.1, 0.25 and 0.5 wt.%	Ball-on-disc	COF ↓ by 24.3%, WTW ↓ by 16.7% (Optimum dose=0.25 wt.%)	Liñeira et al. (2019) [101]
a: Modified MoS₂, b: Modified rGO	PAO 6	Synthesized	a: 0.5-5 μm, b: 3-5 μm	Lamellar	0.1, 0.2, 0.3, 0.4	Four-ball	COF ↓ by 48.3%, WSD ↓ by 31.71% (optimum concentration=0.3 wt.% (5:5))	Wang et al. (2020) [102]
a: W, b: h-BN, c: W+h-BN	PAO 6	Synthesized	a: 20-70, b: 10-80	a: Spherical, b: lamellar	0.01 and 0.1 wt.%	Pin-on-plate	COF ↓ by 20%, 30%, 50% and WR ↓ by 93.9%, 95.4%, 99.3% for a, b and c, respectively (Optimum dose=0.01 wt.% for W, 0.1 wt. % for h-BN)	Bondarev et al. (2020) [103]
<p>APS: Average particle size, AF: Antifriction, AW: Anti-wear, EP: Extreme pressure, COF: Coefficient of friction, WSD: Wear scar diameter, WR: Wear rate, MWV: Mean-wear volume, ↓: Decrease, ↑: Increase/ improvement, LWI: Load wear index, WL: Weld load, LCC: Load-carrying capacity</p>								

2.5. Effect of nanoparticle parameters on tribological performance

2.5.1. Effect of nanoparticle particle size

There are three different ways in which nanoparticle size affects the tribological characteristics of nanoparticle-based lubricants. First, the intrinsic mechanical and physicochemical properties of nanoparticles are determined by their size, affecting their tribological properties. For example, the hardness of materials increases with a decrease in the particle size due to a rise in the number of dislocation pileups for crystals with a size of 100 nm or larger [104]. When a harder nanoparticle comes into contact with a softer mating surface, it causes indents and scratches. Therefore, while designing nanoparticle-based lubrication systems, it is vital to consider the size-induced variations in the hardness of nanoparticles. Second, nanoparticle-based lubrication systems must remain in the contact zone to protect friction surfaces during loading and shearing. In this regard, the effect of nanoparticle size may be relevant [105]. For instance, if the characteristic roughness of rubbing surfaces is less than the radius of the nanoparticles, then there is a tendency of the nanoparticles to escape from the contact zone, resulting in poor lubrication. In contrast, if the characteristic roughness is significantly greater than the radius of the nanoparticles, the grooves of the rubbing surfaces can be filled with nanoparticles, make the friction surface sleek and uniform, and lead to improvement in tribological properties. Third, colloidal stability considerably influences the homogeneity of lubricant formulation, which significantly governs their ability to perform reliably and smoothly. Nanoparticles having large specific surface areas and high surface activities are prone to react with one another, causing nanoparticle aggregation and reducing dispersion stability [58].

2.5.2. Effect of nanoparticles concentration

The concentration of nanoparticles is another significant parameter that affects the tribological performance of lubricating oils. In general, there may be an optimum concentration for a given range of nanoparticles concentrations that results in the minimum friction or wear [104]. The possible explanation is that at very low concentrations, the development of a continuous protective film is hindered. In contrast, nanoparticle congestion increases abrasiveness when concentrations are higher than the optimal value. Both of these factors contribute to inferior tribological characteristics [106]. However, the optimum concentration of the nanoparticle in the lubricating oil is system-dependent. Therefore, lubricant formulation must be examined separately for each operating condition.

2.5.3. Effect of nanoparticles morphology

Another vital factor to consider while designing nanoparticle-based lubricants is the morphology of the nanoparticles. Generally, the nanoparticles exhibit five types of morphology, i.e., granular, onion, sheet, spherical, and tube. The spherical shapes of the nanoparticles are more pronounced than granular, onion, sheets, and tubes. This is because of the rolling action of the spherical particles [107]. Furthermore, the pressure encountered by nanoparticles during loading is directly determined by the morphology of nanoparticles. For example, nanospheres experience the most significant pressure for a given load. In contrast, nanosheets experience the lowest pressure because nanospheres make point contact with counter surfaces, but nanosheets establish a planar contact [104].

2.6. The hypothesis of the lubrication mechanism of nanolubricant additives

The examination of lubrication mechanisms of nanoparticles is regarded as a critical parameter to comprehend the role of nanoparticles in lubricants. However, in various

research studies dealing with nanoparticle-based lubrication systems, identifying the active mechanisms remains a topic of discussion. The researchers have suggested multiple mechanisms using surface analysis techniques to illustrate the advancement in lubrication performance by including nanoparticles in lubricating oil. These mechanisms can be divided into two primary categories. The first direct impact of the nanoparticles is the ball bearing/rolling effect and protective/tribo-film formation. Another is the secondary impact which leads to surface improvement by mending effect and polishing effect [108] as depicted in **Figure 2.5**. (The copyright permission certificate of Figure 2.5 is presented in **Appendix E**).

2.6.1. Rolling/ball bearing effect

The spherical, quasi-spherical, or hemispherical morphology of nanoparticles are expected to act like tiny ball bearings which roll in the contact zone. It is assumed that nanoparticles with such morphology transform the sliding friction into a combination of sliding and rolling friction and also sustain a proportion of the applied load. One of the requirements for this mechanism is low-load conditions be maintained between the rubbing surfaces so that the shape and rigidity of the nanoparticles are preserved [96,108,109].

2.6.2. Mending effect

The mending effect, also known as the self-repairing effect, is characterized by the deposition of nanoparticles in the grooves of interacting surfaces and compensation for mass loss [108]. During this mechanism, the rubbing surface can become hardened by sintering and deposition of nanoparticles in the grooves or macroscopic cracks, resulting in diminished abrasion and improvement in the tribological properties of the nanolubricants [110]. The mending effect repairs the cracks on the rubbing surface and controls the propagation of the cracks. Most studies reported on the mending effect have confirmed the

deposition of nanoparticles on the rubbing surface using energy-dispersive X-ray spectroscopy (EDS) analysis.

2.6.3. Formation of the protective layer/tribo-film

In boundary lubrication conditions, nanoparticles dispersed in lubricating oil can form a protective film that decreases the interfacial shear stress between tribo-pairs and protect the surfaces from micro-damage and scratches. The protective film deposited on the rubbing surface is also known as tribo-film. This tribo-film results from physical or chemical interaction between the nanoparticles and the friction surfaces [58].

2.6.4. Polishing effect

The polishing effect, also known as the smoothing effect, is assumed to be produced when the roughness of the lubricating surface is reduced by nanoparticle-assisted abrasion. The nanoparticles may fill the spaces between rough asperities, acting as solid lubricants (nanoparticles) reservoirs within the contact, as shown in **Figure 2.5**. This procedure of filling up rough valleys is known as the smoothing process. This “polishing” or “artificial smoothing” mechanism may enhance the tribological properties primarily due to reducing surface roughness [110].

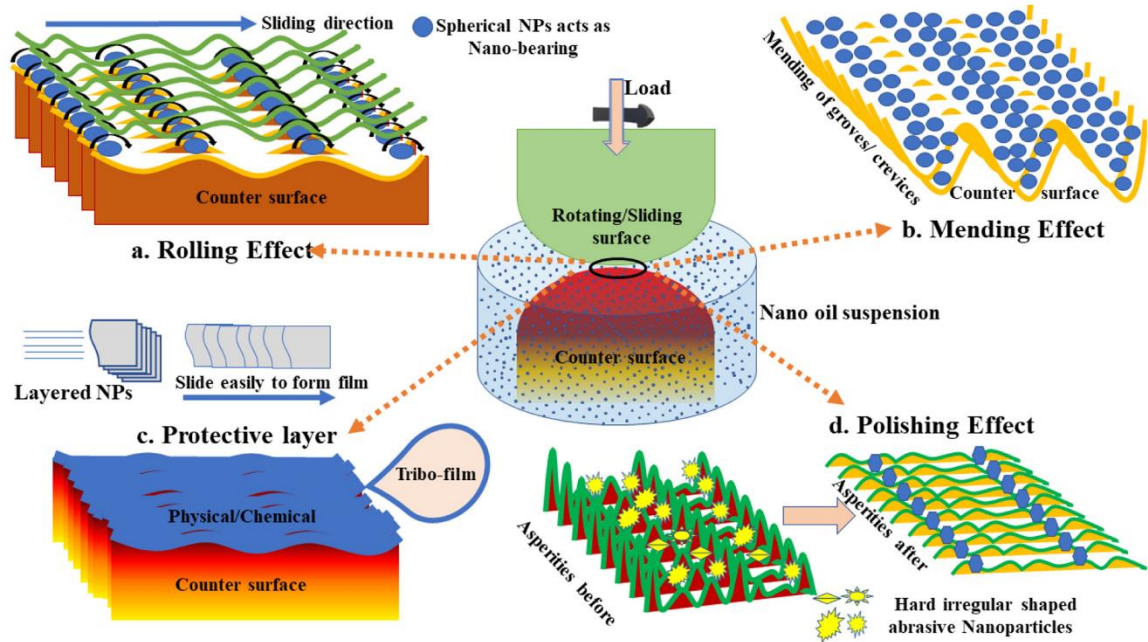


Figure 2.5: Several possible lubrication mechanisms of nanoparticles as lubricants additives [111]. Reproduced with permission from Elsevier- Appendix E.

2.7. Optimization of process parameters

The friction and wear properties of nanolubricants are influenced by various process parameters or control factors such as applied load, the concentration of nanoadditives, sliding velocity, temperature, and viscosity of lubricating oils, etc. Optimizing these parameters to achieve the minimum friction and wear is important from the aspect of cost reduction. Further, optimization helps to identify the most dominant factor that affects the tribological characteristics of nanolubricants. Therefore, several statistical models for the analysis and optimization of tribological parameters have been devised in recent years, such as response surface methodology (RSM), Taguchi method, factorial design, and regression techniques. The Taguchi-based optimization technique has resulted in a unique and powerful optimization methodology that differs from traditional approaches. Thakre and Thakur (2015) applied the Taguchi method to determine the most prominent factor and optimal combination of factors that regulate the tribological properties of nanolubricants. It has been observed that the nanoparticles concentration (contribution 59%) and normal

load (contribution 29%) are found to be more significant factors, followed by sliding speed and nanoparticles size [112].

2.8. Tribological performance of PAOs-based greases

PAOs-based greases are formulated where mineral oil-based greases are unable to fulfil the service requirements. PAOs are one of the most popular high-performance synthetic base oil and offer various intrinsic properties such as high viscosity index, better oxidative and thermal stability, low volatility, lower toxicity, and use in a wide range of temperatures. 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. Schultheiss et al. (2016) have investigated the wear behaviour of grease-lubricated gears under boundary lubrication conditions. The result revealed that the thickener type, especially the additive type, significantly influences the wear behaviour 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 [113]. Shu et al. (2018) have examined the lubricating performance of PAO 10 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 pure greases. Moreover, the polypropylene formulated grease added with a combination of ZDDP and MoDTC additives showed superior lubrication performance compared to lithium complex greases [114]. The summary of some critical literature on the tribological performance of PAOs-based greases with various nanoadditives is summarized in **Table 2.11**.

Table 2.11: Summary of tribological performance of PAO-based greases with various nanoadditives

Base oil	Thickener	additives	Morphology of additive	Size of additive	Optimum concentration	Outcomes	References
PAO 100	Polyurea	a: MoS ₂ , b: KB ₃ O ₅ , c: PS, d: PN	— — — —	— — — —	5.0 wt.%	COF ↓ with all nanoparticles, WR↓ with “a”, “c”, and “d” but WR↑ with “b”.	Wang et al. (2010) [115]
PAO	Lithium soap	CaCO ₃	cubic	l = 45 nm	5.0 wt.%	COF ↓, WSD ↓ and EP ↑	Ji et al. (2011) [116]
PAO 40	Attapulgite /bentonite clay	a: PTFE, b: MoS ₂ , c: CaCO ₃ , d: graphite	— — — —	— — — —	3.0 wt.%	COF ↓ with “a”, “b” and “d” while COF ↑ with “c”. MWV ↓ with “b” while MWV ↑ with “a”, “c” and “d”	Chen et al. (2014) [117]
PAO 40	Bentone soap	graphene	lamellar	t = 1.3 nm	0.1 wt.%	COF↓ by 10.4%, MWV↓ by 25-50%	Fan et al. (2014) [118]
a: PAO, b: mineral oil	Lithium soap, aluminum complex soap	a: RC9505, b: graphite, c: MoS ₂	—	—	a: 4.0 wt.%, b: 4.0 wt.%, c: 4.0 wt.%	Wear ↓ with “a” while wear ↑ with “b” and “c”	Schultheiss et al. (2016) [113]
POA 8	Calcium soap	Phosphate zirconium	—	—	3.0 wt.%	COF ↓, WSD↓, EP ↑	Dai et al. (2017) [119]

PAO 10	Polypropylene soap, lithium complex soap	a: ZDDP, b: MoDTC, c: ZDDP+Mo DTC	— — —	— — —	a: 2.0 wt.%, b: 2.0 wt.%, c: 1.0 + 1.0 wt.%	COF ↓, WSD ↓	Shu et al. (2018) [114]
PAO	Lithium soap	Graphite	Flake type (Platelet)	d= 50 nm, 450 nm, 4 μm, 10 μm	4.0 wt.%	With 50 nm diameter, COF ↓ by 57%, WSD ↓ by 41% EP ↑ by 25%	Kumar, N. et al. (2020) [120]
PAO 40	a: Complex lithium soap, b: polyurea soap, c: complex calcium sulfonate soap	CuO	Nearly spherical	D= 40 nm	1.0 wt.%	COF ↓ WSD ↑ in case of “a” and “c” WSD ↓ in case of “b” (Pure complex calcium sulfonate grease exhibited the best tribological properties)	Wu et al. (2020) [121]

d: Diameter, **l:** Length, **t:** Thickness, **EP:** Extreme pressure, **COF:** Coefficient of friction, **WSD:** Wear scar diameter, **WR:** Wear rate, **MWV:** Mean-wear volume, ↓: Decrease, ↑: Increase/ improvement

2.9. Formulation of the problem

2.9.1. Problem identification

From the above-mentioned literature, it has been observed that the following experimental investigations are needed in the field of lubrication:

- No study was reported comparing the tribological performance of different grades of PAO oils under various lubrication conditions.
- COOH- functionalized MWCNTs and oleic acid-modified LaF₃ nanoparticles are scarcely used as an additive in various grades of PAOs.
- The comparative study on different grades of PAOs by incorporating various nanoparticles is not explored at different contact conditions using various tribo-test rigs.

2.9.2. Motivation

This work is motivated to develop high-performance synthetic lubricants, i.e., PAOs, to succeed the petroleum-based mineral oils. Specifically, numerous mechanical parts work under boundary lubrication in the automobile industry, such as piston-cylinder and submerged gear-box, which require the potential lubricant that can lead to higher performance and reduce frictions and wear, and fuel consumption. In this thesis work, a nominal range of nanoparticle concentration was used to formulate the nanolubricants, which may be efficient and cost-effective.

2.9.3. Problem definition

Nanotechnology has been spread all over the engineering and science domain. The various researchers reported improved tribo-performance of different mineral and synthetic oils with micro to nano-size particles as lubricant additives, but few with PAOs-based

nanolubricants. Because of the past research in the field of nanolubricants, the following research questions must be answered:

- Whether all nanoparticles show good compatibility with all PAO base oil to enhance tribological properties?
- Is there any effect of nanoparticles concentration and shape on tribo-performance on PAO base oils?
- Are all grades of PAOs investigated in the present study have the same affinity with different nano-additives?

All of these questions are being addressed in this work through experimental investigations. Therefore, the objectives of the work were established accordingly.

2.9.4. Objective of work

The following were the objectives of the present research work:

- To investigate the tribological performance of different grades of PAO oils (i.e., PAO 4, PAO 6, PAO 40, and PAO 100) as base lubricants.
- To explore the various nanoparticles-based nanolubricants to verify the tribo-performance in terms of friction, wear, and extreme pressure using different test rigs such as four-ball tribometer, ball-on-disc tribometer, and high-frequency linear-oscillation tribometer (Optimol SRV 5). The details of the investigated additives are as follows:
 - ❖ COOH-functionalized multiwalled carbon nanotubes (MWCNTs), a commercially available lubricant additive.
 - ❖ Oleic acid-modified lanthanum trifluoride (LaF_3), which is synthesized by modified the sol-gel method.
 - ❖ Concentration of additive are 0.025, 0.05, 0.075, 0.1 and 0.15 wt.%

- To study the role of nanoparticles in tribological contexts and understand the mechanism of friction and wear.
- To find out the optimum tribological performance of nanoparticles (i.e., the optimum dose of nanoparticles) in the different grades of PAO oil.
- To explore the dispersion stability of nanoparticles in all PAO grades.
- To optimize the various control parameters by using the Taguchi method to assess the tribological properties of PAOs based nanolubricants
- To explore PAO 100 as a base oil and lithium soap as a thickener for the formulation of greases and examine their physicochemical and tribological performance.

2.10. Justification for selection of different nanoparticles

It is reported that MWCNTs as lubricant additives are effective in many tribological applications by their unique architecture (tubular), high flexural and tensile strengths, high elastic modulus, and excellent thermal properties. The superior mechanical properties and the tubular shape of MWCNTs enable them to sustain high loads in tribological applications. Moreover, hollow-core carbon nanotubes offer slippery as well as rotating action relative to each other. Because of such actions, MWCNTs form close to optimal nano-bearings. LaF₃ nanoparticles were selected because they exhibit relatively low hardness, hexagonal crystal allotrope, high melting point, and good thermal and chemical resistance. Also, LaF₃ nanoparticles have been used as extreme pressure and anti-wear additive in greases and lubricating oil.

2.11. Summary of the chapter

This chapter provides an in-depth understanding of PAO oils, additives, nanolubricants, and their tribological behaviour based on previous research work. The gap in nanolubricants tribology was assessed and consequently defined the objective of the work.