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Functionalization and composition of graphene-based materials: effective approach to improvement tribological performance as lubricant additives

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Abstract

Recently, because friction has a detrimental effect on longevity, effectiveness, and environmental friendliness, it is becoming more and more crucial to reduce friction and wear-related mechanical failures in moving mechanical systems. As a result, researchers are still looking for new materials, coatings, and lubricants (solid and liquid) that help reduce wear and friction. One of the most significant scientific discoveries of this time has been the family of materials called graphene. Researchers have looked into the graphene family of compounds, which provide promise as physicochemically unique additions for various lubrication systems. This review summarizes the studies conducted on the tribological characterization of materials of the graphene group, such as functionalized graphene, and composites of graphene nanoparticle-decorated graphene and other materials. In addition, graphene-family compounds as lubricating additives, open issues, and promising future directions are covered in the article.

Keywords: *Lubricant Additive; Graphene; Tribological properties; Friction*

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1. Introduction

The wear and friction of machine parts frequently result in significant economic losses and carbon emissions, restricting the sustainable growth of human society [1,2]. Therefore, reducing friction and increasing wear resistance are essential. Using lubricants is essential for energy conservation and environmental preservation, in addition to being one of the best strategies to reduce wear and friction. Friction and wear can be decreased by adding lubricant between mating surfaces [3,4]. In light of this, academics have recommended cutting-edge lubricating methods to prolong service life and lower energy loss. The most crucial material is lubricating oil or grease, which is frequently utilized in a variety of contexts. Even though they make up a very tiny amount of the lubricating oil or grease, additives can frequently significantly improve the characterization of the oil or grease in a number of ways [5,6].

Carbon nanotubes have received a lot of attention despite the fact that there have been several studies on inorganic materials because of its inexpensive cost, greatly increased lubrication, environmental friendliness, and anti-wear performance [7-9]. Graphene is very desirable for many applications because of its remarkable mechanical strength, great electrical and thermal conductivity, and other special qualities [10,11]. Due to the low interlayer shear force and small size of the graphene family of materials, they can readily pass through the friction process's friction interface and change the friction pairs' interaction into sheet sliding [12,13]. They can significantly adsorb to friction surfaces and create a stable, protective three-layer coating as a result of their high surface activity, which successfully prevents direct contact with solid friction surfaces [14]. Their high surface activity enables them to strongly bind to friction surfaces and create a three-layer coating that is stable and protective, effectively preventing direct contact with solid friction surfaces. Graphene has a propensity to quickly clump together due to its enormous specific surface area and powerful Van der Waals interactions between its layers [15]. Friction and wear cannot be decreased since only the top of the lubricant has the empty base oil when the graphene additives in the lubricant settle to the bottom. As dispersion stability is seen as being necessary for an excellent lubricant, this affects the performance of the lubricant. Even though graphene offers a lot of potential for a wide range of applications, it is important to remember that it has some inherent limitations due to its lack of band gap and chemical inertness [16,17].

Because of this, scientists are researching how to functionalize graphene through interactions with inorganic or organic molecules, non-covalent interactions, and chemical surface modification [18]. The remarkable lubricating and mechanical characteristics of nanoparticles (NPs) have garnered significant interest. As a lubricant addition, NP has been found to greatly improve lubricating performance [19]. There are many different types of nanomaterials that are used as lubricant additives, including metal-based nanoparticles (such as iron, copper, copper oxide, and molybdenum disulfide), carbon-based nanomaterials like fullerenes, and organic or inorganic materials (such as iron oxide/graphene, copper/graphene, titanium dioxide/polystyrene, molybdenum disulfide/graphene). Graphene and its derivatives have lately become indispensable materials for the development of different techniques because of its remarkable chemical, physical, and three-layer film properties [14,20].

This article reviews recent developments with lubricant additives made from members of the graphene family. It also classifies lubricating additives into materials and explains and analyzes the evolution of research into them in different lubricants. It also describes the structural and synthetic procedures for nanomaterials based on graphene. Both graphene-non-metallic and graphene-metallic nanoparticles are available. Unresolved problems and promising futures for materials from the graphene family as additives are also covered.

2. Synthesis, Structure, and Lubrication Mechanism of Graphene-Based Nanomaterials

The long-standing interest in graphene and the large number of academics working on its synthesis have led to the publication of several ways for the graphite exfoliation into graphene. They can be categorized using both the bottom-up and top-down methods (Figure 1). As carbon sources for the creation of graphene, graphitic materials such fullerenes, nanotubes, and graphite can be chosen [17,21]. By rapidly heating the resulting graphite oxides, they are further expanded into one or more layered graphenes, or by ultrasonically treating them in aqueous solution, they are exfoliated into individual graphene oxide nanosheets. An electrochemical technique for the potentiostatic reduction of graphene oxide was developed by Peng et al.[22] High-quality electrochemically reduced graphene oxide films with adjustable thickness and size were produced by regulating the current, reduction duration, applied voltage, and amount of graphene oxide. In a same situation, Kaminska et al.[23] proposed a straightforward and sustainable technique for the simultaneous non-covalent functionalization and reduction of graphene oxide using dopamine at ambient temperature. As further explained by Cui et al.[24] a new reducing agent system, hydroiodic acid with trifluoroacetic acid, can chemically convert graphene oxide to graphene at low temperatures (i.e., below the freezing point). To enhance the tribological performance and lubricant dispersibility of nanomaterials based on graphene, new production methods must be developed. In general, single-step and multi-step techniques have been documented for producing graphene-based composites and hybrids. [17,25].

The creation of nanomaterials based on graphene has frequently utilized a one-step synthesis methodology. These include chemical deposition, the

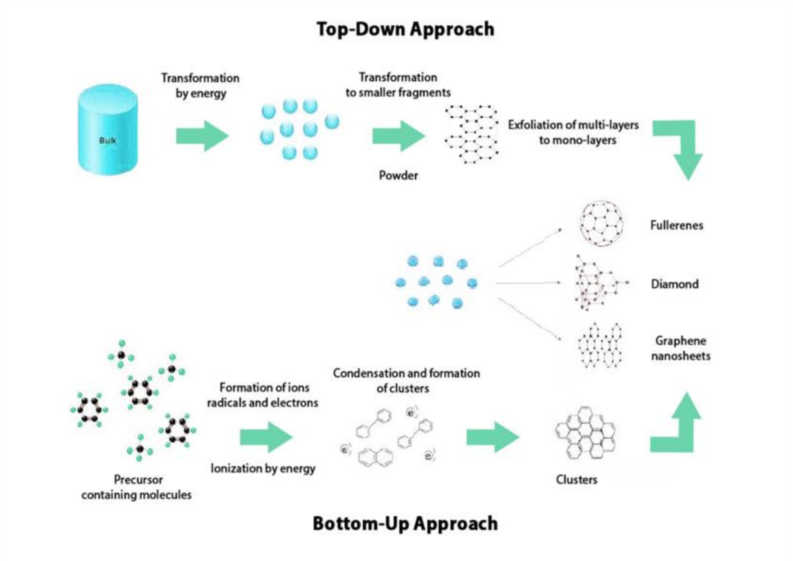

Figure 1. Bottom-up and the top-down approaches in synthesis of carbon-based nanomaterials [26].

hydrothermal technique [27], solvothermal method [28], coprecipitation [29]. reduction method [30], and chemical deposition[14]. Graphene nanosheets can facilitate the growth of crystal cores of modified materials directly on their surface or edge, provided that the right precursors are chosen. The crystal cores can then develop into the required materials in a variety of sizes, such as nanoparticles (NPs), nanorods, nanoblooms, and nanoplates. The capacity to produce materials with high crystallinity without the need for post-treatment, the ability to produce graphene-based nanomaterials without the need for time-consuming procedures, the addition of protective surfactants, or the use of linker molecules are the main advantages of this approach. Using a one-pot hydrothermal process, Zhou *et al.* [31] produced a rGO/ZrO2 nanocomposite. The amount of precursors, such as zirconium oxychloride (ZrOCl2), in the GO dispersion can affect the size of ZrO2 NPs. Graphene-based nanomaterials are often created using multi-step synthetic methods that typically entail prefabrication and reaction procedures. This is a tempting synthetic method for producing nanomaterials based on graphene for use as lubricant additives. Graphene-based nanomaterials with optimum compositions and desirable architectures can be produced by logically designing the multi-step process. Thus, Song *et al.* [32] used a multistep synthesis process to produce MoS2/GO composites. Sodium molybdate was bonded to GO nanosheets in their work, where it decomposed to produce MoO3. L-cysteine might then be used as a reducing agent and sulfur source to further reduce and sulfurize MoO3 in order to produce MoS2/GO composites.

3. Graphene-Based Nanomaterials as Lubricant Additives

3.1 Composites

3.1.1 Metal oxide nanoparticles

3.1.1.1 MoS_2

A large number of layered metal disulfides are known as solid lubricants. These materials have layered crystal structures, which makes it easier for neighboring layers held together by weak van der Waals forces to slide past one another and reduce friction, similar to graphene. One of the most widely used metal disulfides for solid lubrication in dry environments is MoS_2. Its layered structure characteristics, which include covalently bound S–Mo–S trilayers and the presence of inert basal planes in each individual crystallite, account for its excellent tribological performance [33].

graphene nanoplatelets (GNP) and molybdenum disulfide nanoplatelets (MSNP) are two separate 2D materials that Guimarey *et al.* synthesized and employed as additives in the creation of nanolubricants for a steel-steel contact in two different testing configurations (pure sliding and rolling/sliding). As a result, the formulated oil modified with GNP and MSNP as an antifriction and antiwear additive at low concentrations (0.05 wt%) showed significant tribological improvement under pure sliding and rolling/sliding conditions, respectively. Improvements in friction and wear were achieved with stable nano-lubricants without the use of surfactants or functionalizing nano-additives [34].

In a study, Ismail *et al.* produced AGO-C(n)/MoS_2 composites using a hydrothermal technique and examined their tribological characteristics in Group III petroleum-based oil at various weight percentages. Their research resulted in the development of a highly dispersed friction modifier and antiwear additive based on functionalized graphene combined with MoS2. The combination of AGO─C with MoS_2 led to improved tribological performance. It was observed that the tribological behavior was influenced by the mass ratio of AGOC to MoS2. Overall, significant reductions in friction and wear were observed for all synthesized additives, indicating their potential as additive materials in lubricant applications [33].

In the other study, Fan *et al.* used a one-pot hydrothermal technique to produce reduced graphene oxide (rGO)/molybdenum disulfide (MoS_2) hetero-structure nanosheets (rGO-MoS_2-1). The resultant material showed reduced interlaminar shear force, the production of a lubricating thin film, and high dispersion stability in oil. These characteristics collectively contributed to its outstanding tribological performance and provided protection against severe wear for the friction pairs. Due to its unique advantages, the rGO-MoS_2-1 heterostructure shows great potential as an additive in industrial lubricants [35].

3.1.1.2 TiO_2

Because of its low cost, non-toxicity, superior lubricating ability, and extensive application in engineering, nano TiO_2 has become more and more popular as a constituent in engine lubricants in recent years [36].

Zhao *et al.* conducted a study focusing on lubricating oils, where they utilized a hydrothermal method to synthesize titanium dioxide/reduced graphene oxide (TiO_2/rGO) nanocomposites as oil-based lubricant additives. The source of the titanium element was tetra isobutyl titanate. The results showed that the average friction coefficient decreased by 28.4% and wear volumes by 70.7% with the addition of 0.08 weight percent TiO_2/rGO nanocomposites. These nanocomposites showed excellent tribological characteristics at elevated temperatures and showed an extended service life at room temperature and with heavy loads. The creation of a robust multi-gradient tribofilm, the nano-bearing mechanism of TiO_2, and strong dispersibility (facilitating easy and continuous permeation of frictional interfaces) are some of the elements responsible for the outstanding lubricating function of TiO2/rGO nanocomposites [37].

In their study, Wenjie Zhao *et al.* conducted research on the preparation of TiO_2/F-rGO (Fluorinated Reduced Graphene Oxide) nanocomposites using an in situ synthesis method. These nanocomposites were used as additives in lubricants. The findings showed that, in comparison to pure oil, the coefficient of friction (COF) and wear rate were decreased by 33.67% and 88.38%, respectively, when oil containing TiO_2/F-rGO nanocomposites at a concentration of 0.3 mg/mL was employed. In comparison to F-rGO nanosheets, TiO_2 nanoparticles, and a combination of TiO_2 and F-rGO, the TiO_2/F-rGO nanocomposites showed better wear resistance and friction reduction. The TiO_2/F-rGO nanocomposites penetrated the contact areas and formed a protective layer during the friction process, which greatly enhanced the tribological features of the friction pair. Additionally, a synergistic lubricating action between the F-rGO nanosheets and TiO_2 nanoparticles was seen in the TiO_2/F-rGO nanocomposites. This led to improved wear resistance and friction reduction over the use of either F-rGO nanosheet or TiO_2 nanoparticles alone. The protective film generated during friction consisted of two sections: a tribofilm primarily composed of Fe_3C and an oxide film primarily composed of Fe_2O_3. Additionally, the addition of TiO_2 nanoparticles improved the nanocomposites' in-plane mechanical strength because of their ability to support loads, which improved their tribological performance [38].

In a study by Dai *et al.*, the researchers explored the bonding of spherical TiO_2 particles with multilayer graphene in a composite material called graphene-reinforced TiO_2 (MGTC). This attachment process included ball milling with plasma assistance, wet grinding, and surface modification using oleic acid. Anatase TiO_2, expanded graphite, and a wet grinding media were the basic materials used in the experiment. Tribological experiments were performed to evaluate the performance of the resultant products. The results showed that the base oil's viscosity, film thickness, and resistance to wear under high pressure conditions were all considerably increased by the addition of the MGTC composite nanoadditive. The MGTC composite oil, which had 1.0 weight percent of the TiO_2 graphene composite addition, was remarkable for its ability to minimize wear and reduce friction [36].

3.1.1.3 SiO_2

Because SiO_2 nanoparticles are inexpensive, have little influence on the environment, and are simple to prepare, they are frequently added to a variety of base fluids for metal production. The rolling action, mending process, and polishing between tribological contacts are responsible for the remarkable lubricating capabilities of nano-SiO_2 additions [39].

Hongmei Xie *et al.* want to learn more about the tribological characteristics of nano-SiO_2 that was added to GO nanofluids as a partial replacement for GO. They looked at the SiO_2/GO hybrid nanofluids' wear volume and friction coefficient for sliding pairs made of magnesium alloy and steel. The GO/SiO_2 hybrid nanofluids were noteworthy for their exceptional wear resistance, especially when subjected to high loads and demanding circumstances. The GO/SiO2 hybrid nanofluids (with a mass ratio of 0.3:0.2) demonstrated a 50.5% reduction at 5 N and a 49.2% decline at 8 N in comparison to the wear volume of the GO nanofluids. Moreover, the GO/SiO_2 hybrid nanofluids (mass ratio of 0.3:0.2) reduced the wear volume by 46.3% in extreme conditions. This remarkable anti-wear effect is caused by the formation of a dense tribo-film on the worn surface as well as the synergistic interaction between the filling of spherical SiO_2 nanoparticles during the sliding process and the shearing-sliding of the lamellar GO. These mechanisms in the GO/SiO2 hybrid nanofluids successfully minimize wear under high loads and demanding environments [39].

3.1.2 Metallic nanoparticles

3.1.2.1 Cu

Several techniques, including reduced graphene oxide, high-temperature procedures, and Chemical Vapor Deposition (CVD), can be used to produce graphene. Of these techniques, CVD is thought to be the most straightforward and economical way to produce high-quality graphene products. Copper (Cu) is frequently used as the substrate in CVD synthesis because of its easy transferability and poor solubility of carbon and copper at high temperatures [40].

CuO@G, a new nanocomposite made of graphene materials (G) and CuO nanoparticles, was developed by Man *et al.* using copper particles as the main additive material. When compared to the combination of graphene and CuO as well as the individual components (pure CuO or pure graphene materials), CuO@G performed better. The components' synergistic action is responsible for this. The wear scar almost vanished and COF decreased by more than 50% when 0.5 weight percent CuO@G was added to PAO-6 oil. With enormous promise for lubrication applications, the study introduced a promising new technique for creating graphene-based lubrication nanoparticles. Because CuO nanoparticles and graphene sheets interact synergistically, CuO@G demonstrated remarkable lubricating characteristics. Addition of 0.5 weight percent CuO@G to PAO-6 base oil resulted in a considerable reduction of wear rate and COF [41].

Shi *et al.* successfully synthesized hybrid graphene/Cu nanoparticles in a different work by thermally CVD-synthesizing nanographene on copper nanoparticles. The research consisted of two parts: Graphene and nanocopper particles were mixed directly in the first stage to form hybrid graphene/Cu nanoparticles, and the impact of synthesis parameters on the quality of graphene was examined. In the second half, a graphene/Cu/HPMC composite coating was created by combining graphene/Cu hybrid nanoparticles with the biopolymer HPMC (hydroxypropyl methylcellulose). By introducing hybrid nanoparticles, wear and friction coefficients were reduced, leading to excellent tribological performances. The results of the wear tests showed that the macroscopic tribological properties were much enhanced by the inclusion of graphene. Graphene/Cu/HPMC composite films yielded reduced wear volumes and friction coefficients in comparison to Cu/HPMC and pure HPMC composites. The dissipation energy and the surface morphology of the wear scratch verified the delamination of graphene from the surfaces of the copper particles during wear, providing an additional way to accommodate velocity and reduce the wear volume and friction coefficient in the tribological system. Even at modest doses, additives had an effect [40].

Wang *et al.* used an ionic liquid as a lubricant-additive to improve the dispersal stability of synthetic oil, resulting in the development of the $Cu(ReO_4)_2$/Gr composite. The synthesis technique comprised micro-emulsion preparation of copper perrhenate ($Cu(ReO_4)_2$) and ultrasonic processing to attach it to graphene (Gr). Four-ball friction test findings showed that the lubrication performance of a steel/steel pair was greatly enhanced by adding 0.05 weight percent of the $Cu(ReO_4)_2$/Gr additive to the base oil. The composite additive quickly stuck to the contact surface, creating a coating that shielded the friction surfaces from direct contact and efficiently healed wear scars. Strong thermal conductivity and graphene's layered structure also contributed to its improved heat dissipation properties. The native oxides and composite additive at the Si_3N_4/GH4169 contacts combined to provide lubricating properties as the temperature increased. Tribological performance was enhanced at higher temperatures because the protective layer that formed as a result of pressure and friction-induced heat exhibited more stable and consistent deposition on the worn surface. Overall, the $Cu(ReO_4)_2$/Gr composite shows promise as an oil addition for lubricating applications throughout a wide range of ambient temperatures [42].

3.1.2.2 Fe

Compounds containing iron have demonstrated significant promise for lubricating friction. One such substance is iron oxychloride (FeOCl), which uses van der Waals forces to create layers that stack on top of one another. FeOCl's prospective applications have drawn attention in recent years. Microwave-pyrolysis was used in a study by Mengxin Xie *et al.* to manufacture graphene/FeOCl (G/FeOCl) heterojunctions. The investigators investigated the synergistic lubrication of G in liquid paraffin (LP) with FeOCl. The tribological behavior was mostly regulated by the intercalated structure of G/FeOCl. At an ideal dosage of 0.20 weight percent G/FeOCl, the mean wear scar diameter (MWSD) and mean coefficient of friction (COF) of LP were reduced by as much as 44.7% and 66.1%, respectively. In addition, G/FeOCl demonstrated outstanding operational stability, a lengthy service life, and outstanding bearing capacity, highlighting its enormous potential for practical uses [43].

3.1.2.3 Ag

Wang *et al.* introduced a one-step laser irradiation technique for the synthesis of a silver/graphene nanocomposite called L-Ag@rGO. This technique involved attaching uniformly dispersed silver (Ag) nanospheres to graphene oxide (rGO) nanosheets. The L-Ag@rGO composites possessed small particle size and excellent dispersion stability in oil, allowing them to easily penetrate the friction zone. By adsorbing onto the friction surface, the L-Ag@rGO compound formed a protective lubrication film, preventing direct mechanical contact. Moreover, the highly exfoliated layered structure of L-Ag@rGO exhibited outstanding self-lubricating properties. Furthermore, a substantial reduction in wear and friction was achieved through rolling friction's conversion from sliding friction made possible by the distinct spherical morphology of the Ag particles [44].

3.1.2.4 Mu

By modifying graphene oxide with muscovite (Mu) and a silane coupling agent, Zhao *et al.* created a modified graphene/muscovite (MGMu) nanocomposite. Excellent MGMu dispersion stability in oil was achieved as a result of this change. MGMu's lipophilicity made it possible for it to disperse steadily in a base oil over 30 days with little sedimentation. MGMu demonstrated better lubricating qualities than both muscovite (Mu) and graphene oxide (MGO). MGMu, MGO, and Mu improved the lubrication when added as additives to the base oil, which resulted in a lower average friction coefficient than with the base oil. Similar to this, the MGMu, MGO, and Mu oil samples showed lower average wear scar diameters (WSD) when compared to the base oil [45].

It is important to remember that a variety of factors affect the tribological performances of materials in the graphene family, as demonstrated by the statistical information found in Tables 1 and 2 of earlier research. These tables show how little changes in test settings or materials can have a significant impact on tribological performances. Consequently, it is critical to take into account and talk about the variables that may affect the tribological performances of materials of the graphene family.

3.2 Functionalized graphene

To ensure their effective application, it is crucial to functionalize and disperse graphene sheets appropriately. The chemical functionalization of graphene enables processing with the assistance of solvents. This approach preserves the inherent properties of graphene while preventing the clustering or clumping of individual graphene layers during the reduction process [46].

3.2.1 Boron nitride

White graphene, also referred to as hexagonal boron nitride (h-BN), is a substance which may be used in lubrication. h-BN is made up of covalently organized sheets of atomically thin BN, much like graphite does.

Table 1. Statistical data of studies related to graphene-family materials in solid lubrication.

No	Solid lubricants	Test mode	Lubricant	Results		Lubrication Mechanisms	Ref
				COF Reduction	**Wear Reduction**		
1	TiO$_2$/rGO	four-ball tester	pure base oil group II PBO (PBO-GII)	28.4%	70.7%	Protective film	[37]
2	CuPc−(ADB−rGO	four-ball tester	Paraffin oil (PO)	50.80%	55.66%	layered structures	[47]
3	(GO-T154)	ball-on-disk	PAO4	54%	60%	Protective layers	[48]
4	ZrO$_2$@GO	ball-on-disk	Paraffin oil	20.7%	21.5%	Multilayer nanocomposite film	[49]
5	TiO$_2$ + Graphene	four-ball test rig	PAO 20	38.83%	36.78%	Protective layers	[50]
6	(NIL) GO@SiO$_2$	ball-on-disk	water-based (WB)	20.7%	36.6%	tribolayer	[51]
7	Mn$_3$O$_4$@G	ball-on-disk	PAO 6	75%	97%	Protective film	[52]
8	SiO$_2$/G	ball-on-plate	Water	48.5%	79%	Protective film	[53]
9	ZnO@G	four-ball machine	A synthetic ester lubricant (SparkM40)	35%,	32%	Protective film	[54]
10	CeO$_2$/rGO	ball-on-disk	Paraffin oil	15.85%	76.03%	Tribofilm	[55]

Apart from its remarkable solid lubricating properties, its unique chemical, structural, and mechanical attributes have attracted attention as a potential fluidic lubricant. The material exhibits excellent chemical stability against oxidation and high thermal stability, making it suitable as a solid lubricant [56].

In their research, Qi *et al.* investigated the tribological characterization of 3D graphene, 2D h-BN, and their combination in PAO4 oil (polyalphaolefin with a viscosity of 4 cSt at 100 °C) as a potential lubricant for steel-to-steel contacts. The 2D h-BN and 3D graphene dispersed effectively in PAO4 oil and were mixed to create a lubricant for steel-to-steel contacts. The addition of 3 wt% 3D graphene and 3 wt% 2D h-BN significantly reduced the wear rate and friction coefficient under various test conditions. The tribological performance of the mixture of 3D graphene nanosheets and 2D h-BN nanoparticles in PAO4 oil surpassed other combinations with PAO4 oil additives. The combination also exhibited noticeable synergistic lubrication. In other words, using a mixture of 3D graphene and 2D h-BN as an additive in PAO4 oil enhanced the lubrication behavior of the steel contact pair. The frictional effect of the 3D graphene and 2D h-BN mixture varied with different loads. The synergistic lubrication effect was most pronounced at a load of 200 N. The interaction of 2D h-BN and 3D graphene distributed in PAO4 oil produced positive anti-wear properties for the lubricant containing these nanoparticles. The particles in the friction surfaces rolled, polished and self-repaired themselves, leading to facilitation of interaction [56].

Table 2. Statistical data of studies related to graphene-family additives in liquid lubrication

No	**Additive in Base Liquid**	**Test mode**	**Lubricant**	**Results**		**Lubrication Mechanisms**	**Ref**
				COF Reduction	**Wear Reduction**		
1	Modified biodiesel soot/ graphene oxide (MBS–GO)	ball-on-plate tribometer	water	69.7%	60.5%	protective tribofilm	[57]
2	[BMIm][N(CN)$_2$]	ball-disk	PEG200	16%	25.9%	Protective layer	[58]
3	[P$_{66614}$][DEHP]-G	ball-on-plate	Base oil (150 N)	-	~58%	Tribolayer	[59]
4	(GO-EmimN(CN)$_2$)	Ball-on-plate	Water	-	74%	Protective layer	[60]
5	FGO	ball-on-disk	water	41.4%	88.1%	Transfer films	[61]
6	rGO@ODA	ball-on-disc	BIOE oil	34%	71%	Tribofilms	[62]
7	GO/f-CMS	ball-on-disk	engine oil (85W-90)	26 %	54 %	Protective layer	[63]

A study on the application of h-BN solid lubricants and 3D graphene to decrease wear and friction in steel-a-C:H film contact under varied loads was carried out by Qi *et al*. They discovered that the lubricating qualities of 3D graphene and h-BN when utilized independently with a-C:H film were subpar and occasionally even had adverse consequences. Nonetheless, a 1:1 volume ratio combination of 3D graphene and h-BN produced the biggest improvement and decrease in wear and friction. This was explained by the transfer film on the sliding interface forming a more compact and orderly structure [64].

In another study by Samanta and R. Sahoo, an optimized and simple method for exfoliating and chemically oxidizing bulk h-BN powder was demonstrated. Additionally, a chemical functionalization process was carried out to prepare APTMS-grafted h-BN (h-BNAS) by linking oxidized h-BN with (3-aminopropyl) trimethoxysilane (APTMS) as a bifunctional chemical linker. Moreover, h-BNAS's edge sites and basal plane defect were chemically grafted with amino-terminated functional groups using graphene oxide (GO) to create an h-BN/GO nanocomposite (h-BNAS@GO) through covalent contact.

The tribological data revealed that, in lubricating oil, the h-BNAS@GO nanocomposite exhibited significantly superior antifriction and wear resistance properties than h-BN, h-BNOH, and h-BNAS additives under all tested tribological conditions. The macrotribological results showed that the h-BNAS@GO hybrid composite (0.5 wt%) had the best wear resistance performance, reducing the coefficient of friction (COF) significantly (at Pm = 1.95 GPa) by 50.7% compared to the base oil. It also showed a significantly reduced specific wear rate for pairs of steel when sliding in a rotating motion. Additionally, the h-BNAS@GO composite in nanolubricant form demonstrated a considerable wear reduction under microtribological reciprocating sliding circumstances, with a total COF decrease of 41.18% (at Pm = 2.15 GPa) compared to the base oil.

The covalent grafting of GO onto h-BNAS sheets, which enhanced the adhesive capabilities and generated a lubricating barrier at the interfaces, was credited with these improvements. Additionally, it lessened interlayer interaction and encouraged lamellar shearing at metallic contacts. The study showed that under high contact pressure, the ability of h-BNAS@GO nanofluids to reduce COF and wear was more effective compared to other particles. This was ascribed to the adhesion and deposition of composite particles to the metallic substrate in both macro- and microtribological studies, producing a thick, continuous, and cooperative tribofilm at the sliding surfaces. Microscopic and spectroscopic post-tribological analyses of the worn tribopairs verified the formation of a well-organized lubricating tribofilm [65].

3.2.2 Ionic Liquids

Ionic Liquids (ILs) have been a subject of extensive research in the field of tribology, particularly as potential base oil additives and clean lubricants [66]. Researchers have identified a promising IL additive that enhances the tribological properties of turbine oil. The chemical structure of ILs is crucial for their compatibility with non-polar oils. To achieve miscibility with oils, IL cations require long alkyl chains to create non-polar characteristics [66].

In a study by Song *et al.*, a SiO_2@GO@MEIMBScB nanocomposite was developed by wrapping graphene oxide (GO) around SiO_2 nanospheres and modifying them with a 1-methylimidazolium bis(salicylate)borate (MEIMBScB) ionic liquid. The nanocomposite exhibited a core-shell structure and was dispersed in poly(ethylene glycol) 400 (PEG400) as a lubricant additive. The SiO_2@GO@MEIMBScB nanocomposite was successfully synthesized through electrostatic assembly and amidation reaction. Analysis of the wear scar surface revealed that, unlike the SiO_2@GO/MEIMBScB mixture, the SiO_2@GO@MEIMBScB nanocomposite could deposit onto the rubbing surface. This can be attributed to the strong interaction between SiO_2@GO and MEIMBScB on the surface of SiO_2@GO@MEIMBScB, facilitating the adsorption of additives onto the steel surface and the formation of a tribofilm film. The robust bonding capacity of this tribo-boundary film on the steel surface prevents direct contact between the two steel surfaces, resulting in reduced friction and wear [67].

In a work by Hao *et al.*, they bonded silica nanoparticles to graphene oxide (GO) to create a hybrid nanoscale ionic liquid (NIL) GO@SiO_2. In order to display liquid-like behavior without the use of solvents, the hybrid was further functionalized. The inclusion of the NIL GO@SiO_2 hybrid decreased the area of wear scar (AWS) and coefficient of friction (COF) in all tested concentrations. In particular, the COF and AWS of the 4.0 wt% hybrid nanolubricant were lower than those of the water-based lubricant by 20.7% and 36.6%, respectively. Synergistic mechanisms found inside the GO@SiO_2 compound, such as micro-rolling, mending, and polishing, are responsible for the NIL GO@SiO_2 hybrid's improved tribological properties [51].

The use of graphene and ionic liquid (IL) additives in bio-based lubricants was explored in a different study by Hasnul *et al.*, with a focus on dispersion stability, tribological behavior, and lubricating mechanism. Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate was the IL of choice. The mixture of graphene and IL additives demonstrated superior tribological properties compared to samples with graphene additive alone. Trimethylpropane trioleate (TMP) ester's frictional performance was increased by the IL alone, but not to the same extent as when TMP+G+IL were combined. This demonstrates the two lubricating additives' synergistic activity. When selecting an IL as an additive for lubricants, it is crucial to consider the movements involved (static and sliding friction) during application and a wide temperature range, as these factors significantly influence the tribological behavior of IL as an additive [68].

Amann *et al.* conducted a study to optimize the tribological properties of Automatic Transmission Fluid (ATF) oil by using additives. They selected two ionic liquids (ILs) and one IL containing 0.1 wt.% graphene as potential candidates. Among them, the IL known as Trihexyltetradecylphosphonium (2,4,4-trimethylpentyl) phosphinate + 0.1 wt.% Graphene [P_{66614}] [TMPP][G] was identified as the ideal additive to enhance the tribological behavior of ATF oil. Despite slightly higher static friction and coefficient of friction (COF) during the duration test, the wear was significantly reduced. The Stribeck behavior also improved at a temperature of 30 °C and a velocity exceeding 0.8 m/s. However, it was observed that the identified ILs as additives did not uniformly enhance friction coefficients across the entire temperature range, indicating that viscosity is not the primary factor determining tribological characteristics. The interaction between the IL and the surface was suggested to have a significant influence on the observed effects [66].

In their research, Nasser *et al.* examined the effects of combining graphene nanoplatelets (GnP) at various concentrations with three phosphonium-based ionic liquids (ILs) as additives in PAO 32 base oil. The study focused on evaluating their performance in steel-steel contact under mixed conditions at room temperature. The three ILs investigated were IL1 (Trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate), IL2 (Tributylethylphosphonium diethylphosphate), and IL3 (Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate). The findings indicated that the best performance in terms of combined capabilities was achieved by adding both 0.05 wt% graphene nanoplatelets and 1 wt% of either IL1 or IL3, both containing the cation $[P_{6,6,6,14}]^+$. These hybrid lubricants not only enhanced the tribological performance of PAO 32 but also improved the tribological behavior of PAO 32 alone. Consequently, IL1 and IL3, when combined with 0.05 wt% GnP, demonstrated promising potential as additives for PAO 32, offering anti-friction and anti-wear properties [69].

Gan *et al.* employed hydroxyl-terminated ionic liquid coupling agents (ILCAs) to functionalize Multilayer Graphene Oxide (MGO) and improve its dispersity and lubricity in water. The functionalized graphene oxide, known as ILCAs-GO, exhibited better dispersity in water compared to pristine MGO. This was achieved by utilizing ILCAs as a bridge, facilitating potent hydrogen bond interactions between GO and water. As a lubricant additive, ILCAs-GO demonstrated excellent tribological characteristics, particularly in terms of anti-wear capabilities. It significantly reduced wear track width and wear volume compared to DIW and MGO, with reductions of up to 69.5% and 85.4% respectively compared to DIW, and 61.5% and 71.9% respectively compared to MGO. Because of the electrostatic adsorption of ILCAs-GO with the metal ions of the friction pairs, a deposition film of ILCAs-GO developed on the friction interface that demonstrated self-healing and self-wetting properties. This film effectively separated and wetted the tribo-pairs, minimizing material wear [70].

3.2.3 MWCNTs

Single-walled and multi-walled carbon nanotubes (CNTs) are considered one-dimensional nanomaterials due to their large surface area, which gives them unique chemical, physical, mechanical, and biological properties. These properties, including exceptional mechanical, thermal, electrical, chemical, and optical characteristics, have attracted the attention of researchers. CNTs have been investigated for usage in a diversity of tribological applications, like lubricant additives in water and oil [71].

A base oil (15W50) was studied by Kamel *et al.* for its tribological and rheological properties with various concentrations of multi-walled carbon nanotubes (MWCNTs) (0.5, 1, 1.5, and 2 wt%) and a fixed amount of graphene nanosheets (GNSs) (0.5 wt%). The results demonstrated that the addition of the hybrid combination of CNTs/GNs improved the tribological and rheological properties of the base oil. The viscosity and thermal conductivity of the 15W50 oil were enhanced by the incorporation of these hybrid nanoparticles [72].

Mohamed *et al.* investigated the potential use of graphene nanosheets (GNS) and multi-walled carbon nanotubes (MWCNT) as lubricant additives using calcium grease (CG) as the base material without any chemical modification. The study showed that the addition of nano additives significantly reduced the coefficient of friction (COF) and wear scar diameter (WSD), indicating improved lubrication performance. Additionally, the thermal conductivity of the lubricant was significantly enhanced by the inclusion of these nano additives [73].

3.2.4 Fluorinated graphene (FG)

Many studies have been conducted on fluorinated graphene (FG), a promising 2D nanomaterial with special features in electronics, biology, magnetism, and optics. It possesses distinct qualities that differentiate it from other graphene derivatives, including reduced surface energy, increased chemical inertness, improved thermal stability, and lower interlayer shear force, which are expected to enhance lubrication performance [74].

Fluorinated reduced graphene oxide nanosheets (F-rGO) were created in a study by Xiaojing Ci *et al.* by directly gas-fluorinating graphene oxide to various fluorination levels. These nanosheets were then incorporated as a lubricant additive into gas-to-liquid-8 (GTL-8) base oil to enhance tribological behavior. Comparing the effects of adding HF-rGO to pure lubricating oil, it was found that the COF was reduced by 30% and the rate of wear by 90%. Furthermore, the addition of HF-rGO led to a 21% COF reduction and improved wear rate compared to GTL-8 containing rGO [75].

In Wan *et al*.'s work, pure graphite fluoride was converted into functionalized fluorinated graphene sheets (FFGS) via solid ball milling with ammonium carbonate. The interaction between ammonium carbonate and graphite fluoride allowed for the partial substitution of fluorine with nitrogen/oxygen groups and the breakdown of graphite fluoride into nanosized fluorinated graphene sheets. This process performed admirably in a ball-mill environment. The resulting FFGS was more soluble in polar (water) and nonpolar (ethanol and NMP) solvents, and it had incredibly small nanoscale dimensions. The study assessing FFGS as a lubricant additive in lubrication oil found that when added to the lubricant oil, the created FFGS showed good dispersion and stability. Additionally, the lubricant oil's antiwear qualities were markedly improved by the addition of FFGS, suggesting that this additive has a bright future in the field of lubrication engineering [76].

Ma *et al.* developed a microwave-assisted liquid-phase method to synthesize hydroxyl-modified fluorinated graphene (HOFG) with a high fluorine content. By employing microwave heating, they successfully obtained HOFG samples with an abundance of fluorine through a liquid-phase substitution reaction. The researchers investigated the impact of NaOH ratio and reaction time on the chemical composition of the resulting product. Due to the effective preservation of the fluorine content inherited from fluorinated graphene (FG), the HOFG samples prepared in this manner maintained FG's high thermal stability. The water dispersibility tests demonstrated that even with a substantial fluorine content (46 atomic% of F) and a high fluorine-to-oxygen (F/O) ratio, the as-prepared HOFG samples exhibited good dispersion in water. Friction tests revealed that HOFG also contributed to enhancing the friction-reduction and anti-wear properties of water-based lubrication systems. The lubricating performance of HOFG is closely related to its fluorine concentration, along with other properties. The greater the fluorine content of HOFG with suitable dispersibility, the better its performance as a water lubricant [74].

In order to enhance dispersion and lubrication performance, Wu *et al.* conducted a synthesis of sulfonated graphene (SGO) by sulfonating GO. When used as an additive in water-based lubricants, SGO exhibited excellent dispersibility and superior lubrication performance. The addition of 0.2 wt.% SGO increased the viscosity of water by 25.8%. Furthermore, compared to the non-additive lubricant, the application of SGO to the frictional surfaces resulted in a 74% decrease in friction and a 15.7% improvement in wear resistance. SGO demonstrated superior lubricity compared to GO, which can be attributed to the stronger adsorption ability of sulfonic acid groups compared to hydroxyl and carboxyl groups [77].

In a pioneering approach, Liu *et al.* introduced a novel hybrid lubricant additive that combined pyrolytic graphene and serpentine to enhance the tribological performance of paraffin oil. The hybrid lubricant exhibited advanced tribological performance due to the formation of tribofilms consisting of carbonaceous and serpentine components. The wear tracks of the hybrid and base oils showed 3D profiles with furrows. The hybrid additive's remarkable anti-friction properties were demonstrated by the considerable reduction of paraffin oil's coefficient of friction even at a low concentration of 0.2 weight percent. The exceptional tribological characteristics were ascribed to the combined influence of serpentine and pyrolytic graphene on the friction surface [78].

3.2.5 Alkylation

Alkylation is a process that involves grafting alkyl groups onto the surfaces of graphene oxide (GO) and reduced graphene oxide (RGO), resulting in improved mechanical properties [79].

In order to synthesize functionalized graphene oxide (FGO), Han *et al.* attached hydrocarbon chains onto the surface of graphene oxide (GO). Additionally, a gelator known as 1-methyl-2,4-bis(N-octadecylurea)benzene (MOB) was created as well as added to the system to improve the dispersion's endurance. Alkyl FGO, which contained alkyl chains, and MOB, acting as a gelator for GO, were both synthesized for this study. The lipophilic FGO, produced through alkyl functionalization, displayed effective dispersion, and the addition of MOB as a dopant enhanced the long-term stability of the dispersion, as confirmed by a dispersion test conducted over 30 days. The friction test results indicated that the combination of 1.0 wt% IF-WS2, 0.1 wt% FGO6, and 1.0 wt% MOB reduced the friction coefficient and wear scar size by 13.06% and 21.18%, respectively, demonstrating optimal lubrication performance [80].

In a separate study, Wu *et al.* developed an effective method for dispersing graphene in a base oil by chemically modifying graphene with octadecylamine and dicyclohexylcarbodiimide, and incorporating an efficient dispersant. This method achieved remarkable dispersion stability of graphene in polyalphaolefin-6 (PAO-6) lubricant for a period of up to 120 days. Furthermore, the lubricant exhibited significant improvements in tribological performance compared to pure PAO-6. The addition of 0.5 wt% MG (modified graphene) and 1 wt% dispersant together reduced the friction coefficient and wear scar depth by approximately 40% and 90%, respectively, compared to the base oil [81].

Chouhan *et al.* developed aminoborate-functionalized reduced graphene oxide (rGO-AmB) for use in aqueous lubricants. Zeta potential and UV-vis absorbance tests revealed that the high wettability, amino groups in AmB, and residual oxygen functions in rGO were responsible for the remarkable dispersibility of rGO-AmB in water. The water conductivity of rGO-AmB increased by 68% as a result of its exceptional dispersibility and 2D structure. Water infused with rGO-AmB greatly enhanced the steel tribopair's lubricating qualities. The friction and wear track width were reduced by 70% and 68%, respectively, using an optimal dosage of 0.2% rGO-AmB [82].

Ma *et al.* synthesized sulfur-doped graphene oxide (SA-GO) through the sulfurization and alkylation of graphene oxide. SA-GO was found to be an effective green anti-wear additive for engines operating in harsh conditions. SA-GO, at 1.104 weight percent, showed the smallest wear scar diameter (0.25 mm) in the 928 lubricating oil, according to anti-wear testing. Tribological investigations revealed that sulfur-doped graphene oxide (SA-GO) functioned as a potent anti-wear agent [83].

Li *et al.* used chemical bonding to successfully produce functionalized graphene/montmorillonite (FG/MTT) nanosheet, a lubricant additive. Following an investigation into different FG/MTT concentrations, it was found that 0.4 mg/ml had the best results, with a 50.9% reduction in average friction coefficient (FC) and a 19.1% drop in wear scar diameter (WSD). Moreover, the results of the hardness test showed that the grinding surface's hardness increased with the addition of graphene oxide (GO), functionalized graphene oxide (FGO), and FG/MTT [84].

Wenjing Li *et al.* successfully produced reduced graphene oxide (RGO) decorated with the rare earth organic complex Eu(Phen)(OA) using a simple hydrothermal technique. As ligands, phenol and OA modified RGO with Eu^{3+} complexes. π–π stacking was utilized in the hydrothermal procedure to create RGO/Eu(Phen)$(OA)_3$ complex hybrid materials (RGECs). During this process, the decrease of GO and the production of Eu(Phen)$(OA)_3$ happened in turn. Subsequently, the tribological characteristics and application of RGECs as additives in poly-α-olefin base oil (PAO8) were studied. The study concluded that RGECs possess both exceptional wear resistance from Eu(Phen)$(OA)_3$ particles and super lubricity from graphene. Notably, Eu(Phen)$(OA)_3$ particles served as isolators to stop the re-accumulation of graphene nanosheets in addition to contributing to wear resistance [85].

Huo *et al.* studied the impact of the nature and size of graphene nanosheets on tribological performance by alkylating graphene oxide (GO) of various sizes with 1-dodecylamine (DA) and subsequently reducing them. Among the different samples, the smaller-sized DA-GOS, which did not undergo reduction, exhibited the most effective friction reduction and antiwear properties when considering rheological behavior, dispersion stability, and lubricating property. This superior performance was attributed to its monolayer wrinkled structure, smaller size, and abundance of polar groups. However, the lubricating property did not show significant improvement due to notable scratches generated during the initial tribological testing [86].

4. Different oils

Min Xie *et al*. enhanced the lubricity of a wax derived from Codonopsis pilosula by incorporating multilayer graphene. A straightforward magnesium metallothermic reaction was used to synthesize multilayer graphene, which was then incorporated into the wax, designated as P grease, to increase its load-bearing ability and lubricity. The resulting mixture grease, designated as P + Gr grease, exhibited superior lubrication properties. Semi-solid grease and multi-layer graphene combined at room temperature to create a tribo-film with superior lubricity and a large bearing capacity. For AISI 52100 discs, the wear mechanism changed from heavy abrasion and oxidation wear, lubricated by P grease, to light abrasion wear, lubricated by P + Gr grease. At temperatures exceeding 150 ºC, multilayer graphene significantly decreased the friction coefficient, wear, and oxidation of the steel pairs [87].

A quick and scalable approach for generating a graphene additive to improve engine lubricating oil was suggested by La *et al*. Natural graphite was chemically exfoliated in a single step to form graphene nanoplates (GNPs), which were then changed using a surfactant and an organic compound to create a modified GNP additive that is simple to distribute in lubricating oil. The modification process led to uniform coverage of the GNP surface by oleic acid. The modified GNP additive exhibited excellent dispersibility and stability in lubricant oil, remaining suspended for over 30 days without sedimentation. The tribological performance of lubricating oil was greatly enhanced by the addition of GNP, with a maximum reduction in wear scar diameter of 35% occurring at a concentration of 0.05% w/w of the modified GNP. The improved antiwear performance was explained by the formation of a protective graphene layer on the steel surface. Small amounts of the modified GNP additive, which may be generated at low cost, could be used to accomplish this significant gain in lubricating efficiency (around 35% augmentation). This advancement has expanded the application of graphene in reducing energy losses due to wear and friction in mechanical processing and automotive components [88].

The effects of graphene as an addition in n-hexadecane lubricant for a Si3N4-GCr15 friction pair were investigated by Zhang et al. The van der Waals energy between the Si3N4-GCr15 wall regions and the lubricating body was elevated in the presence of graphene. As a result, there was less shear stress between the lubricating body and Si3N4 or GCr15, increased lubricating oil adsorption on the frictional surface, and thicker solid coating on the walls [89].

Raghavulu et al. experimentally investigated the use of graphene nanolubricant additives in vapor compression refrigeration (VCR). They suspended graphene oil nanoparticles in Polyester oil (POE) at various volume concentrations. Increasing the concentration of nanoparticles resulted in higher viscosity and thermal conductivity. The coefficient of friction initially decreased at low concentrations but increased with higher nanoparticle concentrations. The optimal nanoparticle content was found to be 0.010%, which corresponded to the lowest coefficient of friction [90].

Sun *et al.* investigated the effects of varying quantities of carbon-based additives on the tribological performance of the specialty grease IRIS-200BB used in wire ropes through a series of four-ball friction tests. They investigated the fretting tribological behaviors of helically organized steel wires under various lubrication conditions using a specially designed test setup. The study focused on evaluating the impact of varying concentrations of carbon-based additives on the tribological performance of the IRIS-200BB grease. The inclusion of multilayer graphene (MG) or micron graphite (G) in the base grease leads to an improvement in its ability to resist wear, resulting in smaller wear scar diameters compared to the base grease alone. When the base grease is supplemented with 2% MG or 2% G, the COF decreases gradually over time and eventually falls below the COF curve of the base grease during the steady-state phase. This indicates a significant enhancement in friction reduction for both compound greases. The addition of 1% MG and 1% G to the base grease demonstrates noticeable improvements in its tribological characteristics, particularly in short and medium-term friction. However, for prolonged periods of friction, the lubricating effect of this compound grease gradually diminishes [91].

Hou *et al*. evaluated the tribological properties of graphene lubricant additives in two types of diesel oils with different sulfur contents using a high-frequency reciprocating rig (HFRR). The lubricating properties of 0# diesel oil were considerably improved by the addition of graphene lubricant components. For diesel oil with a greater sulfur concentration, the addition of 0.03 weight percent graphene led to a 20% drop in COF and a 28% reduction in WSD when compared to pure 0# diesel oil. Similarly, adding 0.03 weight percent graphene to diesel oil with a decreased sulfur concentration resulted in a 24% drop in COF and a 30% drop in WSD. The creation of a graphene tribofilm in the damaged areas was credited with the improvement [92].

How *et al.* compared the performance of 5W30 PAO+ester completely synthetic oil (SO) with and without the inclusion of graphene nanoplatelets in order to investigate its tribological characteristics. They also looked into how different graphene concentrations affected the oil's tribological characteristics. The least amount of wear and friction was obtained when 0.05 weight percent graphene was added to 5W30 PAO+ester synthetic oil. In addition, the SO+0.05 mixture demonstrated a 34.42% increase in wear protection and a 33.78% decrease in friction when compared to base oil. The creation of a protective graphene coating that lessened surface rubbing was blamed for the reduction in wear and friction. However, higher concentrations of graphene had negative effects on the tribological properties [93].

5. Conclusions and Outlooks

As tiny spheres that can readily penetrate the area of contact with liquid lubricant, the graphene family of materials is generally nano-sized, enhancing wear protection and reducing friction in liquid lubrication. Moreover, the dispersoids included in liquid lubricants perform the role of hard materials capable of eliminating contact surface irregularities. In order to reduce friction and increase wear resistance, the unevenness can be eliminated. This can also result in a flattening of the surfaces and a reduction in surface roughness.

Graphene-based nanomaterials have made significant strides toward becoming lubricant additives, however there are still several obstacles to be overcome: Due to its connection to the instability of liquid-based lubrication systems, dispersal stability is a significant issue that has not yet been entirely solved for additives from the graphene family.

On the othe hand, Because of the friction-induced heat during the friction process, organic modifiers have a tendency to deteriorate, which causes the reaggregation of graphene nanosheets in lubricants. Additional research is needed to better understand the effects of high temperatures on wear and material degradation when using graphene-based additives. The long-term stability of these additives may be significantly influenced by such factors. In the future, it will be crucial to develop new additives that exhibit favorable tribological properties in challenging conditions or diverse environments. For the practical implementation of these additives, large-scale preparation methods and assessments of tribological performance in actual applications are essential. The commercialization of lubrication and wear-resistance technology may use graphene as an addition by solving the aforementioned difficulties.

6. Reference

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