Chapter 39
Carbon-Related Materials for Tribological Application

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Abstract A lot of focus has been laid on the studies of carbon-related materials (CRMs). Owing to self-lubricating properties, high strength, high density, high hardness, and good electrical conductivity, CRMs find a variety of applications. Recent studies have shown that the carbon-related materials have been successfully incorporated in the Al, Mg, Cu and their alloys. Also, they serve as additives in different lubricating oils in order to obtain the improved tribological properties. Further, their use as coating materials also resulted in the enhancement of wear resistant capability of different materials. The aim of this paper is to discuss the recent developments in related to CRMs in field of tribology.

Keywords Carbon · Composites · Lubrication · Coatings · Tribology

1 Introduction

Energy conservation is the most important aspect of sustainable development [1]. Lot of energy is consumed due to the friction between materials under sliding contact. In automobiles, one-third of the losses are incurred in overcoming the friction itself and only one-fifth of the total fuel energy is effectively used to propel the vehicles [2, 3. Tribological studies are aimed at controlling the friction and wear of not only the macro-sized materials but also of the micro-/nano-sized materials [4]. Coatings and surface texturing on the other hand are also the potential ways that can help in reducing the friction [5].

For further reducing of frictional coefficient and wear loss of the materials, small concentration of different additives (anti-wear, extreme pressure, anti-friction, anti-corrosion) are added in lubricants to improve the overall behavior of the lubricating oils. [6, 7. The use of nanoparticles in composite materials is also an important aspect of material development as it results in improved properties (mechanical & tribological) in contrast to the bulk materials [8]. The size and volume fraction of the nanoparticles are key components in this aspect.

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V. Bindhu et al. (eds.), *Proceedings of Fourth International Conference on Inventive Material Science Applications*, Advances in Sustainability Science and Technology,
https://doi.org/10.1007/978-981-16-4321-7_39

Carbon materials are most widely used as additives in bulk material as well as in lubricants because of good corrosion behavior, good mechanical properties, high thermal conductivity and good lubricating properties [9]. Figure 1 shows the number of articles published related to carbon materials in the field of tribology. The data were extracted from SCOPUS database by using the three set of keywords such as carbon + tribology + composites, carbon + tribology + lubrication and carbon + tribology + coatings. Diamond and graphite are the naturally occurring allotropes of the carbon, but they can be synthesized in any size, shape and properties by various physical and chemical methods. Carbon nanomaterials are regarded as most attractive materials for minimizing energy consumption. Apart from the lubricant additives, they can be used as additives in bulk material and for the development of coatings in order to attain the better tribological properties.

Carbon atoms have the ability to form three types of hybridizations and on the basis of that the carbon allotropes are classified in three categories—sp^3 hybridization, sp^2 hybridization and sp hybridization (Fig. 2). Another classification is on the dimensionality—zero-, one-, two- and three-dimensional (Fig. 3). Each of these

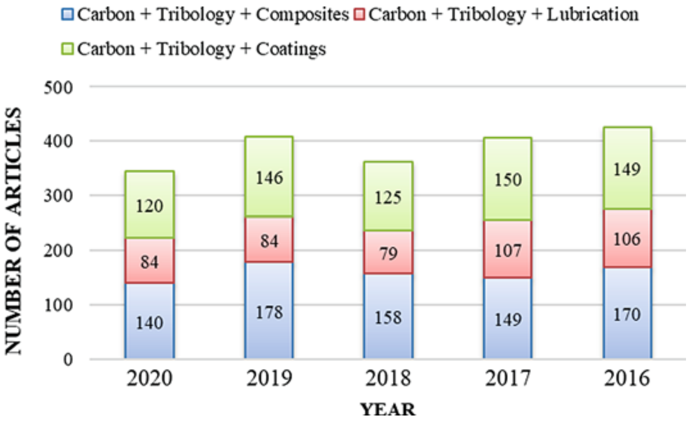

Fig. 1 Number of articles published related to the use of carbon-related materials in last five years. *Source* SCOPUS

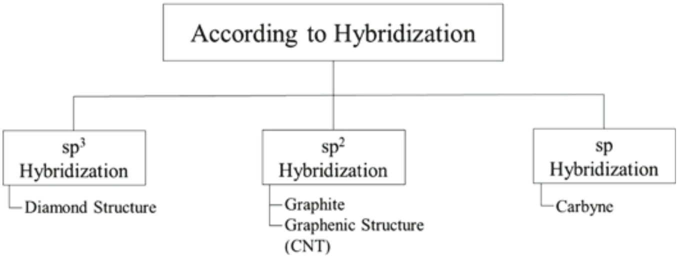

Fig. 2 Classification according to hybridization

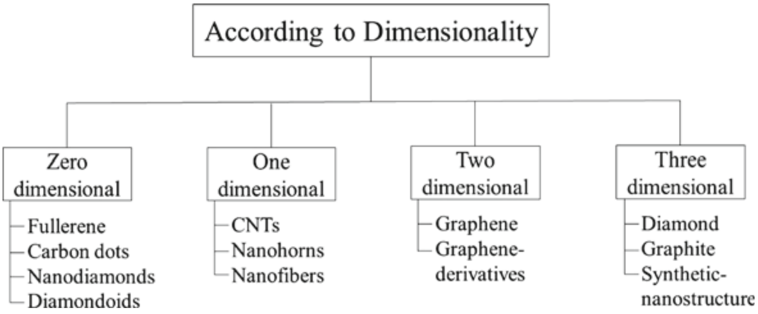

Fig. 3 Classification according to dimensionality

carbon atoms has its own distinct advantages due to which they find their specific application in each field. A brief description of the various carbon atoms used along with their classifications has been presented in Table 1. This paper presents an insight into the different studies carried with the use of carbon related materials. The paper is structured to present the studies related to the use of CRMs in different metal matrix composites. In the next section, their use as lubricant additives in different oils has been presented. Further, their use as coating materials has also been discussed in detail.

2 CRMs as Additives in Metal Matrix Composites (MMCs)

When one or more materials are added in a metal to enhance or tailor its certain properties, it is termed as MMCs. Different types of additives are added to the base matrix for enhancing its mechanical (yield strength, tensile strength, compressive strength, toughness, hardness) and tribological properties (coefficient of friction, wear resistance). In this section, a discussion on the various carbon-based materials in Al-, Mg- and Cu-based matrix has been made.

2.1 Aluminum Matrix Composites (AMCs)

The use of AMCs is one of the active areas in the material development. There is need for the lightweight materials with high mechanical strength and improved wear resistance properties, and different studies have been carried out in this direction [22, 23. Slathia et al. [24] fabricated hybrid composite of AA 2024 reinforced with ZrO_2 (6 wt%) and graphite (1.5, 3 and 4.5 wt%). Density and microhardness decreased while ultimate compressive strength increased with increasing wt% of graphite.

Xiong et al. [25] fabricated graphene nanoplatelets (GNPs)-reinforced AMCs at four different compositions from 0.3 to 1.2 vol.% by spark plasma sintering (SPS).

Table 1 Brief description of the various carbon atoms used along with their applications

Types of carbon atoms	Structure/shape	Hybridization	Particle size (nm)	Advantages & applications
Fullerene (C60)	Spherical with 60 carbon atoms	In between sp^2 and sp^3	0.7 nm	Engineering and Medical industry Offers better lubricating conditions [10]
Carbon dots (CDs)	Quasi-spherical shape	Combined hybridization of sp^2 and sp^3	Below 10 nm	Less toxic, chemically stable and biocompatible Applications in medical and optical industry [11]
Nanodiamonds (nD)	Crystalline	sp^3 hybridized	4–5 nm	Chemically stable, biocompatible & non-toxic Best additive for improving lubricating properties of engine oils
Diamondoids	Cage structure	sp^3 hybridized	1–2 nm	Chemically & thermally stable and biocompatible Good mechanical properties [12]
Single-walled carbon nanotubes (SWCNT)	Single cylinder	sp^2 hybridized	1–2 nm	Energy storage and biomedical applications Thermally stable and conductive [13, 14]
Multi-walled carbon nanotubes (MWCNT)	Several concentric tubular structure	sp^2 hybridized	10–200 nm	Chemically stable and good thermal conductivity Best mechanical and electrical properties Mostly used in energy storage industry [15]

(continued)

Table 1 (continued)

Types of carbon atoms	Structure/shape	Hybridization	Particle size (nm)	Advantages & applications
Carbon nanohorns	Conical cage shapes	*sp*^{2} hybridized	2–3 nm	Porous in nature Improves mechanical properties of nanocomposite Used in biomedical, fuel cells and gas storage industry [16]
Carbon nanofibers	Cylindrical structure	*sp*^{2} hybridized	3–100 nm	Electrochemically stable and porous nature Excellent composite material [17]
Graphene	Hexagonal shape	*sp*^{2} hybridization	25 µm	Chemically inert High Thermal and electrical conductivity Applications in medical industry [18, 19]
Graphene oxide (GO)	Sheet like structure	*sp*^{2} hybridization	1–1.3 nm	Good coating material Biocompatible and highly functionalized [20]
Diamond	Cubic structure	*sp*^{3} hybridized		Best mechanical, lubricating and coating properties Chemically stable and electrically conductive Excellent lubricating and coating material [21]

Chemical bonding improved between the reinforcement material and Al matrix and the load transfer efficiency of the interface has increased. Turan [26] fabricated MWCNT, GNPs and fullerene (C60)-reinforced AMC using semi-powder technique at 0.25 wt% of reinforcement. Enhancement in the yield strength and tensile strength of the composites was observed with the addition of carbon materials. The C60 reinforcement resulted in maximum hardness, tensile strength and yield strength.

Tsemenko et al. [27] fabricated carbon nanostructure (CNS)-reinforced AMC by using powder metallurgy technique and studied the effect of particle size of aluminum powder on the fused carbon nanofibers. İt was observed that prepared matrix resulted in the enhancement of mechanical properties. Liu et al. [28] fabricated graphene nanosheets (GNS)-reinforced AMC by in situ technique. 200% improvement in tensile strength was observed at 2.5 vol.% of GNS. Cavaliere et al. [29] studied the microstructure and the mechanical properties of the AMC reinforced with CNT fabricated by SPS technique at 0.5 and 1 wt%. Higher density was observed at lower wt% of CNT, while the porosity and the tensile strength increased at higher concentration of reinforced material. Kwon et al. [30] fabricated single and dual reinforced AMC with nanodiamond (nD) and MWCNT by mechanical milling and hot pressing technique. Vickers hardness increased by five times, and the flexural strength increased by seven times. From the above studies carried out, it can be observed that addition of various reinforcements can result in the improved mechanical and tribological properties.

2.2 Magnesium Matrix Composites

The use of magnesium matrix composites has also remained an active area of research. In this direction, Say et al. [31] successfully fabricated AZ61/CNT- and AZ91/CNT-reinforced composite by chemical vapor deposition technique. Authors used the different reinforcement at 0.1, 0.2 and 0.5 wt% conc. Increased value of strength was observed with the increase in reinforcement. Further, the maximum corrosion resistance was observed for 0.2 wt% reinforcement.. Du et al. [32] fabricated GNPs-reinforced ZK60 magnesium matrix composite at 0.05 and 0.1 wt% reinforcement by melt stirring, casting and hot extrusion process. Maximum value of hardness was observed at 0.05 wt% reinforcement. Further, it was also observed that yield strength (tensile and compressive both) also increased.

İn another study, Yuan et al. [33] fabricated AZ91-GNS magnesium matrix composite by thermal reduction process at 0.1, 0.3, 0.5, 0.8 and 1.2 wt% of reinforcement. Maximum value of hardness, ultimate tensile strength, yield strength and elongation were observed at 0.5 wt% reinforcement. Turan et al. [34] fabricated fullerene (C60)-reinforced composite using the semi-powder metallurgy technique at 0.5 wt% of reinforcement and studied the microstructure, wear, corrosion and mechanical properties of the reinforced composite. Hardness, yield strength and the ultimate strength increased in comparison with the unreinforced magnesium. Wear rate and COF decreased, while the corrosion rate increased for the reinforced magnesium. In another study, Turan et al. [35] fabricated composite reinforced with MWCNT, GNPs and C60 reinforcements at 0.5 wt% by semi-powder metallurgy. Highest hardness observed for C60 and the MWCNT-reinforced composite exhibited poor corrosion resistance. Thus, from the above studies, it can be determined that addition of reinforcements leads to an improvement in properties (both mechanical

& tribological), but the issues related to corrosion resistance need to be explored further.

2.3 Copper Matrix Composites

Different studies have been carried out with regard to the copper matrix composites. In this direction, Zhang et al. [36] fabricated hybrid composite reinforced with graphene and carbon fiber with fixed 0.5 wt% CF and two contents 0.1 and 0.4 wt% of G reinforcements. Hardness and yield strength increased with increasing wt% of G reinforcement, while elongation decreased. Shao et al. [37] fabricated Cu/GNP-reinforced composite at 0.1, 0.2 and 0.3 wt% reinforcement by electrostatic self-assembly and SPS technique. Mechanical properties increased up to 0.2 wt% reinforcement. Tensile strength and Vickers hardness at 0.2 wt% increased by 27 and 19% as compared to pure Cu. Zhang et al. [38] studied the corrosion and wear behavior of the Cu/GNP-reinforced composite at 0.1, 0.2 and 0.4 wt% reinforcement fabricated by electrostatic self-assembly and SPS technique. Best antifriction properties and corrosion resistance observed at 0.4 wt% reinforcement. Salvo et al. [39] synthesized 1 wt% GNS-reinforced copper matrix composites by sintering technique. 22% improvement in electrical conductivity was observed for composite when compared with base material. At 600 °C sintering temperature, significant improvement in electrical conductivity was observed with insignificant change in mechanical property, but at 700 °C sintering temperature a significant improvement in mechanical properties was observed with a minute decrease in electrical conductivity.

Kumar and Mondal [40] fabricated graphite-reinforced copper matrix composites at 5, 10 and 15 wt% reinforcement by powder metallurgy technique. Wear rate, friction coefficient and density decreased with increasing wt% of reinforcement. Maximum value of hardness for all concentrations of graphite observed at 1000 °C. Compression strength increased up to 5 wt% reinforcement, and after that a decreasing trend was observed. Liu et al. [41] successfully fabricated MWCNT-reinforced copper matrix composites by flake powder metallurgy technique at 0.5 and 1 vol.% reinforcement. 87% increase in tensile strength and 20% in elongation rate for 1 vol.% reinforcement when compared to coarse-grained Cu.

Thus, from the above studies related to the use of CRMs in the MMCs, it can be ascertained that various reinforcements resulted in the improvement of behavior of material. However, magnesium matrix composites resulted in poor corrosion resistance.

3 As Additives in Liquid Lubricants

Reducing frictional and wear behavior of mechanical systems is the major concern in recent studies. For enhancing lubricating properties, certain nanoparticles are added to the base oil. These nanoparticles help in reducing the friction and wear of the machine elements and thus help in improving the life of the sliding components. In this section, the recent studies of various carbon-based additives in different types of oils have been discussed.

3.1 Vegetable Oils

Vegetable oils used for lubrication purpose have resulted in better tribological properties [42]. Different studies have been carried out in this regard [6, 43. Omrani et al. [44] used GNP as nanoadditive in canola oil and studied the COF and wear rate at different concentrations corresponding to varying loads. Anand et al. [19] studied the friction reduction mechanism of rice bran oil with nanoadditives of GNP and TiO_2 and observed the improvement in tribological and thermophysical properties. COF and wear rate were improved by adding the nanoadditives. Zhang et al. [45] used rapeseed oil (RSO) as base and used two additives GO-D (graphene oxide 1-dodecanethoil) and GO-T (graphene oxide tert-dodecyl mercaptan). Coefficient of friction and wear scar diameter decreased by 44.5 and 40.1% at 0.2 wt% GO-D. Krishna et al. [46] formulated a cutting fluid for machining by adding CNT in coconut oil with varying % of nanoparticles inclusions and observed the reduction in cutting force, cutting temperature, tool wear and surface roughness. Sadiq et al. [47] studied the lubricating and thermal properties of coconut oil with nanoparticles of exfoliated nanographene (XnG) at 0.35, 0.7 and 1.05 wt%. It was observed that with the increase in concentration of nanoparticles thermal conductivity and viscosity increased. At 0.35 wt%, minimum value of friction coefficient was observed. Bhaumik et al. [48] used castor oil as base and used micro- and nano-sized additives of graphite, MWCNT and multilayered graphene. Graphene-based oil showed the best anti-wear and extreme pressure properties. Kiu et al. [49] studied the tribological properties of the vegetable oil with additives of GNS, CNT and graphene oxide (GO) at 50 and 100 ppm. Lowest value of coefficient of friction and wear was observed at 50 ppm of GNS. GO at both conc. showed an increase in wear and friction as compared to base vegetable oil.

3.2 Synthetic Oils and Mineral Oils

The use of synthetic oils has resulted in much better lubricating properties owing to their better physical and chemical properties. Lv et al. [50] added 0.5 wt% carbon sphere as additive in 5W30 engine oil and observed the improvement in wear and COF. Pico et al. [51] studied the performance of polyol ester (POE) synthetic oil with 0.1 and 0.5 wt% of diamond nanoparticles and observed an improvement in coefficient of friction and cooling capacity with 4% reduction in friction and 30% reduction in wear.

Paul et al. [52] studied the tribological properties of the dodecylamine-functionalized graphene in 5w-30 engine oil. Coefficient of friction reduced at low speeds for oil with additives, but at higher speeds engine oil served as good lubricant. Raina and Anand [53] studied the friction and wear behavior of PAO (poly-alpha-olefin) synthetic oil containing 0.2% nanodiamond (nD) along with nanoparticles of MoS_2 and WS_2. Coefficient of friction and wear volume decreased by two times as compared to base oil. Raina and Anand [54] studied the influence of various concentration (0.2, 0.4, 0.6 and 0.8 wt%) of nD additives in PAO oil on friction and wear rate. Minimum value of coefficient of friction and wear rate was observed at 0.2 wt% nD additives. Raina and Anand [55] studied the effect of surface roughness and nD concentration on the friction and wear rate of PAO base oil. Minimum value of coefficient of friction observed at higher concentration of nD for rough surfaces, but for smooth surfaces lower concentration of nD showed reduced friction value. In another study by Raina and Anand [56], the influence of nD additives along with copper oxide (CuO) and hexagonal boron nitride (h-BN) in PAO oil was studied. Better frictional characteristics were observed for CuO/nD oil and h-BN/nD oil as compared to single additives in oil. Azman et al. [57] studied the effect of different concentrations of GNP in blended lubricant containing 95 vol.% PAO oil and 5 vol.% palm oil trimethylolpropane ester. 5 and 15% reduction in friction and wear observed for 0.05 wt% of GNP.

Vats and Singh [58] studied the tribological behavior of paraffin oil with GO additives at 0.2 wt% under varying load conditions. GO improved the friction, anti-wear and dynamic viscosity of the oil. COF decreased by 75 and 61.8% in EHD and boundary regime. Majeed et al. [59] studied the tribological properties to improve friction and corrosion resistance of XGnP and Fe_2O_3 nanoparticles in paraffin oil. Yunusov et al. [60] studied the friction and wear behavior of MS-20 mineral oil with nanostructure additives of GO and fullerene soot. Friction force reduced when fullerene soot concentration increased from 0.5 to 2%, but the addition of GO showed no change in the friction force. Khalil et al. [61] studied the tribological properties of paraffinic mineral oil with MWCNT additives at 0.1, 0.5, 1 and 2 wt%. Wear rate decreased by 38% and friction by 49% for mineral oil with MWCNT additives when compared with base mineral oil. Marko et al. [62] added 0.01 wt% nD particles in mineral oil and observed that the average friction coefficient and wear decreased significantly. Peng et al. [63] studied the tribological properties of liquid paraffin with diamond nanoparticles and observed that best values of friction and wear scar diameter observed at 0.5 wt%. Thus, the studies related to the use of mineral and synthetic oils resulted in better tribological properties with the use of different nanoadditives.

4 As Coating Materials

Coatings are deposition of thin films to achieve properties that are not achievable by the base material. Hard coatings are used when the aim is to reduce the wear of the material, and the soft coatings are used when the aim is to reduce the friction.

Multilayered coatings are often used for improving the chemical, mechanical and tribological properties of the materials, and each layer of the multilayered coating has its own distinct function.

Toosinezhad et al. [64] used graphene particles to study the tribological behavior of cobalt-graphene coating. Microhardness increased by 1.6 times as compared to pure cobalt coating and 2.9 times as compared to steel substrate. Mura et al. [65] studied the tribological performance of C40 steel samples with graphene coating using two coatings techniques. Direct growth coated samples for 10 min showed the best wear resistance, and Transferred coated samples gave the least value of COF. Vinoth et al. [66] studied the tribological behavior of vehicle piston rings with DLC coating at different radio frequencies (RF). Better hardness and tribological properties were achieved for DLC at 150 W RF. Siddaiah et al. [67] studied the tribological effect of nickel-graphite (Ni-Gr) coating on steel and found that the presence of Gr in coating aided in reducing the wear and also lowered the friction value. Kim and Kim [68] found that the friction between the 440 C stainless steel ball and plate reduced by 6 times by coating with reduced graphene oxide (rGO) (Table 2).

5 Conclusions

Each carbon nanomaterial has its own properties that help in either one or other way depending on hybridization, dimensionality or uniform dispersion of these nanoparticles in different materials for improving the tribo-mechanical properties of the materials. CNTs, graphite and fullerene are among the most promising materials as nanoadditives for MMCs. They help in improving the strength, hardness and coefficient of friction of the MMCs. Nanodiamonds, CNT and graphene as nanoadditives in oils aimed at achieving the superlubricity. Among the various CRMs fullerene, CNTs, nanodiamonds and graphene are most widely used nanomaterials as they are stable, non-toxic and biocompatible. Carbon-based materials owing to their excellent properties can be explored further for use in different tribological applications. The concept of hybridization with other materials and developing materials, coatings and additives can yield good results. The effect of various parameters, underlying theories and mechanisms needs to be studied further to widen the application area of the carbon-based materials.

Table 2 Comparison of the different studies carried out using different techniques

Author	Material & method	Study purpose	Outcomes
Ogawa et al. [69]	Carbon nanofiber (CNF)-reinforced AMC by ball milling and SPS technique & powder extrusion at 0.5, 1, 2, 3, 4 & 5 vol.% CNF	Study & compare the thermal conductivity & tensile strength of the AMC fabricated by two techniques	Higher thermal conductivity observed for AMCs fabricated by powder extrusion and decreases with increasing vol.% of CNF Lower tensile strength by SPS technique
Yuan et al. [70]	AMC reinforced with CNTs at 0, 1.5 and 3 wt. % by flake powder metallurgy technique	Study the mechanical properties of the fabricated AMCs	Hardness, yield strength and ultimate tensile strength increased with increasing wt. % of CNTs
Ghasali et al. [71]	Fabricate AMC reinforced with graphene (1 wt%) & CNT (1 wt%) by SPS, microwave and conventional method	Study and compare the bending strength and microhardness of composites fabricated by all techniques	Maximum bending strength and density observed for AMC fabricated by SPS technique Maximum microhardness observed by AMC fabricated by microwave technique
Meng et al. [72]	Fabricate AMC reinforced with graphene by hot-press sintering at 580, 590 & 600 °C	Study the microhardness, wear & COF of fabricated AMC samples	Highest microhardness observed at 600 °C sintering temp COF & wear rate decreased with increase in sintering temp
Sedlák et al. [73]	Fabricate B_4C/GPLs composite by sintering technique	Study the effect of graphene platelets (GPLs) reinforcement (0.5, 1, 2, 4 & 6 wt%) on B_4C composites	Highest value of hardness observed at 0.5 wt% GPLs and lowest at 4 wt% COF have not varied much but wear rate decreased with increasing wt% of GPLs
Li et al. [74]	Fabricate CNT-reinforced Mg matrix composite by in situ synthesis and powder metallurgy process at 2, 4, 6 & 8 wt% reinforcement	Study the mechanical properties of the fabricated composite	Breaking elongation, UTS & microhardness by in situ process composite increased by 31.3, 33.4 & 43.5% Mechanical properties of composite fabricated by in situ process were superior than traditional process

(continued)

Table 2 (continued)

Author	Material & method	Study purpose	Outcomes
Wang et al. [75]	Fabricate graphene nanocrystallite embedded carbon nitride (GNECN) coating by plasma sputtering system	Study the friction behavior of graphene coating in ambient and Nitrogen gas	High friction coefficients observed in ambient air while very low friction coefficients observed in N_2 gas
Song et al. [76]	Fabricate MoS_2-GO composite by simple hydrothermal method	Study the tribological properties of fabricated composite in sunshine oil	Lubricity improved (friction & wear reduced) by adding MoS_2/GO composite in sunshine oil MoS_2/GO composite protected the contact interfaces from damaging
Gupta et al. [77]	Mixed the particles in modified canola oil	Effect of MoS_2 particles in canola oil	Improvement in COF and wear by the addition of particles Film formation led to the improvement in tribological properties

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