IOP Conference Series: Materials Science and Engineering

PAPER • OPEN ACCESS

A review on graphite and hybrid nano-materials as lubricant additives

To cite this article: Gautam Anand and Prateek Saxena 2016 *IOP Conf. Ser.: Mater. Sci. Eng.* **149** 012201

A review on graphite and hybrid nano-materials as lubricant additives

Gautam Anand and Prateek Saxena

Industrial Tribology, Machine Dynamics & Maintenance Engineering Centre (ITMMEC), Indian Institute of Technology Delhi, New Delhi, India

E-mail: pra.9000@gmail.com

Abstract. The paper presents a review on use of nano-particles as lubricant additives. Nano-particles have a strong potential to improve the lubrication property of grease when they are used as additives. Nano-grease has several advantages such as improved frictional behaviour, high load bearing capacity and reduced wear, as compared to base oil grease. Current advancements, limitations and challenges in use of nano-grease as a lubricant are discussed. Although, nano-grease has shown outstanding results, more research is required in this field for the commercialization of technology related to nano-grease.

1. Introduction

Friction is an essential feature of contacts in motion. It leads to frictional heat generation and wear which alters the properties of sliding pair. Mechanical components are prone to failure due to wear and thermal fatigue. Friction is a necessary evil, which can't be avoided but can be controlled. Use of lubricants for controlling the harshness of friction dates back to 2400 BC. During the time of construction of pyramids in Egypt, water was used as a lubricant in transportation of stones [1]. Later, oil derived from vegetables and livestock was used as lubricant. Exploration of petroleum resources after industrial revolution lead to use of mineral oil and other petroleum products as lubricants.

Based on their physical state, lubricants are divided in three categories- liquid, solid and semi-solid. Grease falls under the category of semi-solid lubricant. Grease consists of a **base oil** and **thickeners** [2]. Thickeners are generally soap that are metallic salts of fatty acid [2], [3]. More than 60% of grease produced in the world is lithium soap based grease [3]. There are two categories of conventional additives which are used during formulation of grease, to enhance its performance. First category of additives are anti-oxidant and scavengers. They perform in the bulk of grease. The second category of additives perform at surface of grease, these are anti-wear agents, corrosion inhibitors, extreme pressure agents, friction modifiers, metal deactivators etc. [4]. Desire of high load bearing capacity and improved frictional characteristics through additives has attracted the attention of several researchers in the recent years.

Nano-particles as additives are being looked as performance enhancer of lubricants including grease. Increased surface area to volume ratio impart some excellent physical properties to nano-particles. Nano-particles added grease also called as nano-grease can be a promising solution in achieving the desirable characteristics. In this paper, the authors have presented various aspects of nano-grease to be used as lubricant.

2. Nano-additives in semi-solid lubricants

There is a wide range of additives available that can be used in either micro or nano forms. However, it's not possible to use all the additives in their nano form, due to problems such as agglomeration of particles. Nano-additives are mainly inorganic nano-particles, carbon-based nano-particles and hybrid (surface capped) nano-particles.

Inorganic nano-particles include pure metals, metal-oxides, metal-sulphides, metal-fluorides etc. Metal nano-particles have practical limitations of oxide formation in open environment. The limitation can be overlooked by surface modification/capping using certain organic compounds [5], [6]. Surface modified inorganic material functionalized/coated with organic material together is termed as hybrid nano-particles. The organic part of hybrid material system improves their flexibility and stability, while the inorganic part is responsible for hardness [7]. Materials reduced to nano-scale exhibit increase of surface energy with particles [8]. Higher surface energy of nano-particles leads to their agglomeration. [6]. Surface modification helps to reduce the degree of aggregation.

Alkali metal fluorides such as CaF_2, LiF_2 and BaF_2 have low shear strength and stable thermophysical and thermochemical properties at elevated temperature. At low temperature alkali fluoride remains in brittle state but at high temperature they undergo transition from brittle to plastic state. The plastic state at elevated temperature makes nano-additives good to be used in lubricant which operates in high temperature range [9]. Carbon based nano-particles are mainly graphene and fullerene. The shape and structure play an important role in the selection of nano-additives. They influence the functionality of nano-particles in lubricant. In analogy to fullerene, inorganic materials are also developed into these close caged structure, mainly soccer or nanotube, known as 'IF nano-materials'. The IF materials are synthesized from layered inorganic materials such as WS_2, MoS_2, TiS_2 etc. [10]–[13]. Graphene is one-atom thick, 2D planar material of graphite with excellent physical, electrical and thermal properties [14]–[16]. Layered structured materials such as MoS_2 [17] and graphene [18] are used as friction modifier in lubricants .

In order to find suitable nano-additives for grease many nano-particles are tested and reported in literature. These tested nano-particles as additives include CaF_2 [9] , nano-calcium borate (NCB) [19], nano-titanium dioxide [20], [21], CuO [21], nano-silicon dioxide [20], nano-calcium carbonate [22], graphene [18], [23], graphite [18], carbon nanotubes [24] and MoS_2 among others. There are several challenges for use of nano-particles as additives. The biggest challenge is to avoid the agglomeration of nano-particles into grease in order to ensure the uniform dispersion throughout. Therefore, the method of mixing of the nano-particles is a subject to research. The functional improvement of nano-grease is subjected to concentration dependency of nano-additives. Nano-additives can improve the tribological performance of grease but only up to a certain limit. If the concentration is increased further, the tribological performance of grease deteriorates. At higher concentration, nano-particles form micro-clusters due to their tendency to get agglomerated.

3. Preparation of nano-grease

Many researchers have investigated and reported the different methods for preparation of nano-grease. The most commonly used method is the 'Direct mixing method'. In this method, the nano-particles are directly mixed with grease under heavy mechanical stirring [25]. Additionally, in some studies, mixture is passed through three-roll mill for homogeneous dispersion of nano-particles in grease [19]; while in few cases mixture is sonicated using an ultra-sonic probe [26]. Time duration for mechanical stirring and number of times of passing of grease through three-roll mill vary in different cases. In some studies, at first the base oil of grease is sonicated with nano-particles to prepare a dispersion. This dispersion is then poured into a three roll mill and finally grease is prepared from dispersion of base oil and nano-particles by conventional methods [27].

In another method, nano-particles are first mixed with a reagent and sonicated to break the agglomerates of nano-particles to prepare a dispersion. Mixing of nano-particles with a reagent also prevent its oxidization in air and form an additive solution [28]. This dispersion is then added drop wise in hot liquefied grease under heavy mechanical stirring. [23]; or dispersion is mixed in the solution of appropriate solvent of grease [24]. The reagent or solvent gets evaporated in the environment. Finally, mixture is allowed to cool in normal environment conditions to obtain nano-grease.

4. Characterization of nano-grease

4.1. Physical properties

Grease is characterized in terms of its load carrying capacity. Load carrying capacity of CaF_2 added lithium grease showed improvement up to 48% as compared to base lithium grease [9], whereas the load carrying capacity of nano-calcium borate (NCB) added grease exhibited better load carrying capacity as compared to lithium grease [19]. In the research work done carried out by Zhao et al. [19], pure lithium grease was not able to provide effective lubrication above the load of 300N. However, grease with 6% wt. NCB exhibited better lubrication properties up to 600 N.

The study of lithium based grease when added with CeF_3 nanoclusters surface capped with oleic acid showed improved load bearing capacity as compared to base lithium grease [29]. Studies of $CaCO_3$ nano-particles [30] and multilayer graphene [18] as additives to lithium grease and bentone grease, respectively, registered improvement in load carrying capacity of base lithium grease. Further, use of nano-TiO_2 and nano-SiO_2 as additives, were not able to improve the load carrying capacity of titanium complex grease [20]. Thus, the ability to improve load carrying capacity by addition of nano-particles depend upon the correct combination with the type of grease.

4.2. Rheological properties

Rheology of grease is affected by use of nano-additives [31]. The rheological properties are determined by measuring them in either static condition or steady state (dynamic) conditions [31], [32]. Static condition rheology is measured at very low shear rates. At low shear rate, the grease has solid-like or very high viscous behavior; which can be characterized by several consistency tests. Consistency determines flow and sealing property of the grease. The characteristic grease consistency is usually determined by the cone penetration test.

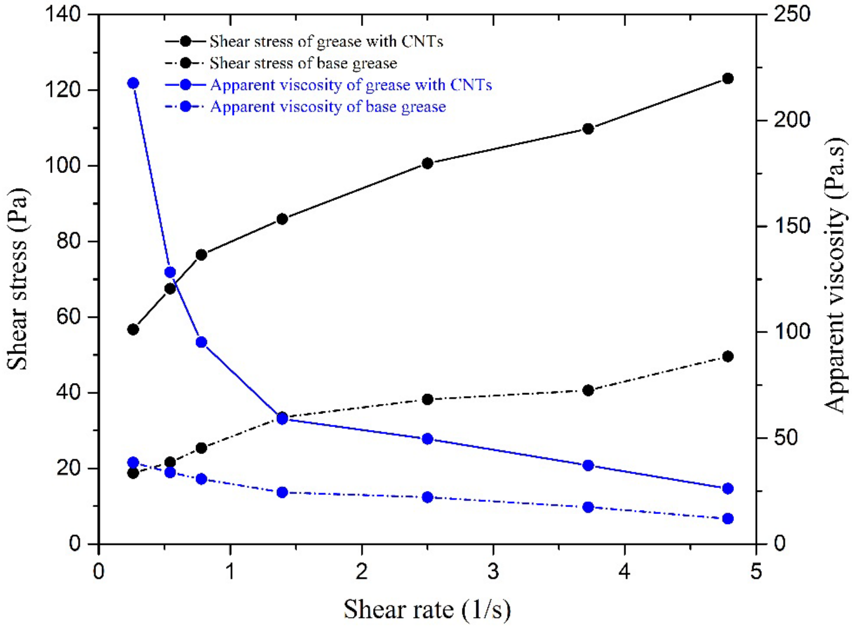

Figure 1: Variation of shear stress and apparent viscosity with shear rate on addition of CNTs

Increase in consistency of grease after addition of nano-particles is reported in literature. Addition of nano-calcium borate [19] to lithium grease showed slight decrease in unworked penetration. The variation in consistency of grease effect the replenishment of grease into contact [33]. The cone penetration test by itself is not sufficient enough to estimate the real consistency at dynamic condition, as it ignores the non-Newtonian flow behaviour of grease. The steady state rheological properties is determined at a relatively high shear rate; to observe viscous behaviour with possible shear thinning. Mohamed et al. [31] studied rheological behaviour of carbon nanotubes added lithium grease. Figure 1 shows variation of shear stress and apparent viscosity with shear strain for lithium grease with addition of carbon nanotubes. It can be seen that shear stress and apparent viscosity can be increased up to 67.3% and 81.8% approximately for CNTs added grease as compared to base lithium grease.

4.3. Thermal conductivity

High thermal conductivity of grease is a desirable property in application of grease as thermal interface materials (TIM) in electronic components. Depending on the combination of nano-particles and grease, thermal conductivity of nano-grease may increase or decrease. CuO, Al_2O_3, TiO_2 and Multiwall carbon nanotubes (MWCNTs) as nano-additives to Mobilgrease-28 showed an improvement in thermal conductivity of nano-grease; on the other hand thermal conductivity was found to decrease for nano-grease based on Uniflor-8623B (grease) [26]. Nam et al. [25] added nano-particles of Ag, Al_2O_3, CuO and MWCNTs to thermal grease (YG-6111) and reported enhancement in thermal conductivity. Among all the other tested nano-additives, MWCNTs was found to be the best additive to enhance the heat transfer capacity of base grease.

Chen et al. [34] reported better thermal transport capacity of carbon nanotube added silicon thermal grease as compared to base silicon grease. Yu et al. [35] studied graphene and graphene oxide based silicon thermal grease and reported that nano-additives are able to enhance the thermal conductivity of base silicon grease. The relative performance of graphene and graphene oxide is concentration dependent. Reduced graphene oxide was able to provide better heat transfer capacity as compared to graphene, at the concentration approximately 1% vol.; but at higher concentration graphene was found to perform better. Graphene (4.25% vol.) added silicon grease was able to increase heat transfer capacity up to 668% compared to base silicon grease. Thus, suitable choice of nano-particles should be made depending upon whether increase or decrease in the thermal conductivity of grease is desired in the application.

5. Lubrication mechanism

The improved tribological performance of nano-grease is attributed to formation of boundary lubrication film. The lubricant film contains nano-particles on the mating surfaces. The mechanism takes place in three stages [9].

Initially, during stage-I rubbing surfaces come in contact through asperities. The gap between asperities is filled by nano-grease providing a lubricating effect. Further, CaF_2 nano-particles are deposited on the rubbing surfaces (stage-II). The low shear strength of CaF_2 due to its low size results in reduction of coefficient of friction. The micro-point of contact has high surface pressure and high temperature, felicitating a complex tribo-chemical reaction. The reaction product together with CaF_2 nano-particles form a complicated wear resistance film on the rubbing surface, which offers the excellent lubrication at the contact (stage-III).

The mechanism of film formation is verified and reported by several authors [9], [19], [21], [22] using X-ray photoelectron spectroscopy (XPS) and/or Scanning electron microscopy (SEM) analysis of the rubbed surfaces after friction test. The results of XPS analysis of rubbing surfaces showed that the boundary lubrication film is composed of deposited NCB and reaction products such as B_2O_3, CaO and iron oxide [19]. The study of layered structured material, such as graphene and MoS_2, as additives in grease show good ability to form conformal protective layer on rubbing surfaces [18], [23], [36]. The planar structure and nano-spaced layer facilitate easy shearing between contacts due to weak vander-wall forces between layers [11]. Further, in the case of IF-materials which are spherical in shape, micro ball-bearing rolling of IF-nano-particles, which reduces contact area may also contributes to improvement in frictional properties of nano-grease [13], [17].

6. Tribological evaluation of nano-grease

Wang et al. [9] evaluated the tribological properties of CaF_2 nano-crystals as lithium grease additives on a four ball tester. Reduction of 29% and 19% in wear scar diameter and friction, respectively was reported. The improvement in tribological properties of CaF_2 added grease is not proportional to concentration of CaF_2. In general, there exists a limiting value (optimum concentration) of nano-additives up to which tribological properties can be improved as shown in figure 2 and figure 3.

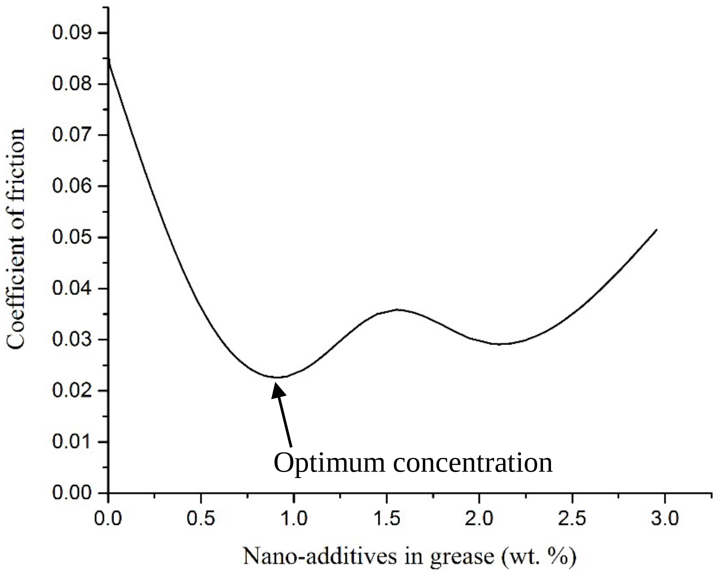

Figure 2: Variation in coefficient of friction with concentration of nano-additives in grease

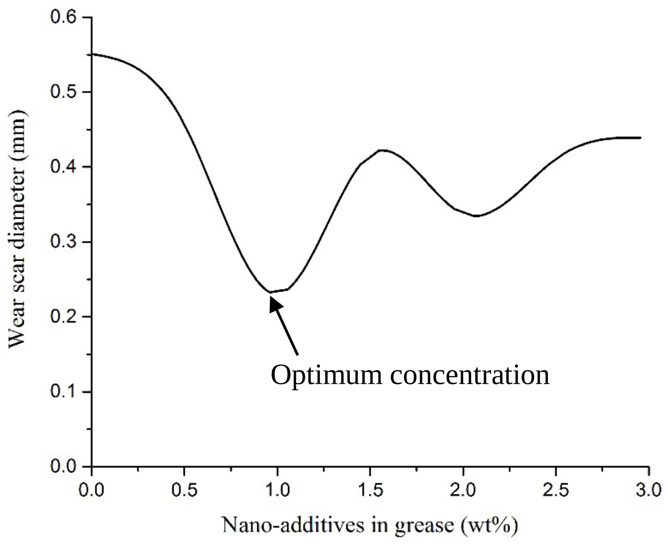

Figure 3: Variation in wear scar diameter with concentration of nano-additives in grease

Zhao et al. [19] evaluated nano-calcium borate (NCB) as additives in lithium grease on an Optimol SRV-IV oscillating reciprocating friction and wear (SRV) tester. They found excellent anti-wear and friction reducing properties subject to an optimal concentration of 6% wt. NCB in lithium grease. The worn surface lubricated with lithium grease shows wider wear scar with deep grooves and wear debris on rubbing surfaces showed relatively small, smooth and shallow wear scar for steel disc lubricated with 6% nano-additives. Table 1 shows influence of different additives on tribological behaviour of the grease.

Table 1: Effect of additives on tribological behaviour of the grease

Type of grease	Type of additives	Effect on tribological behaviour	Reference
Titanium complex grease	(a) Polytetrafluoroethylene (PTFE) (b) Nano-titanium dioxide (c) Silicon-dioxide	Excellent friction-reduction and anti-wear properties with an optimum concentration of approximately 2.0%, 0.5% and 1.5% wt. for PTFE, nano-titanium dioxide and nano-silicon dioxide, respectively.	[20]
Lithium grease	(a) Graphene (b) Graphene oxide (c) Graphite	Decrease in coefficient of friction by 30%, 40% and 60% for grease based on graphene oxide, graphite and graphene, respectively.	[23]
Bentone grease	(a) Multilayer graphene (MLG) (b) Ionic liquid (c) Graphite	Improved friction and anti-wear properties in (a) as compared to (b) and (c)	[18]
Lithium grease	Carbon nanotubes	With 1% wt. of CNTs added, 81.5% decrease in friction and 63% decrease in wear scar diameter was reported.	[24]
Lithium grease	(a) TiO_2 (b) CuO	Improvement in frictional behaviour up to approximately 40% and 60% for TiO_2 and CuO respectively.	[21]

7. Conclusion

Nano-particles as additives are able to modify the functionality of base grease. Nano-grease has better frictional property and anti-wear property. The tribological improvement of nano-grease is not proportional to concentration of nano-particles. There exist an optimum concentration of nano-particles up to which grease is able to perform better as lubricant. Physical property and thermal conductivity may also improve due to addition of nano-particles in grease. The enhanced lubrication property of nano-grease is attributed to film formation containing nano-additives on the contact surfaces. The boundary lubricant film prevent metal to metal contact and facilitate easy shearing between contact surfaces. This shows nano-particles as an excellent additives to grease with ability/potential to improve its tribological performance.

8. References

[1] K. Holmberg, P. Andersson, and A. Erdemir, “Tribology International Global energy consumption due to friction in passenger cars,” *Tribiology Int.*, vol. 47, pp. 221–234, 2012.
[2] E. F. Jones, “The manufacture greases and properties of lubricating,” *Tribology*, vol. 1, no. 4, pp. 161–163, 1968.
[3] V. Mota and L. A. Ferreira, “Influence of grease composition on rolling contact wear: Experimental study,” *Tribol. Int.*, vol. 42, no. 4, pp. 569–574, Apr. 2009.
[4] N. Canter, “Grease additives: Important Contributors not to be overlooked,” *Basics of MWFs*, pp. 19–21, 2013.

[5] J. Zhou, J. Yang, Z. Zhang, W. Liu, and Q. Xue, “Study on the structure and tribological properties of surface-modified Cu nanoparticles,” *Mater. Res. Bull.*, vol. 34, no. 9, pp. 1361–1367, 1999.

[6] V. N. Bakunin, A. Y. Y. Suslov, G. N. Kuzmina, O. P. Parenago, and a V Topchiev, “Synthesis and application of inorganic nanoparticles as lubricant components--a review,” *J. Nanoparticle Res.*, vol. 6, no. 2, pp. 273–284, 2004.

[7] Z. Zhang, D. Simionesie, and C. Schaschke, “Graphite and Hybrid Nanomaterials as Lubricant Additives,” *Lubricants*, vol. 2, no. 2, pp. 44–65, Apr. 2014.

[8] D. P. MacWan, P. N. Dave, and S. Chaturvedi, “A review on nano-TiO2 sol-gel type syntheses and its applications,” *J. Mater. Sci.*, vol. 46, no. 11, pp. 3669–3686, 2011.

[9] L. Wang, B. Wang, X. Wang, and W. Liu, “Tribological investigation of CaF2 nanocrystals as grease additives,” *Tribol. Int.*, vol. 40, no. 7, pp. 1179–1185, Jul. 2007.

[10] S. Sun, Z. Zou, and G. Min, “Synthesis of tungsten disulfide nanotubes from different precursor,” *Mater. Chem. Phys.*, vol. 114, no. 2–3, pp. 884–888, 2009.

[11] R. Tenne, “Fullerene-like materials and nanotubes from inorganic compounds with a layered (2-D) structure,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 208, no. 1–3, pp. 83–92, 2002.

[12] L. Rapoport, O. Nepomnyashchy, I. Lapsker, a. Verdyan, a. Moshkovich, Y. Feldman, and R. Tenne, “Behavior of fullerene-like WS2 nanoparticles under severe contact conditions,” *Wear*, vol. 259, no. 1–6, pp. 703–707, 2005.

[13] A. Margolin, R. Popovitz-Biro, A. Albu-Yaron, L. Rapoport, and R. Tenne, “Inorganic fullerene-like nanoparticles of TiS2,” *Chem. Phys. Lett.*, vol. 411, no. 1–3, pp. 162–166, 2005.

[14] A. Geim, “Beyond graphene,” *Science (80-.).*, vol. 348, no. 6234, pp. 490–492, 2004.

[15] A. K. Geim, “Graphene : Status and Prospects,” *Science (80-.).*, vol. 324, no. June, pp. 1530–1534, 2009.

[16] F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, a. C. Ferrari, R. S. Ruoff, and V. Pellegrini, “Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage,” *Science (80-.).*, 2015.

[17] L. Rapoport, V. Leshchinky, Y. Volovik, M. Lvovsky, O. Nepomnyashchy, Y. Feldman, R. Popovitz-Biro, and R. Tenne, “Modification of contact surfaces by fullerine-like solid lubricant nanoparticles,” *Surf. Coatings Technol.*, vol. 163–164, pp. 405–412, 2003.

[18] X. Fan, Y. Xia, L. Wang, and W. Li, “Multilayer Graphene as a Lubricating Additive in Bentone Grease,” *Tribol. Lett.*, pp. 455–464, Jul. 2014.

[19] W. L. G. Zhao, Q. Zhao, W. Li, X. Wang, “Tribological properties of nano-calcium borate as lithium grease additive,” *Lubr. Sci.*, vol. 26, no. April, pp. 43–53, 2009.

[20] J. Chen, “Tribological Properties of Polytetrafluoroethylene , Nano-Titanium Dioxide , and Nano-Silicon Dioxide as Additives in Mixed Oil-Based Titanium Complex Grease,” *Tribol. Lett.*, vol. 38, no. 3, pp. 217–224, 2010.

[21] H. Chang, C. Lan, C. Chen, M. Kao, and J. Guo, “Anti-Wear and Friction Properties of Nanoparticles as Additives in the Lithium Grease,” *Int. J. Precis. Eng. Manuf.*, vol. 15, no. 10, pp. 2059–2063, 2014.

[22] X. Ji, Y. Chen, and G. Zhao, “Tribological Properties of CaCO 3 Nanoparticles as an Additive in Lithium Grease,” pp. 113–119, 2011.

[23] Z.-L. Cheng and X.-X. Qin, “Study on friction performance of graphene-based semi-solid grease,” *Chinese Chem. Lett.*, vol. 25, no. 9, pp. 1305–1307, Sep. 2014.

[24] A. Mohamed, T. A. Osman, A. Khattab, and M. Zaki, “Tribological Behavior of Carbon Nanotubes as an Additive on Lithium Grease,” vol. 137, no. January, pp. 1–5, 2015.

[25] S. R. Nam, C. W. Jung, C.-H. Choi, and Y. T. Kang, “Cooling performance enhancement of LED (light emitting diode) packages with carbon nanogrease,” *Energy*, vol. 60, pp. 195–203, 2013.

[26] L. Peña-Parás, J. Taha-Tijerina, a. García, D. Maldonado, a. Nájera, P. Cantú, and D. Ortiz,

"Thermal transport and tribological properties of nanogreases for metal-mechanic applications," *Wear*, vol. 332–333, pp. 1322–1326, 2015.
[27] L. Hongtao, J. Hongmin, H. Haiping, and H. Younes, "Tribological properties of carbon nanotube grease," *Ind. Lubr. Tribol.*, vol. 66, no. 5, pp. 579–583, 2014.
[28] N. W. M. Zulkifli, M. a. Kalam, H. H. Masjuki, and R. Yunus, "Experimental analysis of tribological properties of biolubricant with nanoparticle additive.," *Procedia Eng.*, vol. 68, pp. 152–157, 2013.
[29] L. Wang, M. Zhang, X. Wang, and W. Liu, "The preparation of CeF 3 nanocluster capped with oleic acid by extraction method and application to lithium grease," *Mater. Res. Bull.*, vol. 43, pp. 2220–2227, 2008.
[30] X. Ji, Y. Chen, and G. Zhao, "Tribological Properties of CaCO3 Nanoparticles as an Additive in Lithium Grease," *Tribol. Lett.*, vol. 41, no. 1, pp. 113–119, 2011.
[31] A. Mohamed, A. Khattab, T. A. Osman, and M. Zaki, "Influence Of Nano Grease Composite On Rheological Behaviour," *Int. J. Eng. Res. Appl.*, vol. 3, no. 6, pp. 1126–1131, 2013.
[32] M. E. Baghdad, "Rheological properties of lubricating greases," *Wear*, vol. 82, no. 1, pp. 13–25, 1982.
[33] P. M. Lugt, "A Review on Grease Lubrication in Rolling Bearings," *Tribol. Trans.*, vol. 52, no. 4, pp. 470–480, 2009.
[34] H. Chen, H. Wei, M. Chen, F. Meng, H. Li, and Q. Li, "Enhancing the effectiveness of silicone thermal grease by the addition of functionalized carbon nanotubes," *Appl. Surf. Sci.*, vol. 283, pp. 525–531, Oct. 2013.
[35] W. Yu, H. Xie, L. Chen, Z. Zhu, J. Zhao, and Z. Zhang, "Graphene based silicone thermal greases," *Phys. Lett. A*, vol. 378, no. 3, pp. 207–211, Jan. 2014.
[36] D. Berman, A. Erdemir, and A. V. Sumant, "Few layer graphene to reduce wear and friction on sliding steel surfaces," *Carbon N. Y.*, vol. 54, pp. 454–459, Apr. 2013.