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Ultra-thin 2D Carbon Material as Engine Oil Additive for Studying Anti-Friction and Anti-Wear Behaviour

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ABSTRACT

Friction and wear in automobile engines account to 13-18% of the energy losses in the system. The reduced efficiency and life of the engines mandates the search for a better lubricating additives which can help attain super lubricity. These two factors have been areas of concentrated study and play a vital role between any two mating surfaces. Carbon nanomaterial, graphene specifically because of its ubiquitous chemical and mechanical properties have attracted its use for lubricating applications. Layered graphene platelets (LGP's) with few layers (7-10) were prepared using microwave-irradiated thermally expanded graphite flakes

followed by shear mixing using all-purpose mixer. Transmission electron micrographs (TEM), X-ray diffraction and Raman spectrum showed that majority of LGP consist of few layers ranging from 7 to 10 layers. LGP's possessed pristine and crystalline properties validating coherent and distinguishable edges of graphene in TEM. These LGP were used as an additive material in multigrade lubricating oil, and the 4-ball tribological tests were performed to observe the effective role of nanoadditive. LGP based nanolubricant sample and base oil showed coefficient of frictions of 0.06 and 0.10 respectively. Remarkable reduction of 60% was observed in the nano lubricant sample of

1000 ppm concentration ascribed to formation of a protective tribo film on the metal surfaces by LGP preventing the asperities from meeting eventually reduces friction and wear.

Keywords:—Carbon, graphite, exfoliation, graphene, tribology, four-ball test, nano lubrication.

I. INTRODUCTION

Mechanical mating surfaces always have friction at the contact interface leading to energy loss and gradual wear resulting in system failure over a period of time. In automobile engines, this phenomenon specifically draws attention between the piston rings and cylinder liners where these phenomenons cause a condition called 'bore'. Thus reducing friction and wear in engines using various approaches has been an area of interest for tribological studies. Materials with various morphologies; spherical particles, sheet like structures, tubes and rod shaped, etc. are reported to be used as lubricant additives (dry and wet) for macro-scale metallic sliding components and high-pressure mating surfaces. J. Philip et al. suggested ceria-based nanoparticles as lubricating additives and evaluated their surface topology and stability as nano lubricants [1]. Ionic fluid-MoS₂ nanoparticles behaviour for friction reduction using succinimide based dispersants for stability evaluation was cited in study of Pierre Rabaso et al. [2]. Rita Rosentsveig et al. explored tribological properties of fullerene-like WS₂, MoS₂ nanoparticles in ionic fluids and poly-alpha olefin oils and obtained friction coefficients as low as 0.03 [3]. Studies have stated lubrication boosts with various nanoparticles under variously defined lubrication regimes, also illuminating the types of oils, and various metal nano particles used for tribological studies [4-6].

Zhenglin Tang et al. reviewed and categorized lubricants on the basis of functional groups

and summarized the results obtained by using different kinds of friction modifiers for liquid lubricants [7]. M.K Ahmed Ali et al. projected use of hybrid nanomaterials as lubricant additives explaining reduction in scuffing wear in automobile engines [8]. R. Chou et al. used nickel nanoparticles as an additive in poly-alpha olefin oil and found wear reduction in a range of 5% to 45% and reduced friction in a range of 7% to 30% [9]. Joined effect of improved tribological behaviour of MoS₂ and SiO₂ has also been reported for use in magnesium alloy steel contacts studies, while only MoS₂ has been tried in engine bench and road testing, leading to 0.9% reduced fuel consumption and also reduced emissions [10-11].

Carbon nanomaterials draw unique attention owing to their inherent properties and can be eyed as a potential replacement for many present-day commercial additives. Studies performed showed significant reductions in friction and wear were made using carbon nanotubes (CNT's) as lubricant additives in engine oil [12]. Carbon derivatives like graphite flakes, graphene, CNT's and fullerenes have proven as friction modifiers, exhibiting commendable lubricating properties. [13]. Carbon spheres with ultra-smooth morphology were also laid hands on as oil additives in a study documented by Abdullah A Alazami et al. [14].

E.D. Ramón Raygoza et al. formulated nanolubricant with multilayer graphene impregnated copper for automotive applications and achieved reductions in coefficient of friction (COF) and wear of 43% and 63%, respectively [22]. Dan Zheng et al. studied the tribological behaviour of graphene nanosheets as oil additives on textured alloy cast iron surface and obtained a high wear reduction of 90 % [23]. Varrla Eswaraiah et al. used 1 -2 layered graphene prepared by solar exfoliation as a nanofluid additive for engine oil and improvement in

COF, anti-wear, and extreme pressure properties by 80, 33, and 40%, respectively [24]. The engine friction has been a crucial factor to cut down the parasitic losses of energy in any automobile system and simultaneously ramp-up the efficiency and lifespan. The frictional losses in diesel engines have been precisely explained to consume almost 4-15% of total energy input [29]. Victor Wang et al. stressed on the importance of viscosity of different oils and the dependence of friction and wear characteristics of oils on viscosity. Also, current day friction modifiers, viscosity index improvers, anti-wear additives were highlighted [30].

Graphene, which is a peeled-off derivative of graphite, has been widely exploited for its astounding electrical, mechanical and physical properties on a widespread scale [31-33]. Its 2 dimensional structure, sp² hybridization of C-atoms, honeycomb like lattice and layered structure, contributes to its exceptional mechanical properties. Various methods enlisting its synthesis using one-step method and two-step processes are elaborated in multiple studies [34-36]. Graphite in various forms has been used in metal-on-metal hip replacements in biomedical applications [37]. Graphene used as platelets for lubrication [38], and its excellent corrosion inhibition properties on various metals [39, 40] in non-inert conditions and its impermeability to gas molecules [41] has drawn attention for its industrial applications. Graphene and other carbon-based nanomaterials can enhance properties of different lubricants [42-44] with reports of formations of graphite scrolls at the tribological interfaces; these scrolls are assumed to be the cause for decreasing surface energy at the mating junction and reducing friction. Many studies have been reported using graphene as a dry lubricant between steel contacts and as additives in some bio-oils for various applications. The present study was focused to prepare

nanographene sheets in scalable quantity from microwave-assisted exfoliated graphite and use them as nano additive to modify wear and friction. The LGP used is proposed as potential alternative for multiple hazardous additives in commercial oils with improved properties.

II. EXPERIMENTAL WORK

2.1 Exfoliated graphite synthesis via microwave-irradiation and LGP preparation

All chemicals are of reagent grade and used without further purification. The natural graphite flakes (NGF) used were purchased from M/s Oxeeeco, India. NGF's were sieved manually with a mesh size 100 sieves and graphite flakes of size 150 microns were collected. Sulfuric acid (H₂SO₄), Nitric acid (HNO₃), and isopropanol were procured from Sigma Aldrich. The sieved NGF's were intercalated in a mixture of H₂SO₄ and HNO₃ maintaining a ratio of 3:1 (v/v). The mixture was homogeneously stirred using an impeller at 300 rpm for 5 hours and then washed with profuse amount of deionized water till a neutral pH was attained. The graphite intercalated compound (GIC) was separated by vacuum filtration using Watt man filter paper as collecting interface. The GIC was dried at 60°C in a Petri dish for 4 hours. The dried GIC was exfoliated by microwave irradiation (Ken Star) at 450 W for 10 seconds. The exfoliated graphite (EG) prepared using the microwave irradiation with a worm-like structure was further modified to obtain a few layer thick platelets-like particles. This process was carried out by mixing microwave exfoliated graphite in a mixture of water and iso-propanol (3:7 v/v) further processed by probe sonication (SONICS Vibra Cell probe sonicator) at 76% amplitude for duration of 30 minutes (on/off mode). The sonicated compound was further subjected to mechanical grinding in a grinder for 1800 seconds (on/off

mode) to prepare layered graphene platelets (LGP).

2.2 Formulation of nanolubricant

SAE 15W40 was used as base oil for uniform dispersion of LGP. The viscosity of the oil at 100°C was 14 mm²/s, pour point of -30°C and a flash point of 226°C. The nanolubricant were prepared following the two-step method as showed in figure 1 by dispersing synthesized LGP's in varying concentrations in ascending value. The base oil was dispersed with 1000 ppm (1gm./L), 2000 ppm (2gm./L) and 3000 ppm (3gm./L). The LGP's were dispersed uniformly in the oil by using an 'ultra-sonicator' for 3000 seconds followed by probe sonication (SONICS Vibra Cell probe sonicator) at amplitude of 76% for the duration of 900 seconds. The nanolubricant samples were prepared without any surfactants to attain stability of the LGP platelets in the oil. The samples showed excellent stability over a duration of 15 days after being left undisturbed.

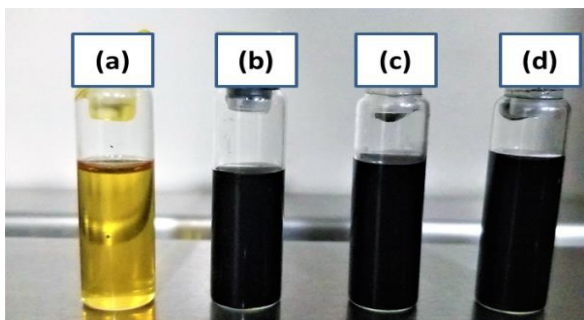
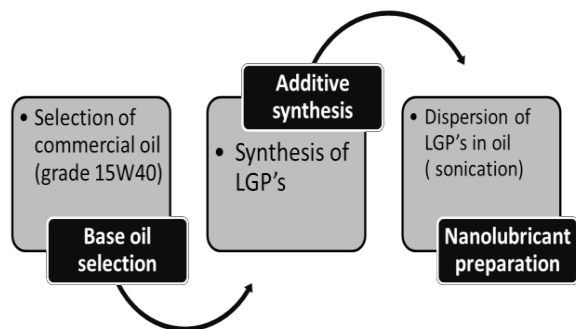


Figure 1: Nanolubricant preparation and samples ; (a) Base oil, (b) 1000 ppm sample, (c) 2000 ppm sample and (d) 3000 ppm sample

2.3 Measurement of tribological properties

The friction and wear characteristics of the formulated nanolubricant samples were evaluated taking the performance of the commercial oil as benchmark target. Four ball test rig (DUCOM MAGNUM), was used to perform the tribological experiments. American Society for Testing and Materials (ASTM) standards D2266, D2596, D2783, and D3233 were referred to set the test parameters. Chrome alloy steel balls of hardness 58 HRC and a surface roughness of 0.2 µm were procured from DUCOM for carrying out the studies. The balls were cleaned with AR grade acetone to remove any contamination from the surface before the test.

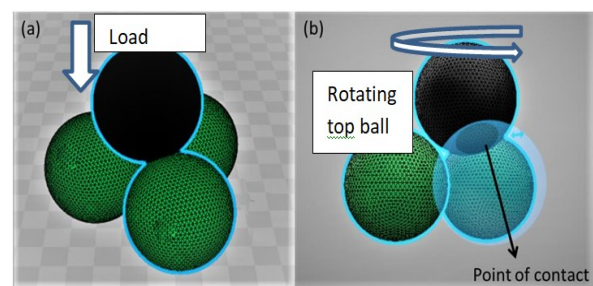


Figure 2: (a) Four ball schematic arrangement, and (b) Point of contact for wear

III. RESULTS AND DISCUSSION

3.1 Morphological and structural characteristics

The images observed in SEM in figure 3 (a) and (b) shows sheet-like platelets, in which each platelet has few layers. Auxiliary decrease in no. of layers was attained after carrying out the grinding process by mixing with isopropanol and probe sonication. The weak Van-der-Waals forces joining the layers are the cause of their self-lubricating property. The layers slither over each other, reducing COF and consequently wear of the material on the mating surface interface. Figure 3(a) depicts the morphology of LGP's. They are platelet-like structures having huge amount of pores. EG worms were split into LGP's using concentrated vibrations

produced by cavitation-induced ultra-sonication and shear mixing. LGP's were characterized to have ultrathin platelet-like structure as illustrated in figure 3(b). The average diameter of LGP's falls in the range of 5-8 μm . The TEM micrograph points out that the LGP's are having 7 layers with distinguishable graphene edges as shown in figure 3(c). It implies, the LGP's have high crystallinity with nominal defects. Figure 3 (d) shows SAED pattern of LGP's with intense bright spots regularly arranged in a concentric rings with hexagonal pattern.

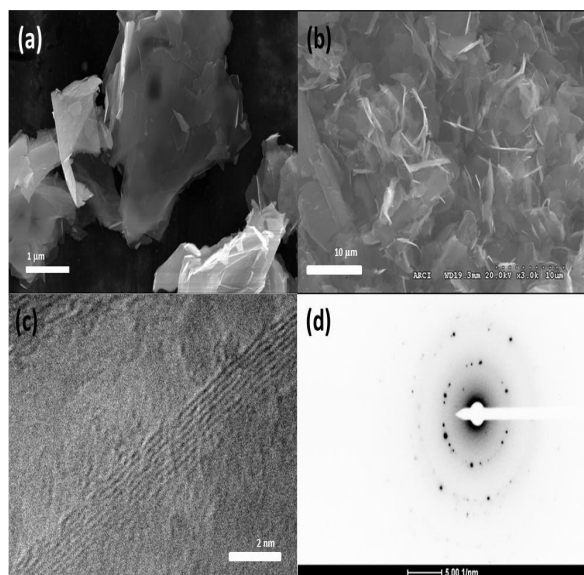


Figure 3: Dynamic viscosities; (a) Base oil, (b) 1000ppm sample, (c) 2000ppm sample and (d) 3000ppm sample

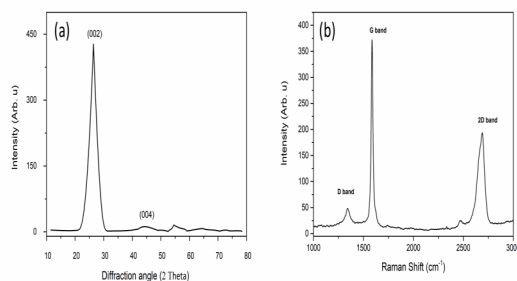


Figure 4:(a) XRD pattern of LGP and (b) Raman spectrum of LGP

At 26 degrees (2 theta) in the figure 4(a) a prominent peak is visible, primarily due to (002) plane which shows predominant

graphitic nature of the LGP followed by a small bump at 45 degrees, which is due to (100) plane. This indicates that a microwave processed LGP's are having less defects and impurities hence can be characterized as pristine graphene with few layers. Figure 4 (b) shows Raman spectrum of LGP's depicting 1st order and 2nd order Raman signatures. Distinct and intense peaks were observed at three points, at 1343.5 cm^{-1} , 1585.7 cm^{-1} and 2688.9 cm^{-1} for D, G and 2D bands, respectively. A minor D band originated due to disorders in sp^2 hybridization of the sample causing resonance in the spectrum, indicating the presence of disordered structures in the LGP's which are possibly induced due to the force induced shearing of the layers. The G band explains the proper stretching of the C-C bond in the graphite flakes after microwave irradiation. The 2D band at 2688.9 emphasises the sp^2 hybridized graphitic nature. Figure 4 (b) trends similar to the Raman spectra of graphite but the absence of secondary peak in the 2D band implies the few layered structure of the LGP's pertaining to their graphitic nature. The full width half maximum (FWHM) for 2D peak is found to be 17.696 which explains the few layered structure of NGS.

3.2 Rheological characteristics

The rheological properties of the lubricating medium between the mating interfaces is of vital importance, as it is governed by various factors like additive concentration, viscosity-temperature behaviour, lubrication regime during operation, etc. These factors in turn affect the prime characteristics like friction and wear resistance. The base oil characterized at ambient conditions at a shear rate of 300 to 600 $1/\text{s}$ exhibited a dynamic viscosity of 0.01 Pa.s. The nanolubricant samples with ascending concentration i.e. 1000ppm, 2000ppm, and 3000ppm were characterized with a high surge in viscosity, values being 0.171 Pa.s, 0.178 Pa.s and 0.181 Pa.s

respectively. This rise in viscosity can be attributed to the LGP's leading to an increased resistance to flow between the fluid layers. The high resistance to flow leads to momentous rise in the shear stress (τ) generated for the applied shear rate. The viscosity characteristics of the base oil and the nanolubricant samples followed the non-Newtonian fluid trend exhibiting shear thickening as seen in figure 5.

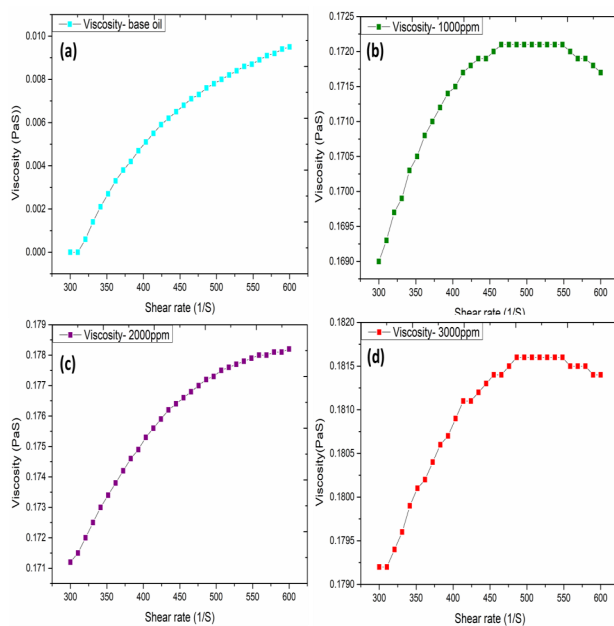


Figure 5: Dynamic viscosities; (a) Base oil, (b) 1000ppm sample, (c) 2000ppm sample and (d) 3000ppm sample

In figure 6 (a) it can be seen that a low shear rate is induced by the applied shear stress. Shear stress is gradually increasing, behaving marginally close to pseudo plastic non Newtonian fluid. However, the nanolubricant samples in figure 6 (b), (c) and (d) depicted an ideal Bingham plastic fluid shear stress behaviour. The nanolubricant samples owing to the LGP's dispersed, developed a high resistance to flow, thus leading to a high shear stress throughout the range of applied shear rate. Comparing the initial shear stress for shear rate 300 1/s the base oil's shear stress is found to be close to 0.5 Pa followed by gradual linear increase. The nanolubricant samples of 1000ppm, 2000ppm, and 3000ppm

concentration exhibited values of 50 Pa, 52 Pa and 56 Pa respectively for the same shear rate value of 300 1/s. At an end value of 600 1/s the shear stress generated in base oil was 5.7 Pa, whereas values as high as 90 Pa, 98 Pa and 104 Pa were recorded for 1000ppm, 2000ppm and 3000ppm respectively. It can be clearly perceived that addition of the LGP's to the base oil led to a reduction in flowing ability of the fluid.

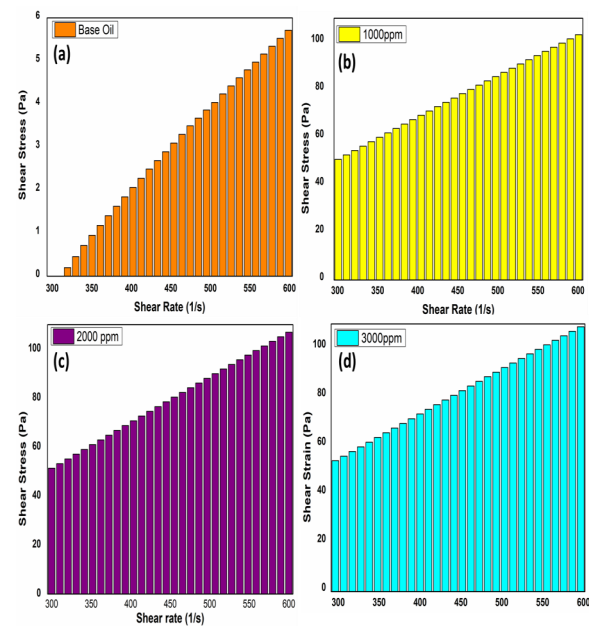


Figure 6: Shear stress; (a) Four ball schematic arrangement, and (b) point of contact for wear

3.3 Friction and wear characteristics

Wear scar diameter (WSD) was measured by using Opto-digital microscope. The WSD recorded were 351.91 μ m, 379.65 μ m, 384.03 μ m and 410.38 μ m for 1000 ppm, and 2000 ppm, 3000 ppm and base oil samples. It is unmistakably visible that the WSD for base oil was greater as paralleled to the nanolubricant samples, precisely 1000 ppm, and 2000 ppm sample. Conversely further increase in additive concentration up to 3000 ppm showed an anomalous increase in WSD as compared to its preceding sample concentrations.

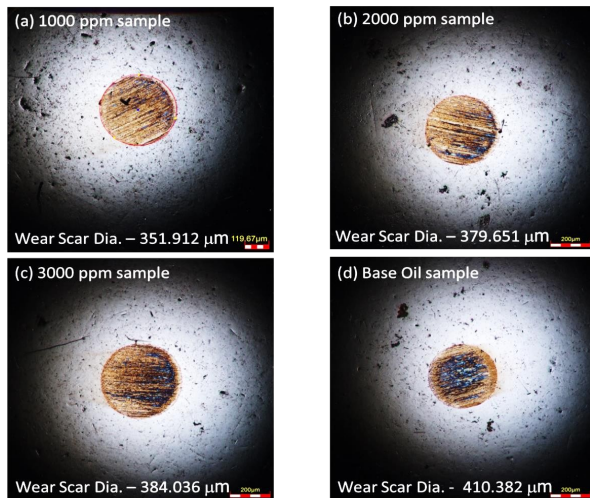


Figure 7: (a) Wear scar diameters (WSD); (a) 1000ppm sample, (b) 2000ppm sample, (c) 3000ppm sample and (d) Base oil

This atypical behaviour can be explicated as the botch of the LGP platelets to form a continuous shielding tribofilm between the balls during the rotary motion under constant normal loading due to very high additive particle concentration leading to faster sedimentation of LGP's, leading to unstable dispersion. Varrla Eswaraiyah et al. reported their work on graphene-based nanofluids and observed a similar trend in behaviour. A lessened performance was witnessed in their samples after the additive concentration was augmented and they concluded that optimized concentration of graphene as an additive is 0.025 mg/mL in their base oil [24]. The nanolubricant sample of 1000 ppm showed a reduction of 15% in WSD while the 2000 ppm sample gave a decrease of 8% and the 3000 ppm sample reducing the WSD only by 7% with respect to the WSD value exhibited by base oil. The nanolubricant samples did not exhibit high wear even on a surface with high surface asperities which is achieved due to the LGP's in the oil. In figure 7 (a), the 1000 ppm sample WSD with a light scratches due to material erosion is seen evidently. Figure 7 (b) and (c) shows 2000 ppm sample and 3000 ppm sample WSD's, exhibiting a similar worn-out surface. The 3000 ppm concentration sample showed denser erosion scratches. From

the figure 7 (d), it can be inferred that the base oil failed to resist wear on the surfaces of balls as a highly eroded surface with dense scratches was observed for the balls tested.

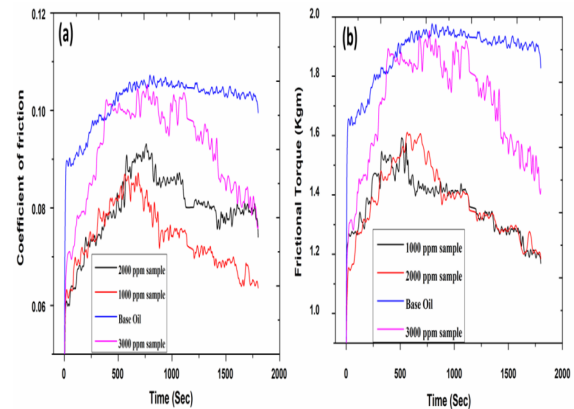


Figure 8: Frictional Characteristics; (a) Coefficient of friction and (b) Frictional torque

Another characteristic studied was the anti-friction (AF) ability of the nano lubricant samples. COF and frictional torque were the frictional aspects taken for consideration. Figure 8 (a) shows the COF graph of the base oil and the nanolubricant samples and figure 8 (b) represents the frictional torque recorded during the tests. A gradual rise in the COF for all the samples can be clearly observed in figure 8 (a) till 500 seconds (X-axis), however a sharp fall is peculiarly seen in the 1000 ppm and 2000 ppm samples. The 3000 ppm sample exhibited a higher value of COF as compared to the former samples but the COF of the base oil was recorded to be the highest. The 1000 ppm sample went up to a COF of 0.085 but steeped back to a low of 0.06. Similar rise and fall trend was replicated by 2000 ppm sample and 3000 ppm sample pertaining to COF values of 0.08 after shooting up to 0.09 and 0.10 respectively. The base oil resulted in a sharp rise of COF till 0.09 followed by a constant COF of 0.10. A COF reduction by 40% can be observed in 1000 ppm sample while the 2000ppm and 3000ppm samples performed with 20% reduction in COF as compared to the base oil.

IV. CONCLUSIONS

Most tribological methods of controlling friction and wear involve use of solid and liquid lubricants. In this study the viscosity of base oil increased almost 17 times after the LGP dispersion in varying ppm concentrations. The nanolubricant samples however showed superior lubricating properties when compared with base oil. This characteristic is attributed to the inherent lubricating property of LGP's. The 4-ball tribological tests distinctly show a wear rate reduction of 15% and 8% using the 1000 ppm and 2000 ppm nanolubricant samples as compared to base oil. Also the frictional torque and coefficient of friction is reduced by more than 40% for the same. However the 3000 ppm sample showed a poor lubrication property as compared to the remaining 1000 ppm and 2000 ppm samples. This can be explained due to the agglomeration and lump formation of LGP's. It can be related to the attaining of threshold for dispersion limit in base oil. The behaviour is a result of instability of the 3000 ppm sample due to high concentration of LGP. The LGP's when dispersed beyond a certain threshold concentration lead to a faster sedimentation of the additive particles leading to formation of heavier lumps, making it a failure exhibiting an anomalous behaviour during lubrication. This defines that lubrication is maintained high until the additives are a certain limit of threshold concentration. This threshold concentration limit can vary for various oils, depending on their viscosities and properties. The studies conclude with wear and friction reduction achieved using LGPs better than the multigrade base oil. The 1000 ppm sample proves to be a stable sample in terms of additive concentration in base oil, 2000 ppm sample which displayed similar trend in its lubricating property. The anti-friction and anti-wear properties of the prepared nano lubricant samples can be recognized as an effect of the LGP's dispersed. The LGP's

prepared from graphite flakes retained its self-lubricating ability and hence ascertained wear and friction reduction.

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