Enhancement of tribological behaviour and thermophysical properties of engine oil lubricant by Graphene/Co-Cr nanoparticle additives for preparation of stable nanolubricant

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Abstract. In the current study the tribological properties of Aluminum alloy (Al 25) with moment in time was examined by adding nanoparticles as additives. Nanoparticles exhibit high thermal conductivity, stable viscosity and can be dispersed well in oil. The purpose of this research is to determine the effect of Al2O3, TiO2, Graphene (G), Co-Cr, Ni nanoparticles on lubricity using linear wear testers under reciprocating sliding motion. SEM and EDX characterization techniques are used to study the composition and morphology on worn surfaces. The findings showed that the tribological properties of the substrate lubricant were significantly increased with the addition of nanoparticles. Friction and Wear are reduced with Graphene, Al2O3, TiO2, Ni & Co-Cr nanoparticles as additives for the same load value and can be used as multifunctional additives. Co-Cr at 0.03wt% has provided best performance among the other nanoparticles and can be used as Nano lubricant in the future.

Keywords: Nanoparticle, Graphene, Nanolubricant, SEM-EDX, Engine Oil.

1. Introduction
Lubrication is among the foremost issues in manufacturing, transportation, and aerospace [1-3]. Automotive engines are completely dependent on lubrication [4]. Engine oil plays a vital role to keep running the engine with sustainability. Performance of engine oil is directly linked by the formulation (Additive content). More than a decade several chemical substances are used as additives in engine oil to succeed in decreasing tribological tests like friction, wear and tear, corrosion, deterioration, and oxidation [5]. Also, massive hard work has been performed in order to attain best thermal performance through multi-grade oils, phosphates, Organic poly sulphides, dithiophosphate, diethio carbamates, molybdenum di-sulphide, zinc di-alkyl dithiophosphates (ZDDP), etc. persist in being famous as anti-wear additives [6]. Meanwhile from previous decade nano particles are being thoroughly inspected as possible performance improver for conventionally used anti-friction and anti-wear additives [7]. Allotropes of Carbon grew attention because of its exclusive morphology as well as properties [8]. Nevertheless, the selected nanoparticles are equitably novel in the lubrication engineering,
astoundingly great thermo-physical and tribological properties have made it a striking research subject [6].

Lubrication is administration of friction and wear by the presentation of a rubbing lessening film between moving surfaces included. The oil utilized be a fluid, solid, or plastic substance. In spite of the fact that this is a legitimate definition, it neglects to understand all that lubrication really accomplishes. Various materials can be utilized in order to grease up the surface. Oil along with grease are the greatest and widely recognized [9]. The nano lubricants earned enormous attention because previous experiment results proved effective in efficiency improvement inferable from diminish frictional improvement power misfortunes straightforwardly as result brilliant working and adjusting as per the car motors necessities. The basics to have chosen this kind of nano-added substances is sufficiently reacted by this examination. The Nanomaterials have captivating highlights as high thermal conductivity and outstanding mechanical properties [10-12]. Nanomaterials offer superior chemical stability, also they can serve adequately in various tribological applications. Graphene have bunch of possibilities, for example, anti-friction/wear, going about as strong oils on sliding worn interfaces, which lead to a more drawn-out life expectancy for motor parts and improving motor toughness. Likewise, nanomaterials give powerless powers of the van der Waals and static communications powers between the 2D layers, that encourage inside the solidness of Nano lubricants [6].

Current research paper aims to investigate the effect of Al₂O₃, TiO₂, Graphene (G), Co-Cr, Ni nanoparticles on lubricity under reacting to sliding movement utilizing Linear Wear Tester. Two types of contact settings are used to measure the friction wear rate. Afterward linear wear test, the morphology and composition of worn surfaces are characterized using SEM and EDX in order to deliver an understanding on the Nanomaterial’s tribological mechanisms [9]. The key reason for resistance and wear of the worn surfaces are vitality dissemination in automobile engines. 17-19% of power produced by engine is wasted due to frictional losses. Now the whole world is looking forward to increasing the efficiency of engine many ways. Among of the ways is to diminish the friction and wear in engine by improving the engine oil. Some of the countries are dependent on importing oil at an extraordinary scale, which can prompt an imbalanced exchange and nation security encounters [13, 14]. If we look at the economic loss worldwide due to frictional losses it will be around US$120 billion per year. From this information we can clearly come to a point that we need to focus on strategies to utilize our natural resources more efficiently [15]. The objectives of this research are to study the structure, characteristics & uses of G, Al₂O₃, TiO₂, Ni & Co-Cr in Lubricants and to mix G, Al₂O₃, TiO₂, Ni & Co-Cr and base engine oil (10W40) in proper concentration and later to evaluate tribology characteristics of newly prepared nano-lubricant and compare the data to show the tribological improvement and lubricants performance [16-19].

2. Materials and methods
The area of this examination is to show the mechanism liable for the tribological properties (anti friction & anti wear) of the piston ring and cylinder body interfaces utilizing nanomaterial enriched nano lubricants compared to the usual engine oil (10w-40) [15, 20, 21]. Moreover, the configuration and morphology of the tribo-science films shaped on the well-used surfaces are studied by tests of SEM, EDS, 3D surface profiler [6].

2.1 Graphene preparation & formulation of nano lubricants
The Graphene is obtained in the form of GO (Graphene Oxide) (8.64 mg/ml). Vacuum Oven was used to make it in Dry form. In this study the commercial lubricant 10W-40 was used as reference oil or base oil. This 10W-40 engine oil chosen because it is one of the widely used engine oil worldwide [22-24]. The technical data of these specific lubricants has been presented in Table 1. The G, Al₂O₃, TiO₂, Ni & Co-Cr nano lubricants were prepared in 3 concentrations (0.01, 0.03, 0.05 wt.%) to obtain a balanced dispersion and to avoid sedimentation in the base oil. The composition of G, Al₂O₃, TiO₂, Ni & Co-Cr nano lubricant is presented in below Table 2. The mixing of nano lubricant samples was
done by a mechanical stirring device for 4 h and 2 hours of ultrasonic mixing for a homogeneous stable suspension [15].

Table 1. Physical Data of sample base lubricant 10w-40.

| Parameters            | Method        | Unit          | Typical Value |
|-----------------------|---------------|---------------|---------------|
| Appearance            | -             | B&C           |               |
| Density 15°C          | ASTM D 4052   | g/cm C²       | 0.875         |
| Viscosity @100°C      | ASTM D 445    | cSt           | 14.2          |
| Viscosity Index       | ASTM D 2270   | -             | 150           |
| Flash Point           | ASTM D 92     | °C            | >200          |
| Point CI. O. C        |               |               |               |
| TBN                   | ASTM D 2896   | mg KOH/g      | 10.0          |
| Pour Point            | ASTM D 97     | °C            | < -30         |
| Foam @24°C            | ASTM D 892    | cc/s          | Traces/0      |

Table 2. The Composition of Gr Nanolubricant sample.

| Lubricant oil type    | Concentration (wt.%) | Reference oil(10W-40) (ml) | Additive Solution (gm) |
|-----------------------|----------------------|----------------------------|------------------------|
| Base Oil              | 0                    | 50 ml                      | 0 % additives          |
| G Nano lubricant      | 0.01, 0.03, 0.05     | 50 ml                      | 0.0004, 0.0013, 0.0021 |
| Co-Cr Nanolubricant   | 0.005, 0.01, 0.03, 0.05 | 50 ml                      | 0.0571, 0.1714, 0.2859 |
| Al₂O₃ Nano lubricant  | 0.01, 0.03, 0.05     | 50 ml                      | 0.0226, 0.0677, 0.1129 |
| TiO₂ Nano lubricant   | 0.01, 0.03, 0.05     | 50 ml                      | 0.0242, 0.0725, 0.1209 |
| Ni Nano lubricant     | 0.01, 0.03, 0.05     | 50 ml                      | 0.0509, 0.1526, 0.2549 |

2.2 Sedimentation
A stable solution of the mixture is necessary for the proper functioning of the nano lubricant to be verified. Achieving sufficient nano lubricant dispersion consistency is an essential problem for the implementation of nano lubricants in any particular application. Graphene has superior properties in its pristine form, but it is enormously susceptible to agglomeration. As a result, in the presence of reducing agents, the pristine Graphene, Al₂O₃, TiO₂, Ni & Co-Cr layers appear to coagulate due to heavy π-π interaction and van der Waals tempting forces between the planes of Graphene, Al₂O₃, TiO₂, Ni & Co-Cr. As Graphene, Al₂O₃, TiO₂, Ni & Co-Cr are propagated in oil-based lubricants, agglomeration is further differentiated [25]. Researchers have found that graphite-derived graphene platelets contain functional groups of hydroxyl and carboxyl on the sheet edges that make them soluble in water. As a consequence, the propensity to coagulate in oil is greater [26]. Few research studies indicate Co-Cr as anticorrosive material and Al₂O₃ being easily available & low cost where as TiO₂ & Ni being used for its special characterization. Visual analysis has been carried to conduct sedimentation test for 1 month and further. Below Fig 1. Shows the Prepared Nano lubricant Samples for visual stability.

2.3 Thermal conductivity & viscosity measurements
The thermal conductivity of the prepared Graphene nano lubricants was calculated using a KD2 PRO thermal conductivity probe (Decagon Devices Inc., USA) [27]. It is the recommended way in the effort to calculate the thermal conductivity of nanofluids used by previous researchers [7, 27-29]. To test the viscosity of the prepared Graphene nano lubricant, a Brookfield LVDV-III Ultra Rheometer (Viscometer) was used.

2.4 Linear wear test & worn surface analysis
The piston skirt-liner tribometer was used to measure the Graphene, Al₂O₃, TiO₂, Ni & Co-Cr Nano
lubricants' friction and wear conduct. Under lubricated sliding conditions, the wear test was performed. Wear checking involves creating a linear motion to a cylinder-piston ring pair working in realistic condition in the same way. The Tribo-tester acts within the engine like a touch piston-ring. Before and after the experiment, all materials are washed in acetone and dried in hot air. Varying loads, velocities and temperatures for all Graphene, Al$_2$O$_3$, TiO$_2$, Ni & Co-Cr nano lubricant sample concentrations as shown in Table 3 [30]. Scanning Electron Microscopy (SEM) by Hitachi TM3000 with Energy Dispersive X-ray Spectroscopy was used to test the morphology and element distribution of the worn surface on the disk (EDS) [30].

Figure 1: Prepared nano lubricant samples.

Table 3. Experimental conditions for tribometer.

| Load (N) | Speed (rpm) | Temp. (°C) | Concentration (wt%) | Nanoparticles                |
|----------|-------------|------------|---------------------|----------------------------|
| 38.5     | 400         | 25         | 0.01, 0.03, 0.05     | Gr, Al$_2$O$_3$, TiO$_2$, Ni & Co-Cr |
| 98.5     | 200         | 25         | 0.01, 0.03, 0.05     | Gr, Al$_2$O$_3$, TiO$_2$, Ni & Co-Cr |

3. Results and discussions

3.1 Thermal conductivity and viscosity
Experimental analysis can declare that one of the chosen nanoparticle Co-Cr is most suitable among Graphene, Al$_2$O$_3$, TiO$_2$, Ni & Co-Cr nanoparticles for using in engine oil because the viscosity readings are most stable. Fig 2. show the thermal conductivity results. High thermal conductivity means more heat dissipation from engine as engine oil’s one of the most important purpose is to keep the engine temperature in control and Co-Cr shows the highest thermal conductivity. Viscosity is preferred to be stable in different condition. One of the main reasons to care about engine oils viscosity is to keep the lubrication in proper manner inside engine. As far we see from the results the most stable viscosity is shown by Co-Cr.

Figure 2 (b) & (c) shows that Co-Cr has the best value for thermal conductivity with 0.3429 W/m-k & 0.3030 W/m-k at 70°c for 0.05 &0.03 wt% respectively. Whereas Graphene is showing the second highest at 0.03% but the most changed according to temperature is Nickel. For 0.03wt% the highest thermal conductivity value obtained for Co-Cr followed by Nickel with 0.2139 W/m-k. Fig 2 (a)
shows the thermal conductivity as highest for Co-Cr and followed by Al₂O₃ with 0.2234 W/m-k and Graphene(G) shows the most gradual increment at 0.01 & 0.05 wt%.

**Figure 2.** Thermal Conductivity for different nano lubricants a) 0.01wt%, b) 0.03wt%, c) 0.05wt%.

**Figure 3.** Viscosity measurements for different nano lubricants a) 0.01wt% b) 0.03wt% c) 0.05 wt%.

The Figure 3 indicates that the most stable viscosity reading is attained by Co-Cr at 0.03 &0.05 wt% at varied speed. viscosity at 0.03wt% shows very critical to choose stable reading but still we can see that CoCr shows the most stable viscosity. In Figure 3 (a) shows the stability almost similar for Co-Cr and Graphene.

3.2 **SEM and EDX analysis (linear wear test nano lubricant)**

For Linear wear test Co-Cr 0.03 wt% nano lubricant has been chosen as it has shown the highest thermal conductivity and most stable viscosity reading among all other materials in different concentration (from Figure 2 & 3). Below Figure 4, shows the nano lubricant SEM images of Co-Cr at 0.03 wt% with linear wear test (200 rpm and 98.5N load). SEM images of Linear wear test (400 rpm and 38.5N load) of Co-Cr 0.03wt% enriched nano-lubricant is shown in Figure 5. It can be clearly observed from SEM images that there are worn surface which contains the layer (of Co-Cr) after Linear wear test. The green highlighted data from EDS result shows the percentage of Cobalt and Chromium found in the layer after linear wear test. Actually, this layer is going to reduce the friction making the surface of components slide. In EDS result Carbon found due to wear and friction, Aluminium found because the friction plate was Aluminium alloy and oxygen found due to decomposition. Aluminium plate was photographed shown in Figure 6.
Figure 4. SEM of Linear wear test (200 rpm and 98.5N load) of Co-Cr 0.03wt% nano lubricant.

Figure 5. SEM of Linear wear test (400 rpm and 38.5N load) of Co-Cr 0.03wt% nano lubricant.

Figure 6. Scanning Electron photograph of plane Aluminium plate.
Linear wear test was done at the 200 rpm for 98.5N load. Scanning electron microscopy was done to understand the surface modifications. The Energy Dispersive X ray testing was performed with elemental analysis, as shown in Figure 7 and the observed elements are listed in the Table 4. Chromium and cobalt were found with the highest weight % as Chromium was 6.610 % and Cobalt was 36.212% respectively.

Table 4. Composition of elements by XRD analysis of Co-Cr 0.03wt% (200 rpm and 98.5N load).

| Element  | Weight % | Weight % σ | Atomic % |
|----------|----------|-------------|----------|
| Carbon   | 50.662   | 0.351       | 80.859   |
| Oxygen   | 2.480    | 0.251       | 2.971    |
| Aluminum | 1.547    | 0.049       | 1.099    |
| Chromium | 6.610    | 0.126       | 2.437    |
| Iron     | 2.490    | 0.123       | 0.855    |
| Cobalt   | 36.212   | 0.318       | 11.779   |

The Figure 8 showing the linear wear test observed under 400 rpm and 38.5 N load conditions. The EDX analysis found that as the rpm increases, and load decreased the amount of Chromium and Cobalt. Table 5 showed Chromium reduced to 4.868 wt% and Cobalt to 24.774 wt% the total percentage reduction observed as by 26% chromium and 31% cobalt.
Figure 8. EDX results of Linear wear test (400 rpm and 38.5N load) of Co-Cr 0.03wt% enriched nanolubricant.

Table 5. Composition of elements by EDX analysis of Co-Cr 0.03wt% (400 rpm and 38.5N load).

| Element   | Weight % | Weight % σ | Atomic % |
|-----------|----------|-------------|----------|
| Carbon    | 53.400   | 0.333       | 79.158   |
| Oxygen    | 7.037    | 0.273       | 7.832    |
| Aluminum  | 2.217    | 0.050       | 1.463    |
| Chromium  | 4.868    | 0.103       | 1.667    |
| Iron      | 6.407    | 0.147       | 2.043    |
| Cobalt    | 24.774   | 0.265       | 7.485    |
| Zinc      | 1.297    | 0.113       | 0.353    |

Figure 9. EDX results of Linear wear test (400 rpm and 38.5N load) of plane aluminium plate.

The aluminium plate was observed under the SEM as shown in Fig. 9. The clear and smooth surface was observed. The energy dispersive x ray analysis found very few numbers of elements observed as listed in Table 6. The total percentage of aluminium was found 77.175 %. Result confirmed that the aluminium plate composed of pure aluminium element.
Table 6. Composition of elements by EDX analysis of plane Aluminium plate.

| Element   | Weight % | Weight % σ | Atomic % |
|-----------|----------|------------|----------|
| Carbon    | 16.125   | 0.695      | 29.662   |
| Oxygen    | 4.905    | 0.260      | 6.774    |
| Aluminum  | 77.175   | 0.681      | 63.196   |
| Silver    | 1.796    | 0.143      | 0.368    |

4. Conclusion
The tribological and thermophysical properties of engine oil were improved by the addition of nanoparticles G, Al₂O₃, TiO₂, Ni & Co-Cr. As additives in the engine oil, G, Al₂O₃, TiO₂, Ni & Co-Cr nanoparticles were used to display good friction reduction, anti-wear activity, improved thermal conductivity and consistent viscosity. This effect may be due to the rolling between the contact surfaces of spheres such as nanoparticles, thereby reducing friction. The thermal conductivity increased with an increasing concentration of nanoparticles with the stability of oil viscosity. The anti-wear mechanism can be due to the accumulation on the worn surface of G, Al₂O₃, TiO₂, Ni & Co-Cr nanoparticles, which in turn reduced the resistance to shearing and thus improved the tribological characteristics. On rubbing surfaces, nanoparticles may be known as nano-bearings. The nanoparticles G, Al₂O₃, TiO₂, Ni & Co-Cr are deposited under mixed and boundary lubrication only. Experimental studies have confirmed that the deposition on the fluid layers of G, Al₂O₃, TiO₂, Ni & Co-Cr nanoparticles improves the tribological properties of the base lubrication oil, showing decreased wear and friction. Aluminum alloy wear (Al 25) was observed to increase with an increased load value over time. As a multifunctional additive, G, Al₂O₃, TiO₂, Ni & Co-Cr nanoparticles can therefore be used. As Co-Cr 0.03wt% has been chosen as the most successful among our other experimented nanoparticles enriched nano lubricant so we can say that in future after considering the health & nature hazard it can be marketed for the usage of lubricant.

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