Analysis On Crystal Formation And Physio-Tribological Properties Of Lithium Based Grease Developed From Coconut Oil (Cocos Nucifera)

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Abstract. The increase in demand for alternative base oil for lubricant has led to the study of non-depleting source like vegetable oils. Some studies have reported the development of grease from sunflower oil and castor oil, which establish the probability of use of vegetable oil as potential base oil. In the present study, an eco-friendly NLGI grade 3 grease was developed using coconut oil as base oil and lithium stearate as thickener. The inherent tribological properties of the coconut oil and grease were evaluated. Tests results of newly formulated grease procured from cone penetration, rolling stability, water wash out, grease leakage, friction and wear are compared to a commercial sample of same grade. Even though the newly formulated grease is found to be competent to the commercial sample, the crystal formation at low temperature has restricted its applications at lower temperatures. Crystal formation at low temperature is due to the agglomeration of saturated fatty acids commonly known as wax occurred due to the low cold flow characteristics of the oil (pour point of coconut oil 26.55°C). The tribological results show that the performance of the newly formulated grease is comparable to commercial greases and its application is restricted to moderate climatic conditions.

1. Introduction
The need for non-toxic, non-depleting and environmental friendly lubricants have paved way to the study of potential tribological properties of vegetable oils. In recent years, tribologists around the world have identified vegetable oils such as sunflower [1], palm [2], rice bran [3], rubber seed [4] and coconut oil [5-7] as good base oil for lubricant formulations. The green lubricants (vegetable oil) with additives were found to be competent to the commercially available oils in a few applications such as engine oils [3-6], lubricating greases [8,9] and cutting fluids [10,11].

The mechanism of vegetable oil film formation over the metal surface can be explained by its head and tail structure of fatty acid. The hydrophilic head of the triglyceride (glycerol molecule) get attracted to the metal surface whereas hydrophobic tail (fatty acids) gets suspended in the oil resulting in the formation of a lubricating film between the interacting surfaces. Vegetable oils also possess inborn tribological properties such as higher flash–fire point and superior friction-wear characterises thereby showing its domination over mineral base oil. The main disadvantage of vegetable oil is its poor oxidative stability due to the presence of unsaturated fatty acids and higher acid value due to the presence of free fatty acids.
Among vegetable oils, coconut oil has superior tribological properties in its natural state. Higher percentage of saturated fatty acids (90%), higher oxidation stability and low acid value promote the use of coconut oil as potential lubricant base oil. Coconut oil with additives has been established as good lubricant in two stroke [5], four stroke engines [6] and as a good cutting oil [10]. Hence, this work focuses on extending the application of coconut oil in the formulation of semisolid lubricants (grease). The influence of tribological properties of coconut oil in coconut oil based grease was analysed in the current study and was found to have high influence over the properties of grease. 

Mechanism of grease lubricant involves the entrapment of lubricating oil inside a network of soap structure. The metallic soap acts like a surfactant resulting in the entrapment of oil inside the network structure [12, 13]. When pressure is applied over the grease, oil moves out from the network structure resulting in lubrication and while releasing pressure, surfactant restructures itself to entrap the oil molecules. Grease (NLGI Grade 3) was formulated using lithium stearate (metallic soap) as thickener and coconut oil as base oil. The tribological properties of the newly formulated grease were evaluated as per ASTM standards and were found to have satisfactory performance when compared to commercial grease sample of same grade.

Crystal formation was observed in newly formulated coconut oil based grease when preserved below 25ºC. Detailed study on crystals was done using gas chromatography technique (GC). The result procured from GC confirms the crystal particles as an agglomeration of longer chain saturated fatty acids, commonly known as wax. Wax formation in the grease was due to the poor pour point property of coconut oil. Hence, application of coconut oil based grease was restricted below its liquid-solid transition temperature (31ºC).

2. Materials and methods
The raw materials (chemicals and coconut oil) used for manufacturing the grease where procured from the resident market.

2.1. Materials
Lithium monohydrate and stearic acid used for the preparation of metallic soap was procured from Chemical house, Ernakulam, India. Magnetic and manual stirrers were used for controlled stirring operations. Deionized (DI) water with conductivity of 18.5 was used for dissolving lithium monohydrate during grease manufacturing process.

2.2. Coconut oil
Coconut oil is an edible vegetable oil extracted from coconut palm tree (Cocos nucifera). The flesh of coconut seed is dried and crushed to extract oil. The extracted oil is later heated to remove the moisture and preserved.

2.3. Metal soap preparation
Formulation of metallic soap is evolved through a chemical reaction as shown in equation 1. One mole of lithium monohydrate and one mole of stearic acid combine to form one mole of lithium stearate (soap) and two moles of water molecule. Lithium stearate metallic soap is extracted by removing the moisture content by heating.

\[
\text{LiOH.H}_2\text{O} + \text{C}_{18}\text{H}_{36}\text{O}_2 = \text{C}_{18}\text{H}_{35}\text{O}_2\text{Li} + 2\text{H}_2\text{O} \tag{1}
\]

Initially, 100g of lithium monohydrate is dissolved in 500ml of deionized water under continuous stirring action for 30 minutes using a magnetic stirrer. Once dilution is complete, solution is poured into the molten stearic acid (678g) at 70ºC under continuous stirring action using a mechanical stirrer. The Li+ ions combine with stearic acid to form lithium stearate by replacing hydrogen ions at the polar head of the fatty acids. The free hydrogen ions (H+) combine with hydroxyl ions (OH-) to from water molecules. The moisture content is removed by heating it above 100ºC.
Heating is further continued up to 190ºC (melting point of lithium stearate 180ºC) to ensure complete soap formulation. The metal soap is cooled and preserved for future use.

2.4. Green formulation
Different grades of grease (NLGI 000 to 6) can be manufactured by varying oil-soap ratio. For manufacturing NLGI grade 3 grease, 1500ml of coconut oil was mixed with molten lithium stearate (previously manufactured) at 190ºC. The mixing was carried out under constant stirring action using a mechanical stirrer for 1hr. Once formulation was complete, the grease was cooled and milled for 3 hrs. The newly formulated grease was preserved for further analysis.

2.5. Tribological test
Tribological properties of coconut oil and grease were evaluated using different ASTM standards. Friction, wear, flash point of the oil was carried out as per ASTM D5183, D4172 and D92 respectively. The thermal degradation and pour point of the oil was studied using thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Viscosity of the oil was measured using a rheometer. The tribological properties of grease such as consistency, rolling stability, grease leakage and water wash out were evaluated as ASTM D217, D1831, D1263 and D1264 respectively.

2.6. Crystal analysis
The crystals formed in the grease were analysed using gas chromatography (GC) technique. Macroscopic structural image of the crystal was acquired using scanning electron microscope (SEM).

3. Results and Discussions
The properties of the lubricating oil and grease where analysed. The tribological properties of the newly formulated grease were compared to a commercial sample procured from the market. Studies were also carried out on the crystals formed in the grease when preserved at low temperatures.

3.1. Physiochemical and tribological properties of coconut oil
Coconut oil mainly consists of 90% saturated fatty acids, 7% mono unsaturated and 2% poly unsaturated fatty acids. The physical properties of coconut oil are listed in table 1. Coconut oil is pale yellow coloured oil with a density of 0.925 gm/cm3. The oil has very low iodine (7) and acid value (0.4) when compared to other vegetable oils [3,4]. The lower percentage of unsaturated bonds of the oil has resulted on low iodine value. It infers the ability of the oil to resist oxidation and thermal degradation. Lesser amount of free fatty acids in the oil has resulted in lower acid values. The resistance of the oil towards corrosion is partially proportional to the amount of free fatty acid present in it. The oil has comparatively higher saponification value of 255. It shows the tendency of the fatty acids to get separated from glycerol molecules to form metal soaps.

Coconut oil has low cold flow properties. Cloud point of the oil is close to 29ºC and solidifies at 26.55ºC. The low cold flow property of the oil is due to the higher percentage of saturated fatty acids in the oil. The oil has high flash point of 289ºC and fire point of 295ºC, which is one of the main advantage of using vegetable oils as base oil. The inherent dynamic viscosity of the oil is 25.1mPas at 40ºC and 5.6mPas at 100ºC. Coefficient of friction of the oil is 0.093, were as wear scar diameter is 0.645mm. Thermal stability of the oil was found through thermo gravimetric analysis (TGA). It was found that coconut oil is thermally stable up to 240.9ºC and starts degrading on further heating as shown in figure 1.
Table 1. Physical properties of coconut oil

| Physical properties of coconut oil |  |
|----------------------------------|--|
| Colour                           | Pale yellow |
| Density [g/cm³]                  | 0.925 |
| Iodine value [g/l2/100 g]        | 7 |
| Saponification value [mg KOH/g]  | 255 |
| Acid Value [mg KOH/g]            | 0.4 |
| Cloud point [°C]                 | 29 |
| Pour point [°C]                  | 26.55 |
| Flash point [°C]                 | 289 |
| Fire point [°C]                  | 295 |
| Viscosity at 40°C [mPas]         | 25.1 |
| Viscosity at 100 °C [mPas]       | 5.6 |
| Coefficient of friction          | 0.093 |
| Wear scar diameter mm            | 0.606 |

Figure 1. Thermo gravimetric analysis (TGA) conducted of coconut oil.

3.2. Tribological properties of CO grease
The tribological properties of the newly developed grease (CO grease) and commercial grease (COM grease) was evaluated using different test methods as shown in table 2.
Table 2. Comparison of tribological properties of CO grease with COM grease

| Tribological properties      | CO grease | COM grease |
|------------------------------|-----------|------------|
| Unworked penetration         | 222       | 230        |
| Penetration after 60 strokes  | 240       | 231        |
| Rolling stability test (2 hrs)| 246       | 231        |
| Water wash out test (39°C)   | 0.31 grams lost | 0.23 grams lost |
| Water wash out test (79°C)   | 0.43 grams lost | 0.25 grams lost |
| Grease leakage test (6 hrs)  | No leakage | No leakage |

The unworked penetration of the newly formulated grease was found to be 222; it signifies that the newly formulated grease (CO grease) was under grade 3 (NLGI Grade 3 range 220-250). After completion of 60 stokes, a penetration difference of 7.5% (222 to 240, grade 3) was found when compared to unworked sample. The commercial grease seemed to be stable even after 60 strokes (230 to 231). Both samples (CO, COM grease) remained under same grade even after 60 strokes.

The shear stability of the grease was analysed by rolling stability tester. The stability of the grease was found satisfactory as the penetration variation of 9.7% (222 to 246) was observed when compared to unworked sample. Commercial sample was stable throughout the test (230 to 231). Both samples have passed the test as they remained in same grade even after continuous shearing operation.

The resistance of the grease towards water was analysed through water wash out test. The results infer the loss of 7.75 % (0.31g) and 10.75% (0.43g) of CO grease lost when tested at 39°C and 79°C respectively. Whereas, in the case of commercial sample 5.75% (0.23g) and 6.25% (0.25g) of grease was lost during testing. Even though the commercial sample seemed to be more resistant to water, a variation of 2% and 4.5% was only observed between CO and COM grease at lower (39°C) and elevated (79°C) temperatures respectively.

The bleeding tendency of oil from grease under running condition was analysed through grease leakage test. While testing both samples (CO, CMO grease), the grease collectors of the machine was found empty after 6 hours test. It infers the rare chances of oil to bleed under operating conditions. CO and COM grease have dropping point of 180°C (melting point of lithium 180°C) hence it did not exhibit any bleeding tendency throughout the test.

Friction-wear characteristics of coconut oil and grease samples were compared using four ball tester (1200rpm, 40kg, 75°C) as shown table 3.

Table 3. Comparison of friction-wear properties of coconut oil, coconut oil grease (CO grease) and commercial grease (COM grease).

| Property                  | Coconut oil | CO Grease | COM Grease |
|---------------------------|-------------|-----------|------------|
| Coefficient of friction   | 0.081       | 0.065     | 0.096      |
| Wear scar diameter [mm]   | 0.606       | 0.712     | 0.892      |
The COF of CO grease is 19.6 % (0.065 mm) lesser than that of coconut oil (0.081) and 32.3% lesser than commercial sample (0.096). The reduction in frictional properties is due to the combined action of oil and metallic soap [14]. The newly formulated grease (CO grease) seemed to be consistently giving lesser COF than oil and commercial grease (COM) as shown in figure 2.

In the case of wear, crude coconut oil showed more resistant to wear when compared to grease samples. The capacity of the oil to dissipate heat at the contact surface and the hydrodynamic action would have resulted in lesser and uniform material removal as shown in figure 3. The anti-wear property of the newly formulated coconut oil grease is 20.2% (0.712mm) more when compared to commercial sample (0.892mm). The wear scars on the steel balls of the commercial sample have a uniform pattern and the load seemed to be equally distributed over the region when compared to CO grease in figure 4 and 5. This might be due to the presents of extreme pressure additives in the commercial sample.

![Figure 2. Comparison of COF of coconut oil, CO grease and COM grease](image)

![Figure 3. Microscopic image of wear scar over steel ball when tested with coconut oil.](image)
3.3. Crystal formation
Crystal like formation was observed in CO grease when preserved below 25°C. Most of the crystals were spherically shaped as shown in figure 6. Detail study on the composition of crystals was done using gas chromatography technique. The results confirmed the presents of saturated fatty acids in agglomerated form as shown in figure 7. Thus the crystals found in CO grease were confirmed to be wax crystals. The structural images procured from SEM (scanning electron microscope) confirm close resemblance of crystal structures to that of paraffin wax as shown in figure 8 and 9.
Figure 6. CO grease sample along with crystals spread over a petri dish.

Figure 7. Gas chromatography analysis of crystals.

Figure 8. SEM image of crystals found in grease
Figure 9. SEM image of paraffin wax

Wax formation is one among the main challenges faced by petroleum industries while transferring crude oil below liquid-solid transition temperature [15-17]. The liquid-solid transition temperature of coconut oil and grease was found using differential scanning calorimetry (DSC) as shown in figure 10. The structural changes in coconut oil and CO grease was observed between 9ºC to 33ºC and 10ºC to 31ºC respectively, when heated from -50ºC to 50ºC at a constant rate of 10ºC/min [18]. The peak value of the samples was observed as 26.55ºC for oil and 25.52 ºC in the case of grease. The close resemblances of structural changes in the samples infer that grease exhibits similar phase change characteristics to that of its base oil. This is due to the presents of higher percentage of base oil (70%) when compared to total grease composition. Hence when coconut oil grease was preserved below 25ºC, micelle structure with saturated fatty acid in the CO grease solidified to form wax crystals. Hence, the application of coconut oil grease was restricted below 31ºC.

Figure 10. Differential scanning calorimetry of coconut oil.
4. Conclusions
The results procured from tribological test conducted on coconut oil based lithium stearate grease seemed to be satisfactory when compared to a commercial sample of same grade (NLGI grade 3). The coefficient of friction and wear characteristics of the newly formulated grease is seen superior than commercial grease by 32.3% and 20.2% respectively. Commercial grease is more resistant towards water when compared to newly formulated grease, a variation of 2% and 4.5% is only observed between CO and COM grease at lower (39ºC) and elevated (79ºC) temperatures respectively. The worked penetration and shear stability of commercial sample is better when compared to coconut oil grease (CO grease), but both samples retained their grade after testing (penetration, rolling stability), thereby satisfying the requirements of the standards.

The wax crystal formation in coconut oil grease is due to the low pour point characteristics of the oil, thereby restricting its application below 31ºC. The properties of the newly formulated grease can be improved by chemical processes or by adding suitable additives.

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