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Experimental Evaluation on the Tribological Properties of Coconut Oil by the Addition of CuO Nanoparticles

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Considering the environmental problems created by mineral based lubricants, exploring the possibility of the use of vegetable base oils as automobile lubricants has been a growing worldwide trend. In the present study, analysis of coconut oil as a lubricant has been carried out in the perspective of its tribological behaviour using a pin-on-disc tribometer. Copper oxide nanoparticles are added to the oil on weight-percentage basis, the variation of its friction-reduction and anti-wear properties are analysed. At an optimum concentration of nanoparticles, the coefficient of friction and the specific wear rate are found to be the lowest. Viscosity of oil is also seen to increase by an increase of concentration of nanoparticles. Flash-point remains constant while the fire-point increases as the nanoparticle concentration is increased. From dispersion analysis it is seen that the nano oil is not suitable enough for long stationary applications. Surface structure of the worn surfaces obtained by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) shows that the optimum concentration of nanoparticles in this lubricant causes the roughness of the worn pin surface to reduce to a low value after sliding. Wear scar obtained in the presence of nano oil is smoother compared to that with bare coconut oil. When the level of nanoparticles increases above the optimum level, friction coefficient and wear rate are seen to increase.

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1. Introduction

Lubrication is an art that has been practiced for thousands of years from the early days of human civilization. There has been growing concern on the use of mineral oils as lubricants because of the worldwide interest in environmental issues. In this regard, vegetable oils constitute a suitable alternative for replacing ‘mineral oils’, as they are wholly biodegradable, non-toxic, and ‘Generally Regarded as Safe’ (GRAS) products.[1] Indeed, vegetable oils possess many of the desirable properties of lubricants, such as good contact lubrication, high viscosity index (i.e., minimum changes in viscosity with temperature), high flash-point and low volatility. Continued use of cutting fluids which are mainly petroleum-based creates several techno-environmental problems, such as environmental pollution and biological problems to the operators.[2] Bio oils provide intrinsically strong lubricating film and as such possess higher lubrication properties than conventional mineral oil metal working fluids.[3] Biological oil cutting fluid has several superior features compared to the petroleum-based cutting fluids, such as, reduced overall volume of fluids due to higher viscosity, minimized health risk to workers and minimized bio-contamination.[4] Vegetable oils are particularly effective as boundary lubricants as the high polarity of the entire base oil allows strong interactions with the lubricated surfaces. However, the main weakness is their relatively poor oxidation stability.[5] At extreme loads vegetable oil-based lubricants become significantly less effective.[6] With the current interest in lubricants from renewable sources, studies of vegetable-oil-based lubricants and means of predicting their performance are important.

Coconut oil finds mention as a lubricant among other widely used vegetable oils such as olive oil, rapeseed oil, etc. during the pre-mineral oil era.[7] Coconut oil is widely being used as a two-stroke engine lubricant in autorikshaws and scooters in Kerala, a southern state of India. There are many advantages obtained by the use of coconut oil including improved mileage, better pick up (acceleration), smoother engine operation, less smoke etc..[8] Coconut oil shows good lubricant properties, such as high viscosity index, good lubricity, high flash point and low evaporative loss.[9]

One of the drawbacks of coconut oil when used as a lubricant is that the wear rate in sliding in its presence is higher compared to that of mineral oil based lubricants.[10] Coconut oil has very high pour point because of the predominantly saturated nature of its fatty acid constituents precluding its use as base oil for lubricants in temperate and cold climatic conditions.[11] Vegetable lubricants generally show good lubricating properties under boundary lubrication mode.[6]

Tribology is based on the study of lubrication, friction and wear at macro level. Nanotribology deals with the variation in properties of lubricants and contacting surfaces at micro/nano level. The term "nano-lubricant" in the present context represents a lubricant which is used for nano applications or a lubricant obtained by the addition of nanoparticles. In the present study nano-lubricant is used to represent the natural coconut oil with copper oxide (CuO) nanoparticles as the additive.

There have been many investigations on the tribological properties of lubricants with different nanoparticles added. Several investigators have reported that the addition of nano particles to the lubricants is effective in reducing wear and friction.[12-14] Experimental studies have been carried out on the variation in properties of SAE-40 and coconut oil as base lubricants and boric acid solid lubricant of 50 nm particle size as suspensions.[15] The results show a reduction in temperature at the contacting points when nanoparticles are used. The friction-reduction and anti-wear behaviours are dependent on the characteristics of nanoparticles such as size, shape and concentration. The size of nanoparticles used has been mostly in the range of 20-150 nm.

The objective of the present study is to evaluate the tribological and thermo physical characteristics of coconut oil by the addition of CuO nanoparticles at different concentrations. In this study, the variation of viscosity and friction-reduction characteristics of the nano-lubricant is analysed. Dispersion and sedimentation properties of nanoparticles in the nano-lubricant, surface topography of pin surface are also studied.

2. Experimental Procedure

2.1 Preparation of Nano Lubricant

In the present work, CuO nanoparticles were suspended in commercially available coconut oil in different concentrations to formulate the nano-lubricant which is used in small quantities at the sliding interface between aluminium alloy (Al 98%, Si 2%) and steel in a pin-on-disc tribometer. 500ml of coconut oil was used for making the nano-lubricant. Density of the oil was measured on weight to volume basis using a 25ml flask and a precision balance. Commercially available nanoparticles in the range of 20-150nm supplied by M/s Sigma Aldrich Ltd. Bangalore were used in the experimental study, for which the size and true density have been provided by the suppliers. The size distribution of the particles was verified using Field Emission Scanning Electron Microscopy (FESEM).These nanoparticles were added to the oil on weight percentage basis, such as 0.1%, 0.2%, etc. The oil was then agitated using ultrasonic shaker for 40 minutes to ensure uniform dispersion and good suspension stability. Temperature was maintained at 30ºC.

2.2 Tribological Study

The tribological studies were conducted using a pin-on-disc tribometer in accordance with ASTM G-99 standards. The pin material used was aluminium alloy and the disc was of steel with a hardness of 60 HRC. The diameter of the pin was selected to be 8mm and length 27mm. After the turning operation of the aluminium pin, its surface was polished using emery paper of 600 grit size; the same polishing method was adopted for steel disc also. The surfaces were then cleaned by acetone. Profilometer readings showed that the roughness value Ra of pin surface varied from 0.28μm to 0.31μm, and disk surface, 0.14 to 0.15μm.The sliding distance was taken as 1000m and track diameter of the disc was 90mm. The speed of rotation of the disc was varied from 1.4 to 5.6 m/s. Oil was supplied at the interface in a drop-wise manner in order to maintain boundary lubrication / thin film conditions. Frictional force was measured directly by using a load cell and an electronic display. Three trials were conducted for each speed and concentration. The average values of the three trials were taken for the calculation of coefficient of friction. Normal load applied at the interface was varied between 1 and 2MPa.

2.3 Viscosity Analysis

The viscosity of the nano-lubricant was measured using a Redwood Viscometer. 125ml of oil was used for each trial. Time required for emptying 50ml of oil was measured and viscosity was calculated using Redwood formula. Three trials were conducted for each sample. The variation of dynamic and kinematic viscosities were obtained at a temperature range of 30-90^{o}C.

2.4 Flash and Fire point Measurements

Flash and fire points were measured by standard methods using a Cleveland open cup flash and fire point apparatus.

2.5 Dispersion Analysis

The analysis of dispersion of nanoparticles in the nanolubricant was done by Ultra Violet Spectroscopy analyzer. Coconut oil was filled in two cuvettes and base line correction was done. Cuvette is a square shaped 3.5ml capacity bottle made of quartz. Then in one cuvette nano-lubricant was added and bare coconut oil in the other. The absorbance level of visible light, which is proportional to the dispersion of nanoparticles in the oil, was measured using visible spectroscopy over different time intervals.

3. Results and Discussions

Copper oxide nanoparticles in the range of 20-150nm were used for the analysis.

Fig. 1 shows the Scanning Electron Microscopy (SEM) image of CuO nanoparticles. Some of the nanoparticles which are seen to be agglomerated would get separated during agitation by ultrasonic shaker. The degree of agglomeration can be obtained using dispersion analysis. Since the degree of agglomeration can be given in terms of settling trend, absorbance level in UV Spectroscopy may be considered as a measure of degree of agglomeration. For the present study, absorbance measured is 4.3%, 80 hours after the formulation of nano-oil.

3.1 Frictional Force Analysis

Frictional force has been measured using pin-on-disc machine for various sliding velocities of the disc and at various concentrations of nanoparticles in the lubricant. It is observed

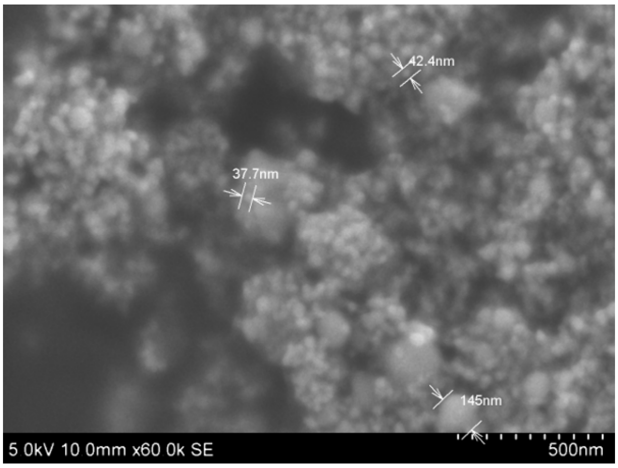
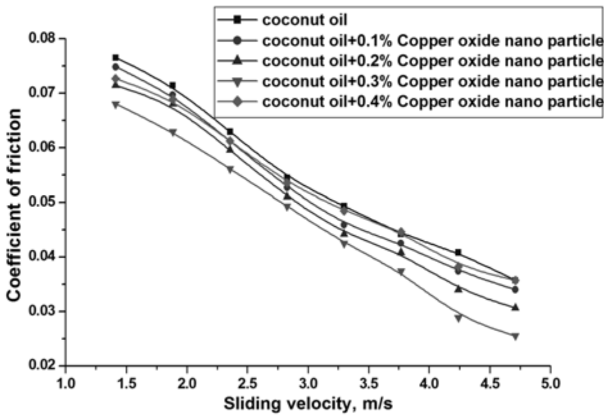
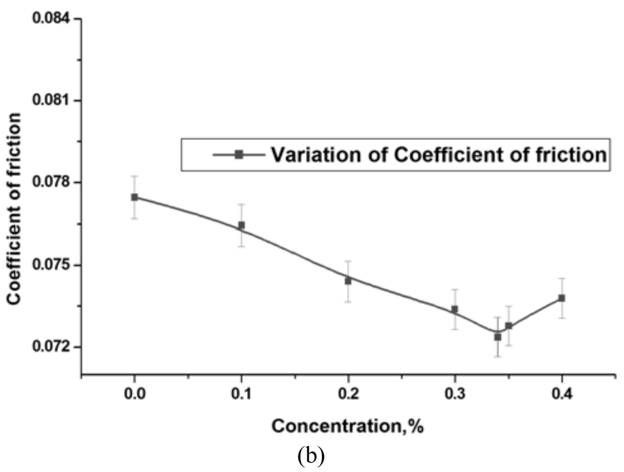


Fig. 1 SEM image of copper oxide nanoparticles



(a)



(b)

Fig. 2 (a) Variation of coefficient of friction at 98N load (b) Variation of coefficient of friction at variation in concentration at 1.5m/s sliding speed, 2MPa load

(Figure 2(a)) that an increase of sliding speed causes the coefficient of friction to decrease gradually. Figure 2(b) illustrates the variation of coefficient of friction with increasing nanoparticle concentrations for a sliding speed of 1.5 m/s. It is seen that the coefficient of friction decreases by increasing concentration of nanoparticles in the lubricant, shows the lowest value for a concentration of 0.34% and then increases.

This reveals the presence of an optimum concentration level at which the coefficient of friction is a minimum, for a given speed and normal load.

This trend may be attributed to the fact that the nanoparticles in the lubricant at lower concentration levels develop a third body rolling effect between the sliding surfaces causing a reduction in friction, whereas larger concentrations causes interaction between the solid particles themselves, thus increasing friction.

Figure 3 shows the variation of specific wear rate with nanoparticle concentration for various sliding velocities. It is observed that as the concentration of the nanoparticles increases, specific wear rate reduces gradually, takes a minimum value at 0.34% and then increases, showing the presence of an optimum concentration for minimum wear too. With increasing sliding velocity, the specific wear rate decreases, still showing the same trend with nanoparticle concentration. The experiment was conducted up to 0.6% concentration of CuO nanoparticles. Higher concentration levels cause faster sedimentation rates and also make the nano-oil more costly. Above 0.34% the wear rate is continuously increased. This may be due to the presence of more solid to solid contacts at higher concentration levels, whereas, at lower concentration levels, solid to liquid contacts are more prominent. While drawing the error bar, the variation in wear values shown for each trial was very low. The values lie within the statistical distribution curve.

The stribeck curve was drawn for bare coconut oil and coconut oil with CuO nanoparticles. From the curves below, it is clear that up to a speed of 5.6 m/s the lubrication regime is boundary or thin film.

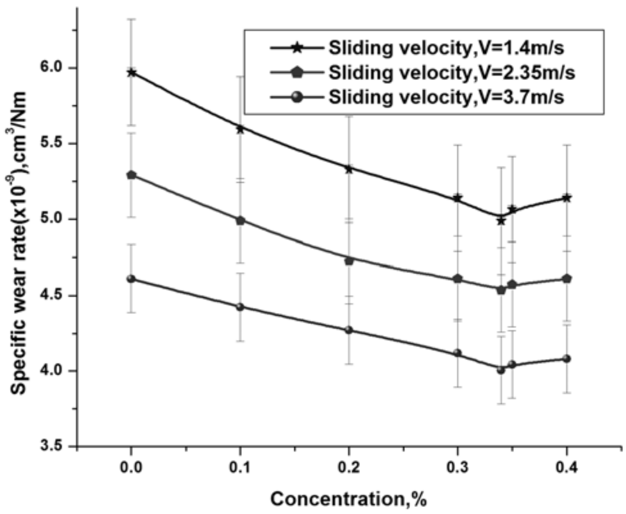


Fig. 3 Wear rate at 2MPa and at different concentrations of addition of CuO nanoparticles

3.2 Viscosity Analysis

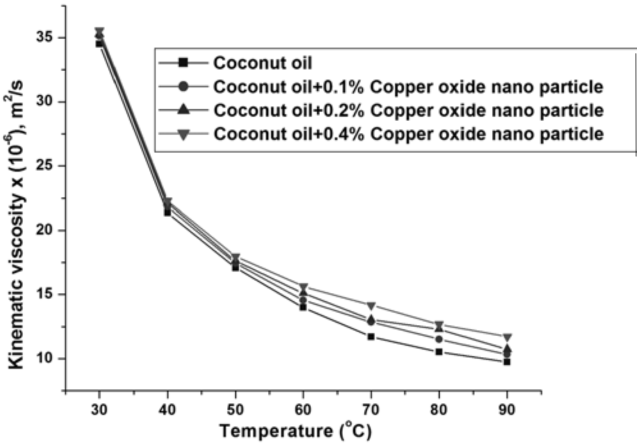
The viscosities of the nano-lubricant at various temperatures and at various nanoparticle concentrations have been measured using Redwood Viscometer. Three trials were conducted for each sample and the average values are taken for analysis. The trial values are comes within the error lever/standard distribution. As expected, the viscosities generally decrease as the temperature increases. From the experiments it is observed that the kinematic and dynamic viscosities increase to some extent by the addition of nanoparticles (Figure 4(a), (b)). The variations at lower temperatures are marginal but at elevated temperatures, higher increases in viscosities are observed for increasing concentrations. The flow ability did not reduce much while small percentage of addition of CuO nanoparticles.At higher temperatures, the decrease in density has caused larger variations in kinematic viscosity compared to dynamic viscosity.

As shown in Figure 5, flash point of coconut oil does not change with the addition of nanoparticles, whereas fire point shows an increase with increase in concentration of nanoparticles. It may be due to the variation in chain structure of the fatty acid at elevated temperatures.

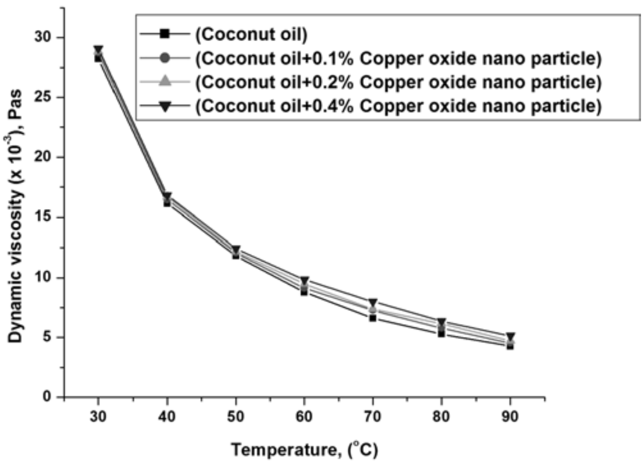
CuO nanoparticles are not flammable. As the temperature, of the oil is increased, flash point refers to the condition when the fumes produced from the oil are just sufficient to produce a flash. This remains to be the same irrespective of the nanoparticle concentration, which is a property unique for coconut oil. For continuous burning (i.e. fire point), continuous vapour formation is necessary. Since CuO nanoparticles are not flammable, higher temperatures are necessary for continuous burning of the oil when the concentration of CuO is higher. This could be the reason for an increase in fire point with increase in concentration of nanoparticles.

3.3 Dispersion Analysis

From dispersion analysis using UV spectroscopy, it is understood that the nanoparticles in the lubricant are likely to settle down after a period of time (Figure 6). So this type of nano oil is suitable only for somewhat short term applications. It can also be used for automobiles where the stationary time is low. It is required to develop techniques to formulate nano-lubricants which are stable over a longer period of time. By the addition of surfactants the settling trend can be suppressed to a certain level.



(a)



(b)

Fig. 4 (a) Variation of kinematic viscosity for different percentage of addition of copper oxide nanoparticles (b) Variation of dynamic viscosity for different percentage of addition of copper oxide nanoparticles

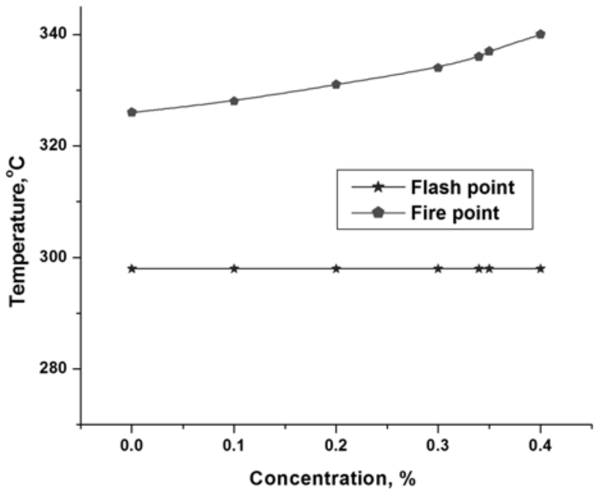


Fig. 5 Variation of flash and fire points of lubricant for different concentrations of nanoparticles

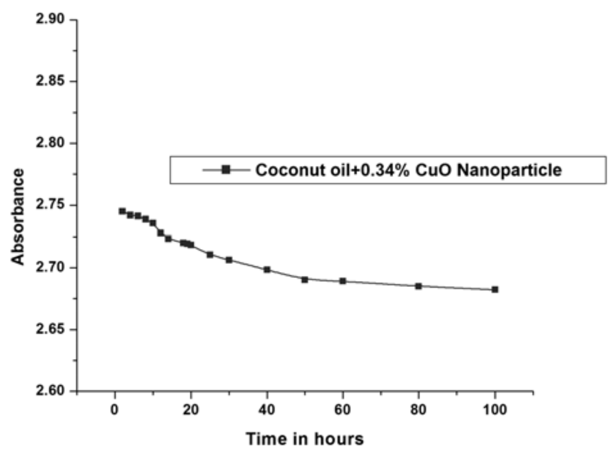
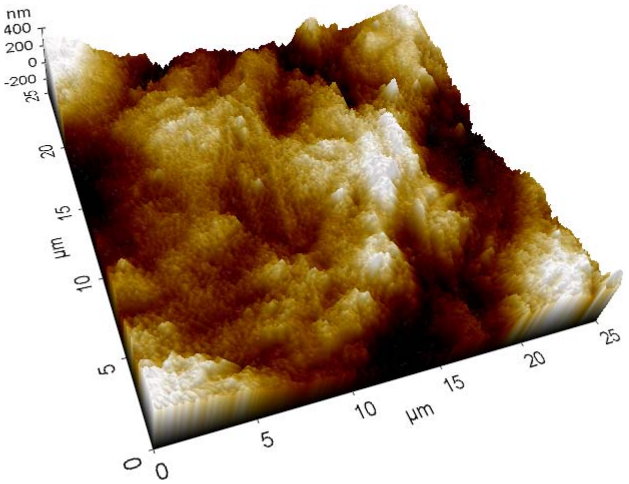


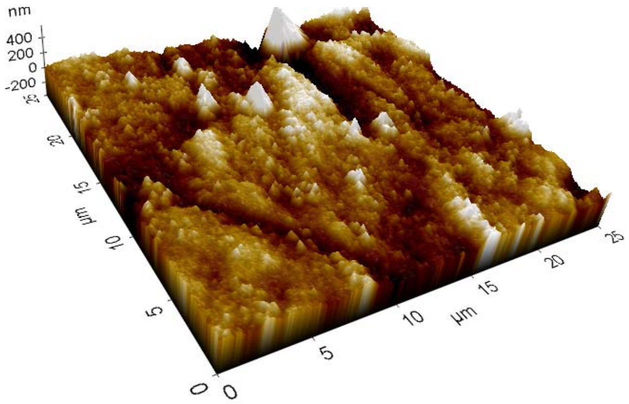
Fig. 6 Variation of absorbance levels of visible light at different time intervals for nano lubricant with 0.34% concentration of nanoparticles at 429nm wave length

3.4 Surface Roughness Analysis

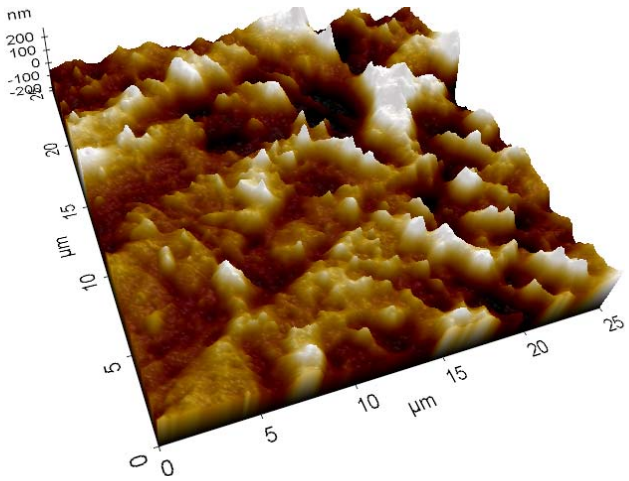
To evaluate the changes in topography during the lubrication tests, an atomic force microscope (AFM) which enables observations of topographic features in 3D was employed. The images were obtained by the use of non contact mode, and the cantilever tip was taken as chromium coated with gold. Area was taken to be 25×25μm so that the surface roughness of a small region could be obtained clearly.



(a) Surface before test



(b) Surface after test with base lubricant (without nanoparticles)

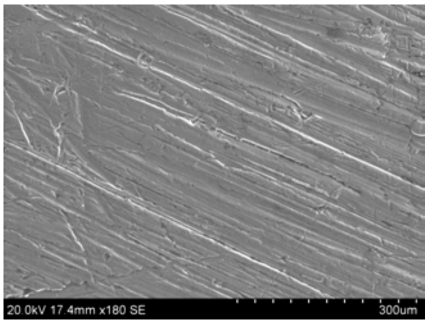


(c) Surface after test with nano lubricant (0.34% concentration of nanoparticles)

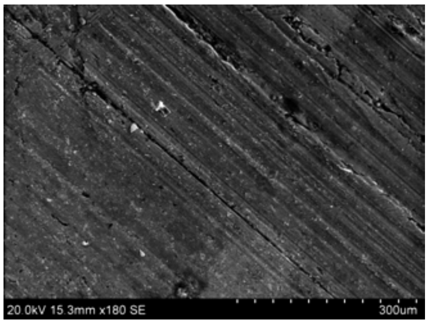
Fig. 7 (a), (b) and (c) AFM images of the friction surfaces of the pin (speed, 1.5 m/s & Load, 98 N)

Figure 7 shows an AFM image of the surface of pin subjected to sliding on the pin-on-disc tribometer under a sliding velocity of 1.5 m/s and a normal pressure of 2MPa. The average roughness of the pin before testing was 97nm (Fig. 7(a)). After the experiment by using bare coconut oil as the lubricant, the average roughness was changed to 61nm (Fig. 7(b)) and the surface got slightly irregular in shape. By the use of oil added with nanoparticles at the optimum concentration level, (Fig. 7(c)) the roughness level was changed to 23nm. The topography of the surface shows that the surface is almost plane at optimum concentration mode with little irregular scuffing.

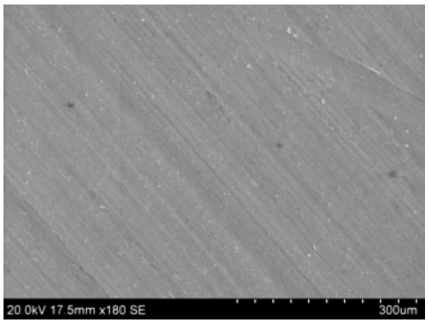
Surface roughness of the disc was taken before and after sliding using profilometer (SJ301, Mitutoyo), with cut-off length 0.25mm. The roughness before the test was 0.18μm and after trial with bare coconut oil it was 0.15μm. After sliding with optimum concentration level of CuO nanoparticles the roughness was recorded to be 0.11μm. For the pin surface the corresponding roughness's were 0.28, 0.16, and 0.09μm. The hardness of the steel disc was not changed after the tests. The hardness of aluminium alloy and CuO nanoparticles are close to each other, and from EDX analysis, it was clear that nanoparticles were not sticking to the pin surface.



(a) Before sliding



(b) After sliding in presence of Coconut oil



(c) After sliding in presence of nanolubricant with 0.34% concentration of nanoparticles

Fig. 8 SEM images of the friction surfaces of the pin

Scanning electron microscopy (SEM) images are taken for the analysis of surface topography. From Figure 8 it is clear that while using at optimum concentration addition of CuO nano particles the wear scar obtained is smooth (Fig. 8 (c)) as compared to the test conducted with bare coconut oil (Fig. 8(b)). SEM mages are taken by using secondary electrons and the image taken with a scale of 500nm.

4. Conclusions

The following conclusions have been drawn from the reported work:

(1) As a lubricant, friction-reduction properties of coconut oil are enhanced by the addition of CuO nanoparticles to a moderate concentration.
(2) There exists an optimum concentration of CuO nanoparticles (0.34%) at which the coefficient of friction is the least.
(3) At concentrations lower than 0.34%, the reduction in friction is attributed to the change of contact configuration from sliding to more of rolling, due to the presence of nanoparticles. When the concentration is further increased, the contact configuration reverts back to more of sliding, thus increasing the coefficient of friction.
(4) The kinematic and dynamic viscosities are slightly increased by the addition of nanoparticles in coconut oil.
(5) The flash point of oil does not change with variation in addition of nanoparticles, but the fire point increases.
(6) From the dispersion analysis it is clear that nanoparticles tend to settle down after a long time if oil is kept stationary. Hence proper measures are required to be taken to reduce this tendency.
(7) The surface structure obtained by using AFM and SEM shows that surface roughness is high while doing experiment using bare coconut oil but it is smooth while using the optimum level of nanoparticles.

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