Experimental studies on viscosity and tribological characteristics of blends of vegetable oils with CuO nanoparticles as additive

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High biodegradability, renewability and low toxicity of vegetable oils make them excellent lubricating base oils. Coconut oil (CO) when used as a lubricant at metallic interfaces exhibits a low coefficient of friction but high wear rate compared to mineral oils, which limits its application as a commercial lubricant, whereas mustard oil (MO) exhibits better wear resistance. The main objective of this work is to obtain an optimal blend of MO and CO to be used as an environment-friendly base oil and to add an optimal concentration of nanoparticles as an additive to improve the viscosity and reduce the friction and wear rate. The experiments are performed on the blends with MO/(CO + MO) ratio ranging from 10 to 50% and the addition of CuO nanoparticles with concentrations ranging from 0 to 0.4 wt.%. The viscosity and tribological analyses of the CO, MO, their blends, and mineral oil (SAE20W40) are carried out and compared. Both the coefficient of friction and wear scar diameter are found to be lower than those of mineral oils. Further improvements in the tribological characteristics of the blends are attained by the addition of CuO nanoparticles in small concentrations, 0.2 wt.% being optimal.

1. Introduction: Conventional lubricants used in machinery are derived from mineral oils. High cost and environmental issues associated with mineral oils forced researchers to strive for the development of eco-friendly lubricants. Vegetable oils are seen to be contrasting options to mineral oils for lubricant development on account of their innate specialised properties and their capacity towards biodegradability [1–4] together with reduced cost. Vegetable oils are very effective in boundary lubrication as the high polarity of the oil permits strong interactions with the lubricated surfaces.

It has been reported that the blending of vegetable oils with other lubricants [5, 6] or with different additives [7] enhances their tribological characteristics. Different investigators [8–10] anticipated the unrivalled tribological execution of vegetable oils in both boundary and hydrodynamic regimes. Guo *et al.* [11] investigated the lubrication performance of a mixture of castor oil with other vegetable oils and reported that the performance of mixed oil was superior to that of castor oil. The prevailing wear reduction quality of vegetable oils is because of the propensity of vegetable oils towards lubricated surfaces to form a stable lubricant film [12, 13]. Jayadas *et al.* [14] compared the performances of coconut oil (CO) and commercial engine oil as lubricants and observed lower coefficient of friction, but higher wear rate for CO compared to those of the commercial lubricant. Mia and Ohno [15] investigated the physical properties and compared the phase diagrams of CO and mustard oil (MO) with those of mineral oils and found that CO imparts the lowest coefficient of friction and MO, the lowest wear scar diameter. Hence it is better to blend CO with MO for improving the tribological characteristics.

According to the available literature, many studies were focused on lubrication by various vegetable oils, but few studies were reported for the blended vegetable oil-based lubricants. Though CO shows a low coefficient of friction, the high specific wear rate and pour point of CO limits its extensive application as a lubricant in the industry. According to Hashempour-Baltork *et al.* [16], mixing of vegetable oils possessing various useful properties is one of the simplest strategies to make new particular products with several desirable properties. MO shows lower specific wear rate and pour point than CO. Hence, in this work, MO is mixed with CO to obtain an optimal blend possessing the best lubrication characteristics in the boundary lubrication regime.

Recently, the addition of nanoparticles to the base oil for improving rheological and tribological characteristics has become an interesting research topic. The concentration, size and shape of nanoparticles play an important role in reducing the coefficient of friction and wear rate. Many researchers [17–22] detailed that adding a very small weight percentage of nanoparticles to the MO improves its rheological and tribological properties greatly. However, the reported researches are very limited in the area of the addition of nanoparticles to enhance the rheological and tribological characteristics of the vegetable oils [23–26]. Thottackkad *et al.* [27] examined the tribological behaviour of CO added with CuO nanoparticles and reported that at a concentration of 0.34%, the coefficient of friction is the least. Koshy *et al.* [28] examined the tribological performance of CO and MO-based nanolubricant containing CuO nanoparticles and reported that the coefficient of friction and wear rate are considerably reduced with the optimal concentration of 0.35 and 0.4%, respectively. The literature survey reveals that the addition of few weight concentrations of CuO nanoparticles to the vegetable oil, especially CO, improves rheological and tribological characteristics.

The objective of this work is to evaluate the viscosity and tribological efficiency of blended vegetable oils viz., CO and MO for developing new biodegradable vegetable oil lubricants that can substitute commercial mineral oils (e.g. SAE20W40). Enhancement of the tribological characteristics of the developed lubricant by adding CuO nanoparticles is also envisaged.

2. Materials and methods: In this work, five distinct oil blends were made by adding MO varying from 10 to 50% in CO as given in Table 1. Correspondingly, the blends were designated as B1, B2, B3, B4 and B5. The mixed oils were continuously stirred on hot plate agitator at 80°C for 2 h with a rotational speed of 1000 rpm to guarantee homogenous blending of the oils and were permitted to cool down to room temperature before testing.

A Redwood Viscometer was used for measuring the viscosity of the lubricants at a temperature varying from 40 to 100°C as per ASTM D-445 standards. Each sample was subjected to three trials of measurements and the average was taken. ASTM D 2270 was chosen as the basis for determining the viscosity index (VI).

Thermo-gravimetric analysis (TGA) was carried out for CO, MO, blends B5 and mineral oil for getting the degree of thermal stability,

Table 1 Volume and blend ratio of oils

Designation	Blend ratio, %	CO, ml	MO, ml
B1	10	900	100
B2	20	800	200
B3	30	700	300
B4	40	600	400
B5	50	500	500

using PerkinElmer STA6000 for a temperature range of 0–500°C with a heating rate of 20°C/min.

The tribological studies were carried out using a four-ball tester. Here, the coefficient of friction (as per ASTM D 5183-05) and wear scar diameter (as per ASTM D4172-94) for different oils including blended oil with and without nanoparticles were evaluated. The operating parameters are speed, 600 rpm, load, 392 N (1 GPa), and temperature, 75 ± 2°C. The balls used in the test are made of GCr15 bearing steel with a diameter of 12.7 mm and a hardness of 64 HRC.

The tribological characteristics of different blends can be enhanced by the addition of CuO nanoparticles. CuO nanoparticles with physical properties shown in Table 2 were procured from M/s. Nano Labs Pvt. Ltd., India. The Cuo nanoparticles are characterised by XRD spectrum (Fig. 1) and SEM image (Fig. 2).

In this work, nanoparticles were added to the oil at different concentrations, viz., 0.1, 0.2, 0.3 and 0.4 wt.% and nanolubricants of 500 ml are prepared at each concentration of nanoparticles. Then 2 ml of span 80 (Sorbitan-Monooleate) was poured into the nanolubricant as a surfactant for improving dispersion stability of nanoparticles. The mixture was then agitated using an ultrasonic shaker for 2 h at room temperature for uniform dispersion and stability. The dispersion stability was tested quantitatively by UV–vis spectrophotometer.

3. Results and discussions: Both CO and MO have similar densities, better miscibility and better biodegradability due to their intrinsic molecular structure and chemical composition. It is observed that CO consists of 90% saturated fatty acids (a major portion is contributed by lauric acid), 7% monounsaturated fatty acids and 2% polyunsaturated fatty acids, whereas MO contains only 4.4% saturated fatty acids, 74% monounsaturated fatty acids (a major portion is contributed by erucic acid) and 19% polyunsaturated fatty acids. The fatty acid components' percentage of blend B1, B2, B3, B4 and B5 are in the middle of CO and MO. The unsaturated fatty acids are responsible for the low pour point.

Table 2 Physical properties of CuO nanoparticles

Property	Value
purity	>99.5%
average particle size	30–50 nm
colour	brownish black
morphology	spherical
specific surface area	>10 m^2/g
true density	6.4 g/cm^3

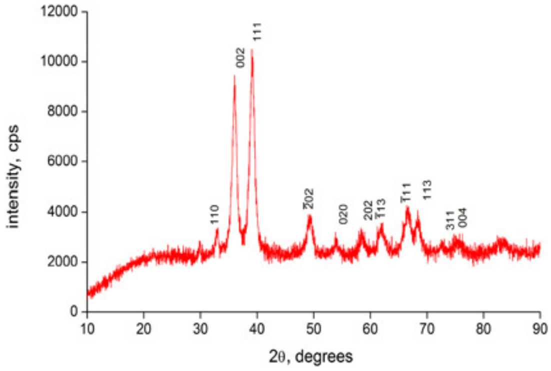

Fig. 1 *XRD spectrum of CuO nanoparticles*

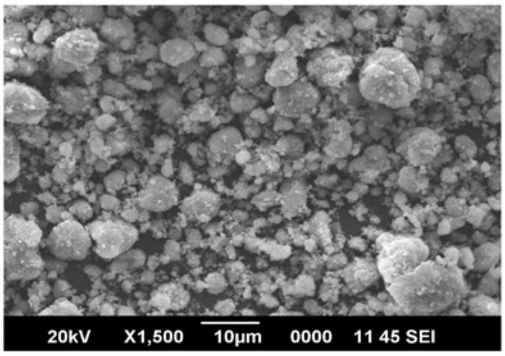

Fig. 2 *SEM image of CuO nanoparticles*

The kinematic viscosity and VIs are summarised in Table 3. The variations of dynamic viscosity at temperatures varying from 40 to 100°C for different blend ratios are shown in Fig. 3. The viscosity range of vegetable oils such as CO, MO and their blends is almost the same. The viscosity variation with temperature of vegetable oils and mineral oils are measured and compared. It is found that the VI is more for vegetable oils. The kinematic viscosity of MO is greater

Table 3 Rheological properties of different oils

Oil	Kinematic viscosity, mm^2/s		VI
	At 40°C	At 100°C	
CO	27.82	7.07	170.9
B1	29.11	8.72	179.3
B2	29.87	9.52	180.6
B3	31.40	10.32	180.0
B4	32.14	11.12	180.2
B5	32.88	11.95	180.0
MO	36.61	15.30	176.9
mineral oil (SAE20W40)	102	14.4	142

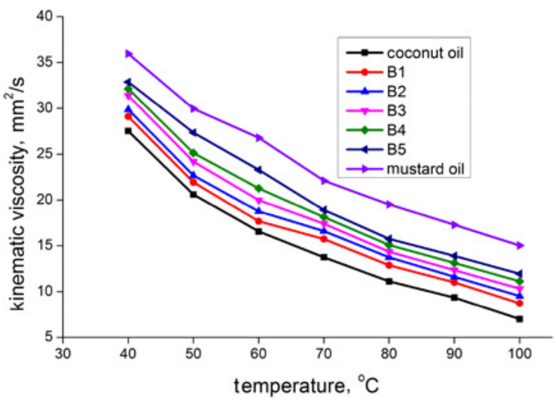

Fig. 3 *Variation of kinematic viscosity with temperature for different blend ratios*

than that of other oils. The viscosity of all types of oils decreases with the increase in temperature.

The TGA to compare the thermal stability of mineral oil, CO, MO and blend B5 (Fig. 4) indicates the onset temperatures of thermal decomposition 290, 300, 334 and 311°C, respectively. Fig. 4 shows that the blend (B5) has better thermal stability (described in terms of onset temperature) than that of mineral oil.

Tribological studies are conducted using four-ball tester in which the contacting surfaces are rotating. The test using four-ball tester can be considered as a screening test for comparing the developed lubricant with the existing oils. Coefficient of friction and wear scar diameter are evaluated for CO, MO, their blends and SAE20W40 oil, using four-ball tester and the results are tabulated in Table 4. The variation of coefficient of friction with time is shown in Fig. 5.

It is seen that, with the increase in the blend ratio (%), the coefficient of friction increases, but the wear scar diameter decreases. The low frictional characteristics of vegetable oils are due to the presence of triglyceride chain in it. The CO gets saponified at elevated temperatures and water vapour in the air generates detrimental products, which result in more wear. The coefficient of friction of all the blends is lesser than that of mineral oil, but the wear scar diameter is greater than that of mineral oil except B5. Table 4 also shows that B5 provides a lower coefficient of friction and wear scar diameter than those of mineral oil.

From these discussions, it is observed that all the blends (with blend ratio 10, 20, 30, 40 and 50%) have got advantages of both CO and MO. Further, to improve the tribological properties, CuO nanoparticles are added to the blend in varying concentrations, viz., 0.1, 0.2, 0.3 and 0.4 wt.%. Few drops of span 80 (Sorbitan-Monooleate) are also poured into the nanolubricant as a surfactant for improving the dispersion stability. The samples of B5 (blend ratio – 50%) added with different concentrations of CuO nanoparticles and surfactant and kept stationary for two weeks after preparation are shown in Fig. 6.

UV–vis spectrophotometer tests were conducted at a wavelength of 445 nm, with a repeatability of 1 nm. In UV–vis spectrophotometry, the absorbance level depends on the amount of particles per unit volume and can be used to indicate variations in particle concentration in the solution with time (Amiruddin *et al.* [29], Yu and Xie [30]). Fig. 7 shows the absorbance level of nanolubricant with CuO nanoparticles at room temperature and 100°C throughout 72 h. It is observed that the variation in absorbance level is slightly higher for nanolubricant at 100°C. However, the dispersion stability for samples at both conditions is quite good. It is understood that DLVO theory is the basis for the stability of particles in suspension. Nanoparticles tend to attract each other through vander Waals forces, and do not depend much on temperature. However, change in temperature may weaken the stabilising electrostatic repulsion until the dispersion becomes unstable.

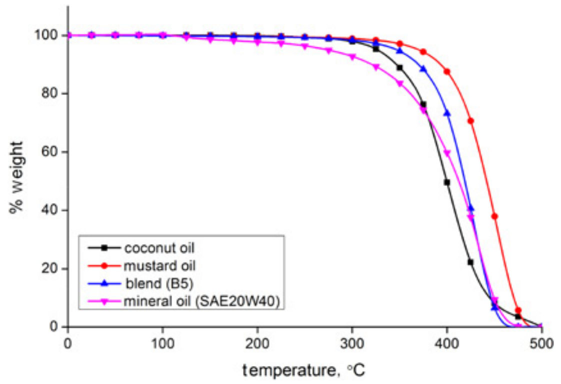

Fig. 4 *TGA curve of CO, MO and their blend B5 (50%)*

Table 4 Test results using four-ball tester for different oils without nanoparticles

Oil	Coefficient of friction	Wear scar diameter, mm
CO	0.090	0.587
B1	0.092	0.585
B2	0.095	0.546
B3	0.096	0.536
B4	0.098	0.514
B5	0.099	0.489
MO	0.120	0.478
SAE20W40 oil	0.103	0.496

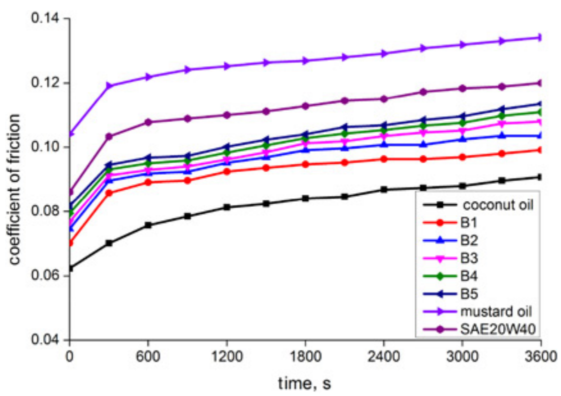

Fig. 5 *Variation of the coefficient of friction with time for different oils*

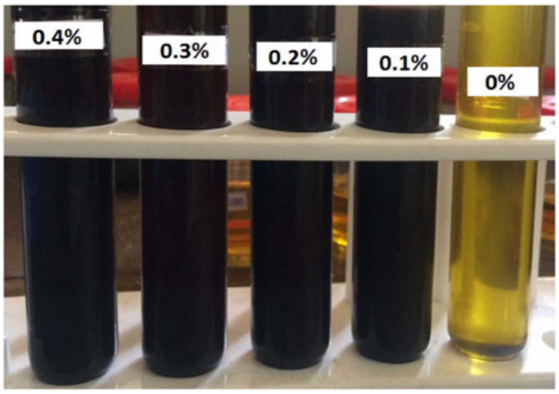

Fig. 6 *B5 with different concentrations of CuO nanoparticles*

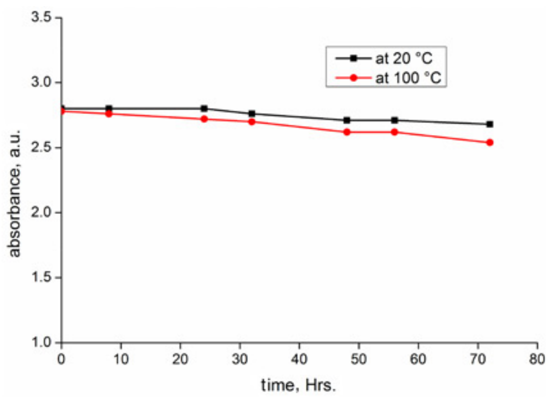

Fig. 7 *Dispersion results of nanolubricant samples over time*

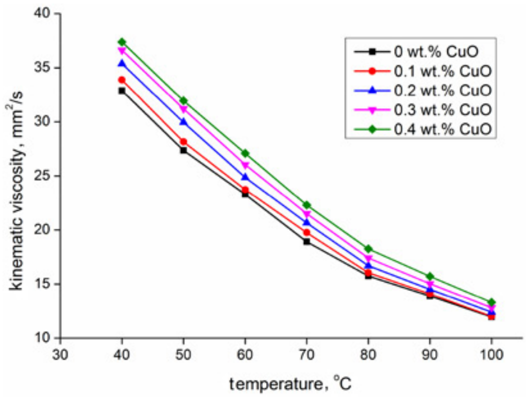

Fig. 8 *Variation of viscosity with temperature for different concentrations of CuO in B5*

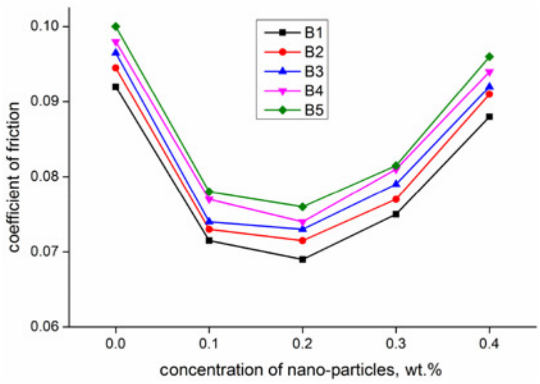

Fig. 9 *Variation of the coefficient of friction with concentration for different blended oils*

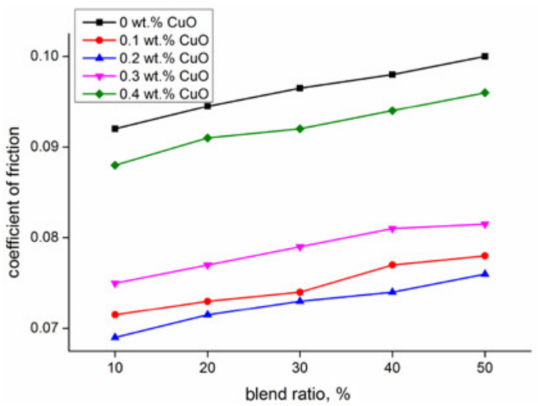

Fig. 10 *Variation of the coefficient of friction with blend ratio for different concentrations of CuO nanoparticle*

The variation of kinematic viscosity with a temperature of B5 added with different concentrations of CuO nanoparticles is shown in Fig. 8. It is shown that the viscosity increases with increase in the concentration of nanoparticles. The viscosity of B5 is enhanced by 6.1, 10.2, 13.8 and 15.2% with the addition of nanoparticles for the concentration of 0.1, 0.2, 0.3 and 0.4 wt.%, respectively.

It is shown in Fig. 9 that the coefficient of friction is the minimum when the concentration of CuO nanoparticles is 0.2 wt.%, for all the blends. CuO nanoparticles have lower hardness compared to many other nanoparticles. The thin oxide film formed

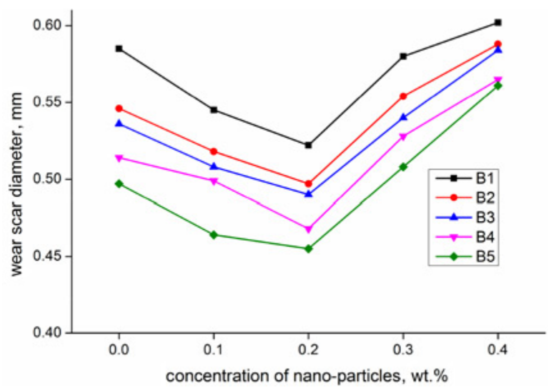

Fig. 11 *Variation of wear scar diameter with nanoparticle concentration for different blended oils*

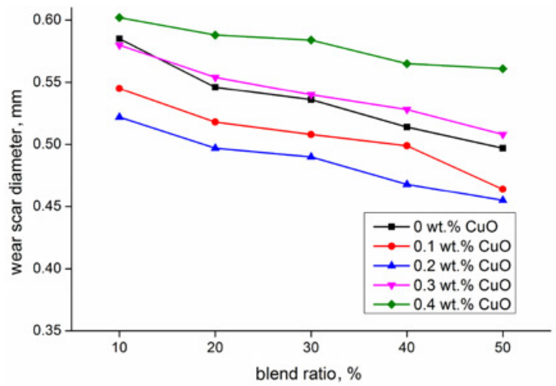

Fig. 12 *Variation of wear scar diameter with blend ratio for different concentrations of nanoparticles*

at the contacting surfaces due to the presence of nanolubricant is removed easily by sliding when the nanoparticles are softer. Hence, B1 added with 0.2 wt.% nanoparticles shows the lowest coefficient of friction. It is shown in Fig. 10 that, the coefficient of friction shows an increase with the increase in blend ratios for all nanoparticle concentrations. For a good lubricant, wear scar diameter needs to be less. It is shown that, wear scar diameter decreases with increase in blend ratios for all concentrations and it is the least for B5 added with 0.2 wt.% nanoparticles as shown in Fig. 11. The wear scar diameter is the least for 0.2 wt.% CuO for all blend ratios and the same is illustrated in Fig. 12.

4. Conclusion: In this study, the viscosity and tribological studies of the blends of CO and MO are carried out and the results are compared with those of CO, MO and mineral oil (SAE20W40) samples. The superior tribological and viscosity properties of the blends of CO and MO make them a biodegradable and environment-friendly alternative for mineral oil-based lubricants. These blends possess the advantages of both CO and MO, depending on the % of MO in the blend. The blend with ratio of 50% (B5) showed a low coefficient of friction and wear scar diameter in comparison with that of SAE20W40 mineral oil. Further, to improve the tribological and thermal properties, CuO nanoparticles are added with Sorbitan-Monooleate as a surfactant. Tribological studies on nanolubricants of blends containing CuO nanoparticles using four-ball tester show that the coefficient of friction and specific wear rate are decreasing with an increase in concentration of nanoparticles in the lubricants up to 0.2% concentration; further increase in concentration increases the coefficient of friction and wear rate, indicating the presence of an optimum concentration of nanoparticles.

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The developed blended vegetable oil based nanolubricant exhibits high VI (∼180), high flash and fire point, and relatively moderate thermal stability as per the requirements of commercial mineral oils. Thus blended vegetable oil based nanolubricant can be used as a promising biodegradable lubricant for many applications like two-stroke engine oil, hydraulic fluid, gear oil, textile lubricant etc.

The main limitation of the blended oils used for developing nanolubricant is their relatively high pour point and poor oxidation stability compared to mineral oil. At extreme loads and under cold climate, the developed nanolubricants become significantly less effective.

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