Micro and nanoparticles blended sesame oil bio-lubricant: study of its tribological and rheological properties

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Non-renewability, depleting resources and damage caused to the environment by mineral oil-based lubricants are the greatest concerns of this century. Recently, these issues have triggered a global trend to use vegetable oil-based lubricants in industries. Sesame oil (SESO) extracted from widely cultivated tropical crop – sesame (‘*Sesamum indicum*’) possesses distinctive characteristics such as low pour point and reasonable oxidation stability. However, the poor tribological properties of SESO limit its application as an industrial grade lubricant. Further improvement of these properties can aid its use as potential bio-lubricant in industries. This work encompasses the blending of micro and nanoparticles in SESO with the aim of enhancing its tribological properties to suit many industrial purposes. The tribological properties of SESO with nanoparticles having morphology variation spherical-shaped titanium dioxide (TiO_2) and rod-shaped zinc oxide (ZnO) are used. The significance of adding microparticles is also dealt with by using molybdenum disulphide (MoS_2). Tribological properties and stability of the above-formulated lubricants with and without the addition of surfactant to particles are studied. The rheological properties of the oil blends are examined using a rheometer. Studies indicate that rod-shaped ZnO blended SESO reduces the coefficient of friction and wear scar diameter by 24.04 and 13.74%, respectively.

1. Introduction: Depleting resources and damages caused to the environment and living organisms by the lubricants derived from mineral oil are the greatest challenges faced by the world in this century [1]. The use of these mineral oil-based lubricants in various complex systems made them an imperative factor for multiple purposes such as industrial and automobile applications [2]. Towards the end of the 20th century, the potential hazards of mineral oil-based products are identified, which promoted the research on bio-lubricants [3]. Good lubricity, higher thermal stabilities, renewability, biodegradability and non-toxic nature are few merits of the vegetable oil-based lubricants. Conversely, they possess poor tribological, rheological, low temperature properties and low oxidative stability [4, 5]. The presence of allylic protons and bis-allylic protons in unsaturated vegetable oils leads to their poor oxidative stability [6, 7].

Sesame is known as the ‘queen of oilseed crops’ and is a widely cultivated tropical oil seed crop [8]. Sesame oil (SESO) is extracted from the seeds of the sesame plant. SESO is one among the rare vegetable oils which are readily available; possess low pour point due to the presence of unsaturation and reasonable oxidative stability due to the presence of natural antioxidants sesamin, sesamolin, sesamol, sesaminol and γ-tochopherol [9]. However, from the preliminary studies, it has been identified that raw SESO exhibits poor tribological properties [8].

Layered molybdenum disulphide (MoS_2) is a solid lubricant material which can be used as an antiwear (AW) additive in lubricants. The use of nanoMoS_2 is not advisable since the cytotoxic influence increases with its exfoliated structure and nanosize [10]. In this context, the study utilises microstructured MoS_2 as one of the AW additives in SESO. The metallic oxide nanoparticles (NPs) are observed to be better AW additives for biodegradable lubricants than the corresponding metal NPs due to their inert nature towards oxidation during lubrication [11]. Titanium dioxide (TiO_2) NPs show self-repairing capability and are considered to be excellent AW additives for the biodegradable lubricants. Zinc oxide (ZnO) NPs get deposited on the wear track leading to the formation of tribo films with low surface roughness [12]. The effect of morphologically varied NPs on tribological properties of lubricants is scarce. Here, we report the enhancement of tribological properties of SESO by blending with suitable AW additives having a difference in morphology such as spherical-shaped TiO_2 as well as rod-shaped ZnO. These AW additives are blended individually in SESO samples, and the AW properties of the resulting nano and microlubricants are evaluated using a four-ball tester.

2. Materials and methods: SESO used for this study is procured from the local market in Calicut, Kerala. MoS_2 microparticles (MPs, average size <44 μm) are purchased from Alfa Aesar, whereas TiO_2 (average size 21–50 nm) and ZnO NPs (NPs, average size 30–80 nm) are purchased from Sigma-Aldrich. The surfactant used is Sorbitan monooleate and is procured from Sigma-Aldrich. The individual blends of oil with the above particles are prepared using magnetic stirring at 600 rpm followed by 45 min of ultrasonication. Tribological properties such as coefficient of friction (COF) and wear scar diameter (WSD) are obtained using a four-ball tester apparatus under the operating conditions of 1200 rpm, 75°C, 60 min and 40 kg load. The specimen balls used are of size 12.7 mm and hardness 61–64HRC [13]. Rheological properties of the oil blends are estimated using a rheometer with parallel plate geometry (Anton Paar MCR 102). Dynamic viscosities of the oil samples are calculated from 15 to 120°C. Viscous flow curves of the samples are also measured at 15, 60 and 120°C for a shear rate ranging from 1 to 1500 s^{-1}. Worn out portions of the ball specimens and morphology of NPs are imaged using a field emission scanning electron microscope (FESEM Hitachi SU6600). All experiments are repeated thrice, and graphs show the standard deviation as the error bar.

To reduce the agglomeration of MPs as well as NPs, Sorbitan monooleate (span 80) is used as the surfactant. The weight fraction of span 80 is 25 wt% of the additives. The required amount of AW additives is added into the solution of span 80 in o-xylene. The mixture is then thoroughly stirred at 50°C for 2 h followed by 3 h of ultrasonication. The solution is then filtered and washed thrice with toluene. The mixture is then dried overnight in a vacuum furnace at 60°C.

3. Results and discussion: The morphologies of MPs and NPs purchased in the unmodified form are shown in Fig. 1. The FESEM images of these particles reveal the flake structure of MoS_2 MPs, spherical shape of TiO_2 and rod shape of ZnO NPs.

Figs. 2 and 3 represent the WSD and COF obtained from the four-ball tester tribometer for various AW additive-blended oil samples, respectively. The layered MoS_2 particles possess strong covalent bond between the molecules in same layers and experience shearing of weak van der Waals forces between layers. While the mating surfaces contact each other in the presence of MoS_2 particles, exfoliation of particles takes place leading to a tribochemical film, which helps in reduction of wear in these contacting surfaces. However, from our studies, it is seen (Fig. 2) that with increasing concentration of MoS_2 MPs, the WSD initially decreases and then increases. The microsize of the particles hinders the penetration of them into the sliding surfaces which leads to the poor tribofilm formation. However, with the addition of NPs, improvement in the wear resistance of the blended oil has been observed. The WSD reduced from ~0.642 to ~0.5773 and ~0.583 mm with the addition of 0.4 wt% of ZnO and 0.5 wt% of TiO_2, respectively. This might be due to the rolling or mending effect produced by these NPs between the contact surfaces [14]. On further addition of additives, the WSD is observed to increase, which might be due to the agglomeration of NPs [15].

The evaluation of COF with various AW blended oils is considered for the study. From Fig. 3, it is observed that the COF increased with the addition of TiO_2 NPs to the SESO base oil which might be due to the inefficient rolling effect of NPs between the mating surfaces. In the case of SESO blended with MoS_2 MPs, the COF slightly decreases at initial concentrations and then increases further. However, with up to 0.4 wt% addition of ZnO NPs, reduction in COF is observed due to the effective rolling effect between the surfaces by the NPs. On further addition of ZnO NPs, the COF increases due to agglomeration of the NPs and hence hindrance to rolling of the NPs between the surfaces [14].

Figs. 4*a–c* show the photographs of 0.3 wt% MoS_2 (span 80 coated) in SESO (SESO + 0.3%-s-MoS_2), 0.5 wt% TiO_2 (span 80 coated) in SESO (SESO + 0.5%-s-TiO_2) and 0.4 wt% ZnO (span 80 coated) in SESO (SESO + 0.4%-s-ZnO) immediately after sonication and Figs. 4*a′–c′* show these samples after 14 days without any disturbance. From the visual analysis of the samples, it is clear that even after adding surfactant the MoS_2 MPs settle faster, which might be due to its higher particle size. However, the settlement of TiO_2 and ZnO NPs is greatly reduced by surfactant addition. The hydrophilic head of SPAN 80 attaches to the NPs leaving the oil loving tail pointing towards the oil molecules. Hence, the addition of surfactant to the NPs results in micelle formation as shown in Fig. 5*a*, preventing coalescence of NPs and thus reduces agglomeration of NPs. The schematic diagram representation of these hydrophilic head and lipophilic tail of SPAN 80 is provided in Fig. 5*b*.

The tribological properties of SESO blended with surfactant-modified NPs (SESO + 0.5%-s-TiO_2 and SESO + 0.4%-s-ZnO)

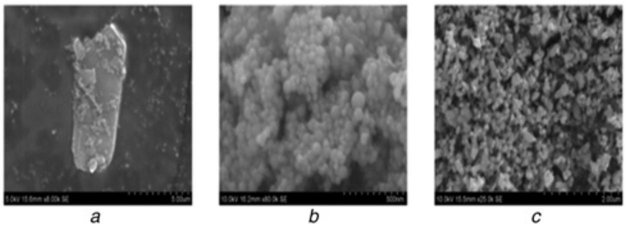

Fig. 1 *FESEM images of*
a MoS_2 MPs,
b TiO_2 NPs,
c ZnO NPs

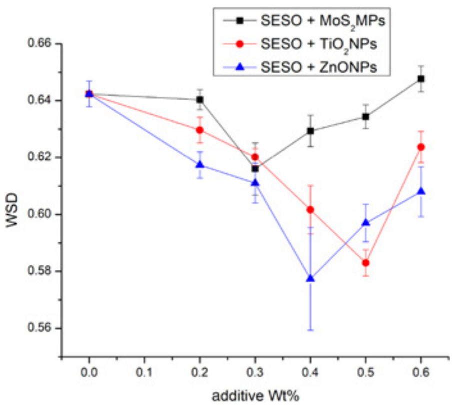

Fig. 2 *WSD of NPs and MPs blended in SESO*

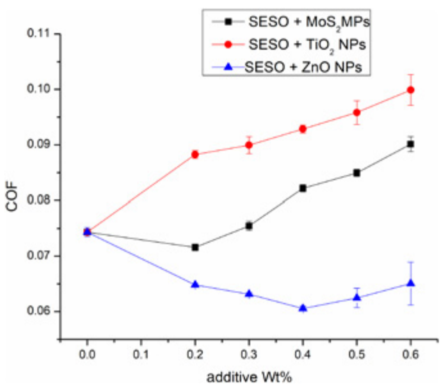

Fig. 3 *COF of NPs and MPs blended in SESO*

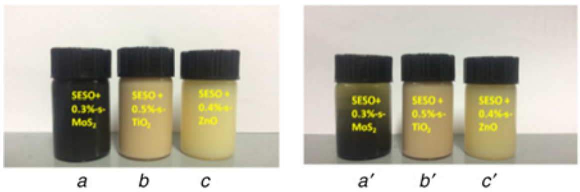

Fig. 4 *Dispersion stability of surfactant coated micro/nano particles in SESO*
a–c Blends just after sonication
a′–c′ Blends after 14 days

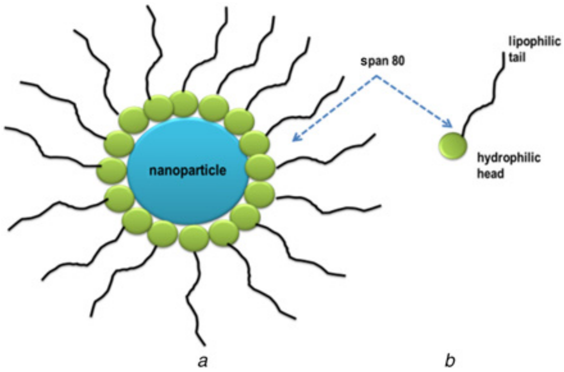

Fig. 5 *Surfactant action on NP*
a Micelle formation
b Structure of SPAN 80

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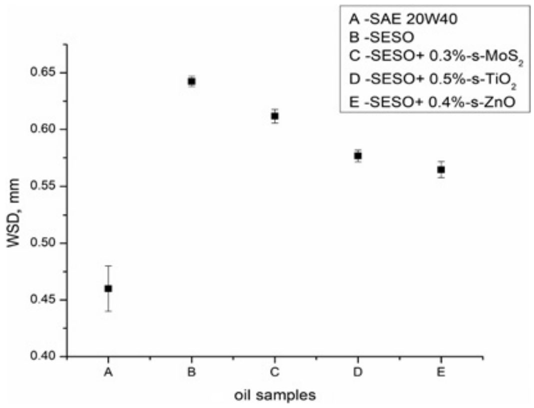

Fig. 6 *WSD for SAE 20W40 and SESO blended with surfactant-modified additives*

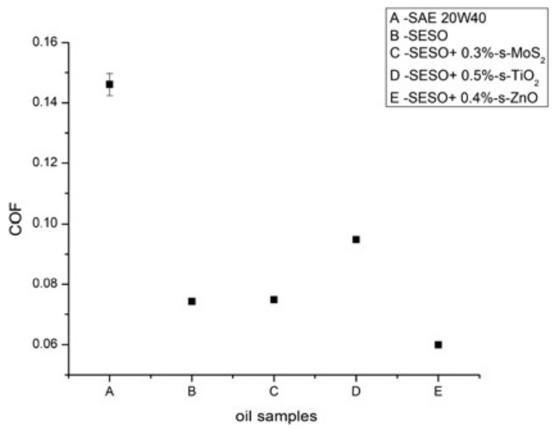

Fig. 7 *COF for SAE 20W40 and SESO blended with surfactant-modified additives*

and MP (SESO + 0.3%-s-MoS_2) are evaluated using four-ball tester. The results are then compared with those obtained for commercially available mineral oil lubricant SAE 20W40 and for neat SESO, which are taken from our previous studies [8] and are shown in Figs. 6 and 7. It can be observed from Figs. 6 and 7 that even after the surfactant-modification of NPs and MP, WSD and COF remained unchanged. Figs. 8*a–e* represent the FESEM images of WSD of the bottom ball of the four-ball tester lubricated with SAE 20W40, SESO, SESO + 0.3%-s-MoS_2, SESO + 0.5%-s-TiO_2 and SESO + 0.4%-s-ZnO, respectively.

It is clear from the FESEM images that MoS_2 MP considerably reduced the abrasive wear. Even though the WSD of TiO_2 blended SESO sample is observed to reduce, the existence of abrasive marks still retains in the surface which might cause an increase in COF with an increase in concentration as discussed earlier. The formation of abrasive marks on the surface with TiO_2 blended SESO sample can be attributed to its spherical morphology, which results in its rolling in between the mating surfaces as illustrated in Fig. 9*a*. However, in the case of ZnO blended sample, the existence of both adhesive and abrasive wear can be seen, but rather lesser abrasive tracks are observed on ZnO than TiO_2. The presence of lesser abrasive marks indicates the deposition of rod-shaped ZnO NPs on the wear tracks, leading to the formation of tribofilm with lower surface roughness [12] than TiO_2 NPs as depicted in Fig. 9*b*. This tribofilm formed with ZnO NPs leads to lowering of the WSD and COF in SESO/ZnO blends.

The variation of dynamic viscosities from 15 to 120°C on AW additives blended SESO is shown in Fig. 10. The detailed investigations of the rheological properties of neat SESO are done in

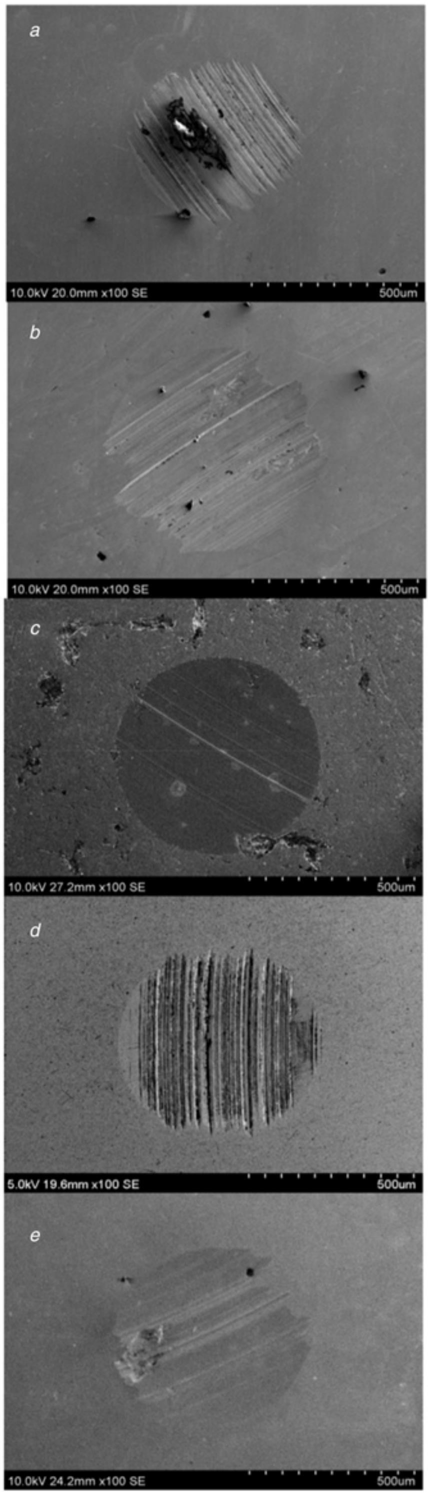

Fig. 8 *FESEM images of WSD of balls lubricated with*
a SAE 20W40
b SESO
c SESO + 0.3%-s-MoS_2
d SESO + 0.5%-s-TiO_2
e SESO + 0.4%-s-ZnO

our previous studies [16]. However, in this study, the addition of additives to SESO causes slight enhancement of viscosity compared to that of neat SESO at lower temperatures. Among the additive blended SESOs, SESO + 0.4%-s-ZnO blend shows a slender hike in viscosities in comparison to SESO + 0.3%-s-MoS_2 and SESO + 0.5%-s-TiO_2 which may be due to the rod shape of ZnO

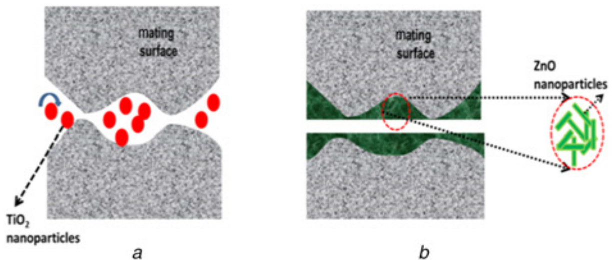

Fig. 9 *Mechanism of AW action*
a Rolling effect of TiO_2 NPs
b Tribofilm formation due to ZnO NPs

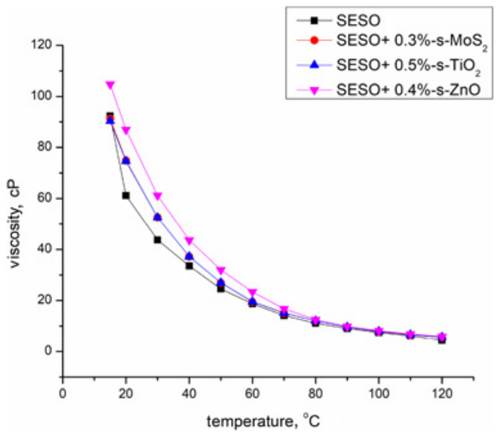

Fig. 10 *Viscosity versus temperature curves for neat and additive added SESO*

NPs. Linear characteristics are obtained for the flow curves of SESO and additive blended SESO which illustrates the Newtonian behaviour of all samples.

4. Conclusion: This study emphasis on the enhancement of the tribological properties of SESO with three additives having morphological differences through, microsized MoS_2 particles of flakes form, nanosized spherical-shaped TiO_2 and nanosized rod-shaped ZnO particles. It is observed from the tribological studies that SESO added with MoS_2 MPs exhibits poor tribological performance, which might be due to its larger size. Among the NPs, rod-shaped ZnO develops better friction and wear compared to spherical-shaped TiO_2. The surfactant modification of the additives improves their stability in SESO. However, in laboratory conditions, substantial enhancement of tribological properties has not been observed after coating with a surfactant. Slight improvement in viscosities is observed for SESO at lower temperatures after the addition of additives. All blends exhibit Newtonian – like flow curves at lower and higher temperatures. Hence this study shows that the rod-shaped NPs are effective in enhancing tribological properties than its spherical counterparts.

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