Investigation on the Impact of Zinc Oxide Nanoparticles with Varied Surface Modifications in Soybean Oil on Tribological Properties

Sekar Mohan¹, Ibrokhim. B. Sapavev², Ahmad Hussein Alawady³, Senthil Kumar⁴ and Primmia Devaraj Rosemary⁵

¹Department of Mechanical Engineering, AAA College of Engineering and Technology, Sivakasi, Tamil Nadu, India
²Head of the department Physics and Chemistry, Tashkent Institute of Irrigation and Agricultural Mechanization Engineers' National Research University, Tashkent, Uzbekistan, Western Caspian University, Scientific researcher, Baku, Azerbaijan
³College of Technical Engineering, The Islamic University, Najaf, Iraq
⁴Department of Electrical and Electronics Engineering, New Prince Shri Bhavani College of Engineering, Chennai, Tamil Nadu, India
⁵Department of Electronics and Communication Engineering, Prince Shri Venkateshwara Padmanabthy Engineering College, Chennai, Tamil Nadu, India

Abstract

Soybean oil nano-additives of surface capped zinc oxide (ZnO) were studied for their tribological characteristics and adsorption behavior with respect to surface modifier and particle size structure. To study their adsorption behavior in soybean oil, researchers used a quartz crystal microbalance. A four-ball friction and wear tester were also used to assess their tribological qualities. The soybean oil contained four different kinds of ZnO nanoparticles as additives: ZnO nanoparticles that had been methylated (DNS-2, 14 nm and DNS-3, 5 nm), RNS-D, 5 nm, and RNS-E, epoxy-modified, 5 nm (5 nm). DNS-2 can reduce the size of the wear scar on the steel ball by forming a strong tribo-film on the surface during shear sintering, thanks to its bigger particles. A viscoelastic adsorption layer can be created on rubbed steel surfaces by utilizing smaller particle sizes of RNS-D, DNS-3, and RNS-E. Increased polarity of the modifiers enhances their friction-reduction capabilities, extreme pressure properties, and anti-wear capabilities. The RNS-E surface capped with the highest polar epoxy group has an equilibrium adsorption mass 16 times larger and an adsorption rate 34 times greater than the DNS-3 surface coated with methyl. Combining ZnO nanoparticles with highly polar organic species could enhance their tribological properties in soybean oil and boost their adsorption on rubbed metal surfaces.

Keywords

Soybean oil, Zinc oxide nanoparticles, Tribological properties, Adsorption behavior, Quartz crystal microbalance

Introduction

Nanoscale lubricating additives are attracting a lot of attention in the tribology community as a result of their good anti-wear and friction-reducing properties under high pressure and different temperatures [1, 2]. These additives are also very effective and ecologically benign. The tribo-film formed by nano-additives has a low shear strength and a high load-bearing capacity when subjected to both normal loads and friction-induced shear stress, according to research [3, 4]. The high activity and huge specific surface area of the nano-additives are responsible for this. Research on the formation of continuous zirconia tribo-films in situ using zirconia nano-additives under shear force of atomic force microscope tip revealed that zirconia nanoparticles can undergo friction sintering to grow into continuous tribo-films over a broad temperature range of 25 °C to 100 °C [5]. Other oxide nanoparticles that have been found to have anti-wear and frictional properties include ZnO and cerium dioxide [6, 7].
Conventional wisdom holds that their anti-wear and friction-reducing properties stem from the effective adsorption of nano-additives onto the friction pairs’ contact surfaces. According to research, polar base oil dissoctylelsbatec and oleamide-modified WS\textsubscript{2} nanosheet can avoid competitive adsorption, leading to improved tribological properties of dissooctylelsbatec [9]. This is because the WS\textsubscript{2} nanosheet is dual modified with oleylamine and a strongly polar molecule, such as dodecyl maleic anhydride. ZnO nanoparticles treated with amino groups outperform those modified with carboxyl, phenyl, or alkyl groups in terms of anti-wear performance, according to research.

This research serves as a useful reminder that nanoparticles can have their tribological properties improved with the correct surface modifiers, leading to better adsorption on rubbing metal surfaces and, eventually, better performance from lubricant base stocks [9, 10]. The correlation between the adsorption behavior and tribological properties of nano-additives is not completely understood, including how the size and structure of nanoparticles impact their adsorption behavior (adsorption rate, adsorbed mass, and adsorption layer structure).

Considering the aforementioned factors, we settle on biodegradable and environmentally friendly soybean oil as our base oil. Then, we study the adsorption behavior of different surface-capped ZnO nano-additives on rubbed steel surfaces and how they impact the tribological properties of the base oil. This study details the effects on soybean oil’s tribological characteristics brought about by the adsorption behavior of four types of surface capped ZnO nanoparticles with varying particle sizes and surface functionalities on rubbed metal surfaces. It clarifies the design and synthesis of new, highly efficient nano-additives by dealing with the quantitative relationship among the adsorption behavior, anti-wear abilities and friction-reducing, load-carrying capacity, and surface-capped ZnO nanoparticles.

**Experimentation**

**Materials**

The particle sizes of these additives ranged from 14 nm to 5 nm. To make the lubricating base oil, we used soybean oil that is commercially available; table 1 shows its physicochemical parameters.

A Fourier transform infrared (FTIR) spectrometer was used to study the unique chemical groups of organic chains that were modified on ZnO nanoparticles (between the 500 cm\textsuperscript{-1} to 4000 cm\textsuperscript{-1}) spectrum. The thermal stability and organic modifier content of surface capped ZnO nanoparticles were examined using a thermogravimetric analyzer (TGA) in a nitrogen environment from 25 to 800 °C with a temperature increase rate of 10 °C/min.

**Friction and wear test and worn surface analysis**

After being added to the soybean oil in varying amounts (mass fraction: 0.25%, 0.45%, 0.65-0.85%, 1.05%, 1.25%, and 1.45%), the four different types of surface capped ZnO nanoparticles were well dispersed using ultrasonic technology (dispersion stability). Soybean oil’s high concentration of organic acids is one of the key reasons why ZnO dissolves so well in it [11]. An experimental technique of lubricant anti-wear performance standard, SH/T 0189–92, was followed in order to assess the tribological characteristics of the nano-additives in soybean oil using a four-ball wear and friction tester. The GCr15 standard bearing balls (hardness HRC 61 ~ 64, diameter 12.7 mm) were subjected to 60 min of sliding tests at 75 °C, 1200 rev/min, and 392 N. The diameter of the wear scar was measured using an optical microscope to an accuracy of 0.01 mm following the completion of the wear and friction tests. Soybean oil containing nano-additives had its extreme pressure properties (PB and PD values) assessed using an MRS-1J four-ball machine in accordance with Chinese national standards GB 3142-82 and GB/T 12583-98. The sliding tests were performed for 10 sec at 1450 rpm at ambient temperature. After adding ZnO to the oil, its viscosity remained unchanged when measured using a viscosity-density integrated equipment. The distribution of important elements on the surface of the worn steel was also examined using energy dispersive X-ray spectroscopy, which employed a 15 kV collecting voltage.

The samples were imaged optically at room temperature and 75 °C at their optimal concentrations. Even after three months of room temperature storage, no precipitate formed at the base of the bottles containing the four distinct groups of modified ZnO that had been uniformly disseminated in soybean oil. The samples remained clear and bright after opening the bottle cap and placing them in the oven at 75 °C for 24 h; furthermore, no precipitation was observed at the bottom of the bottle.

**Adsorption performance tests**

We used a quartz crystal microbalance device (QCMD) to study the adsorption behavior of the four different types of surface capped ZnO nanoparticle dispersions in soybean oil. Soybean oil contains surface capped ZnO nanoparticles, and we were able to study their tribological characteristics by grafting functional groups onto their surfaces. Here, the piezoelectric effect of quartz crystal is utilized by the QCMD, a sensor. It has the ability to detect the change in vibration frequency (Δf) of quartz crystal very sensitively when nano-
additives are adsorbed [12, 13]. In addition, it determines the nano-adsorbents’ mass by describing the link between frequency change and adsorbed mass using the Sauerbrey equation (equation 1) [14]:

$$\Delta m = \frac{\rho \cdot h_q \cdot \Delta f}{f_0} \times \frac{\Delta f}{n} = -C \Delta f$$  \hspace{1cm} (1)

Where $\Delta m$ stands for the adsorbed mass in relation to the surface area of the crystal; $\rho$ represents the density of the quartz crystal; $h_q$ indicates its thickness; $f_0$ represents the fundamental frequency; $n$ denotes the number of pan frequencies, which indicates the number of adsorption layers; and $C$ is a constant associated with the quartz crystals characteristics.

Equation 2 is used to calculate the number of adsorption layers $n'$:

$$n' = \frac{\Delta m}{\rho \cdot R}$$  \hspace{1cm} (2)

Where the nanoparticles' diameter and density are denoted by $\rho$ and $R$, respectively.

What follows is a description of the experimental process. We used petroleum ether to clean the sample tank, pipeline, and wafers, and dry nitrogen to purge them before the experiment. Afterwards, a pristine gold-plated wafer was set up and linked to the QCMD. An appropriate quantity of soybean oil was then added and maintained for 10 to 15 min until the $\Delta f$ value was 2 Hz or lower, providing the baseline. After the baseline measurement was finished, the nano-additives dispersions that were going to be examined were added and left to be absorbed for approximately 3 h. The temperature and flow rate used for all the measurements were 25 °C and 80 μl/min, respectively. We chose gold (Au)-plated wafers because their adsorption effects are comparable to those of iron (Fe)-plated wafers.

Adsorption tests were performed on Fe-plated wafers to mimic real-world working circumstances and study metal-to-metal friction. But the Fe surface isn’t reusable because it’s so susceptible to chemical alterations even after washing. Any imperfections in the Fe plating will not show through on the Au-plated surface. On the Fe- and Au-plated wafers, the adsorption curves of 0.50% copper nanoparticles in n-dodecane and particle size distribution are displayed in figure 1 and figure 2, respectively. The outcomes of the adsorption tests conducted on both wafers were comparable.

**Results and Discussion**

**Structure of surface capped ZnO nanoparticles**

Figure 3 is a schematic representation of the surface structures of the four types of surface capped ZnO nanoparticles. In this case, methyl functional groups modify the surface of DNS-2 and DNS-3, vinyl functional groups modify RNS-D, and epoxy functional groups modify RNS-E.

We used FTIR spectroscopy to determine which functional groups were attached to the ZnO nanoparticles’ surfaces. Figure 4 displays that the four types of surface capped ZnO nanoparticles exhibit Si-O-Si absorbance peaks at 1260, 1010, and 630 cm$^{-1}$, which are ZnO nuclei. The stretching vibrations of the O-H bonds in ZnO-bound water are reflected by the absorbance peak at 3555 cm$^{-1}$, while the DNS-2 and DNS-3 C-H bonds are represented by the bands at 3095 cm$^{-1}$ and 1260 cm$^{-1}$, respectively. The epoxy group of RNS-E is responsible for the absorption peaks at 1045 cm$^{-1}$, whereas the stretching vibrations of the C=C double bond and the carbonyl group of RNSD are reflected in the bands at 1815 and 1870 cm$^{-1}$.

Figure 1: Copper nanoparticles adsorption curves in n-dodecane at a concentration of 0.5% on Fe- and Au-plated.

Figure 2: (a) DNS-3, (b) RNS-2, (c) DNS-E, and (d) RNS-D particle size distributions.

The presence of specific absorbance bands at 1095 and 1010 cm$^{-1}$, as well as these FTIR data, along with the fact that all four types of surface capped nano ZnO exhibit these bands, indicates that the organic modifiers (DNS-2) and methyl (DNS-3), along with vinyl (RNS-D) and epoxy resin (RNS-E), are chemically bonded onto the surface of ZnO nanoparticles.

TGA was used to assess the thermal stability of the organic modifiers and surface capped ZnO nanoparticles. Figure 5...
shows that at 116 ~ 550 °C, the weight of each of the four types of surface capped ZnO nanoparticles decreases as a result of the organic modifications being removed or decomposed. Specifically, DNS-2, DNS-3, RNS-D, and RNS-E lose 8.2%, 3.9%, 12.9%, and 9.6% of their weight, respectively. Based on these results, we can deduce that 8.2%, 3.9%, 12.9%, and 9.6% of RNS-D, DNS-3, and RNS-E, respectively, are organic modifiers. Additionally, in terms of thermal stability, DNS-3 is better than DNS-2, RNS-E is better than RNS-D. It follows that organic modifiers containing very active radicals are not good for keeping nano-ZnO thermally stable, but they might improve the surface-capped nano-ZnOs chemical reactivity with other species.

**Tribological properties of surface capped ZnO nanoparticles in soybean oil**

To study the impact of four different types of surface-capped ZnO nanoparticles on the tribological characteristics of soybean oil, a four-ball wear and friction tester was utilized. The test was conducted in the context of boundary lubrication [15–17]. Figure 6 shows that the tribological properties of soybean oil are affected in many ways by the nano-additives.
of DNS-2, which has a large particle size and surface methyl, is exceptional in base oils. Within the additive concentration range of 0.45 - 0.85%, it decreases the wear scar width by 30% when compared to using soybean oil alone for lubrication, while maintaining it at a minimum of 0.47 mm. Raising the concentration of the DNS-2 nano-additive causes a little increase in the diameter of the wear scar.

Equation 3 shows that the layer thickness ratio (λ) can be used to approximate and anticipate the lubrication condition (Equation 4).

\[
h_m = 3.63R_x^* G^{0.49} U^{-0.58} W^{-0.033} (1 - e^{-0.68k})
\]  
\[
\lambda = \frac{h_m}{R_q^*}
\]

In equation 3, the minimum film thickness is denoted as \( h_m \), the corresponding ball radius is denoted as \( R_x \), according to the Hertz contact theory, the steel ball’s radius in the four-ball friction test is 6.35 x 10^{-3} m, and \( R_q \) is equal to 3.175 x 10^{-3} m. The dimensionless speed parameter (\( U^* \)) is 7.66 x 10^{-12}, the contact point sliding speed is 3.84 x 10^{-2} m/s, the lubricant’s dynamic viscosity is 0.012 Pa·s at 75 °C, and the rotation speed is 1200 rev/min, according to equation 5.

\[
U^* = \frac{n^2 U E^*}{\eta_0 R^*} = 5.32 \times 10^{-13} \eta_0 n
\]

\[
G^* = \alpha E^* = 2.28 \times 10^{11} \alpha
\]

\[
W^* = \frac{W}{E^* R^*} = 1.776 \times 10^{-7} W
\]

\[
k = 1.03 \left( \frac{R}{R_q^*} \right)^{0.64} = 1.03
\]

With these values entered into equation 3, the lowest possible oil sheet should be 19.48 nm.

In this experiment, a steel ball with a surface roughness of 0.05 μm was employed, and the root mean square deviation of the balls’ surfaces, denoted as \( Rq1 \) and \( Rq2 \), respectively, was about 1.2 and 1.25 times the arithmetic squared mean deviation. The lubrication state is defined quantitatively by \( RNS-D \) and \( RNS-E \), which have particle sizes that are equal to DNS-3, outperform DNS-2 in terms of anti-wear capabilities. One possible explanation is because shear sintering produces thick tribo-films with ease with bigger ZnO nanoparticles, whereas surface adsorption makes this process harder with smaller nanoparticles.

Consequently, DNS-2, being larger, increases soybean oil’s anti-wear ability more than DNS-3, which is smaller. Meanwhile, the inclusion of DNS-2 in the base oil causes a little rise in the coefficient of friction (more than 0.06), which may be due to the comparatively high shear strength of the dense tribo-films that DNS-2 forms. On top of that, at the sweet spot for addition concentration, RNS-E with a surface epoxy group gives a low friction coefficient of around 0.05 and shows a moderate benefit of drag reduction. Soybean oil’s viscosity was unaffected by the addition of ZnO nanoparticles throughout the test, and table 2 lists the coefficients of friction and wear scar diameters at the optimal concentration of the nano-additives.

Figure 7 shows the friction coefficient-time curves of Soybean oil is in the border lubrication phase when λ = 0.3, which is smaller than 1, as stated in equation 4.

This follows previous reports that 100 nm ZnO nanoparticles can reduce the diameter of wear scars by filling grooves on rubbed metal surfaces and forming a protective coating by shear sintering under normal load [18, 19]. While DNS-2 demonstrates anti-wear effects across the concentration range, DNS-3, which has the same surface functional group as DNS-2 but smaller particles, fails to do so. In contrast, RNS-D and RNS-E, which have particle sizes that are equal to DNS-3, outperform DNS-2 in terms of anti-wear capabilities. One possible explanation is because shear sintering produces thick tribo-films with ease with bigger ZnO nanoparticles, whereas surface adsorption makes this process harder with smaller nanoparticles [20, 21].

\[
R_q^* = \sqrt{R_{q1}^2 + R_{q2}^2}
\]

Table 2: Soybean oil lubricated steel-steel contact measures average coefficient of friction and wear scar diameter at optimal concentration of surface capped ZnO nanoparticles.
the steel-steel contact that is lubricated with soybean oil that contains an optimal concentration of surface capped ZnO nanoparticles. Soybean oil’s high concentration of long-chain fatty acids makes it ideal for reducing friction when rubbing against metal, however this film can't withstand the intense pressures experienced in the contact region because of its low load-bearing capacity. For this reason, the friction curve of a steel-steel contact that is lubricated solely with soybean oil is quite unstable. The addition of surface-capped ZnO nano-additives to the base oil makes the friction curves smoother and less fluctuating. Specifically, the nano-additives in soybean oil rank higher in terms of their ability to reduce friction than RNS-D, DNS-3, and DNS-2 (DNS-2 is an outlier because it slightly increases the friction coefficient), suggesting that the nano-additives’ friction-reducing effect tends to augment with increasing surface functional group polarity.

The deposition of ZnO particles onto rubbed steel surfaces to fill the grooves thereon and the creation of a nano-ZnO protective coating through shear sintering could be the reasons behind this. Tribological behavior of the superfine ZnO nanoparticles (DNS-3, RNS-D, and RNS-E) used in this study is dictated by the polarity of the surface functional groups. Increases in both the friction-reduction and anti-wear effects are proportional to the surface functional groups’ polarity. Soybean oil’s nano-additive, RNS-E, has the most impressive set of tribological characteristics overall (the greatest capacity to reduce friction, moderate capacity to prevent wear, and load-carrying capacity).

The ideal concentration of several surface capped ZnO nano-additives for the steel-steel contact is shown in figure 8, along with the extreme pressure properties of soybean oil. To a certain degree, the four varieties of surface capped ZnO nano-additives can raise soybean oil’s PB value, which is the highest non-seizure load. In particular, the PB value of soybean oil goes raised from 637 N to 749 N when 1.05% RNS-D or RNS-E is added. Incorporating 0.65% DNS-3 raises the PB value to 702 N, whereas incorporating 0.85% DNS-2 raises the PB value to 684 N. Lubricant film-formation rate and load-bearing capability of the tribo-film are both correlated with the PB value, which measures the lubricant’s ability to keep rubbed metal surfaces from seizing after 10 sec of sliding. Soybean oil’s load-bearing capacity can be enhanced to a certain degree by all four types of nano-additives that were evaluated.

The oxide tribo-films can only be formed after around 3000 shear cycles, which is far lower than the 300 shear cycles measured in 10 sec during PB experiments. Among the nano-additives tested, DNS-2 (0.85%) in soybean oil had the lowest PB value. This could be because of its relatively large particle size, which causes abrasive wear, and its low film-formation rate. Nevertheless, DNS-2 is capable of shear sintering into tribo-films that have an impressive load-bearing capacity. The adsorption rate on the friction surfaces increases with increasing surface polarity and the introduction of polar organic modifiers; however, RNS-D, DNS-3, and RNS-E with smaller particle size cannot create sintered tribo-films. A higher PB value is the end consequence of the as-deposited nano-additives forming deposition layers that prevent metal contact surfaces and boost load-bearing capacity.

**Adsorption behavior of ZnO nanoparticles**

Analyzing the adsorption behavior of ZnO nanoparticles capped with various materials and having diverse surface functions was done using a QCMD. All four types of surface capped ZnO nanoparticles exhibit comparable variations in adsorption rate with increasing adsorption duration, as demonstrated in figure 9. Because the ZnO nano-additives adsorb quickly to the surface of the quartz crystal, their vibration frequency tends to drop sharply as the adsorption process progresses. The adsorption rate reaches a plateau after an initial time, which corresponds to the adsorption equilibrium of ZnO nano-additives on the quartz crystal surface. Furthermore, the four varieties of surface capped ZnO nanoparticles were rinsed with soybean oil after the adsorption tests; they continued to retain any remaining adsorption mass. This suggests that they have a high ability to adsorb onto the surface of the quartz crystal.

Table 3 displays the adsorption mass of several ZnO types at adsorption equilibrium, as determined using the Sauerbrey equation. The equilibrium adsorption mass of RNS-D, DNS-3, and RNSE with lesser particle sizes is 3.4 x 10^{-3} mg/cm², 3.8 x 10^{-3} mg/cm², and 2.1 x 10^{-3} mg/cm², respectively, when the adsorption equilibrium is achieved. Their surface functional group polarity is directly related to their equilibrium
adsorption mass, as seen above. As a result of their tribological characteristics and their role as nano-additives in soybean oil, DNS-3, RNS-D, and RNS-E are believed to have anti-wear and friction-reducing capabilities that are connected to the polarity of their surface functional groups. Notably, as the surface functional group’s polarity increases, the competitive adsorption between the nano-additives and soybean oil tends to intensify. Together, these factors and the low shear strength of the adsorbed-deposited tribo-film that forms on the metal surface serve to shield rubbing metal surfaces from one another, which in turn greatly reduces friction and wear. The RNS-E that has the most strongly polarized surface epoxy group has the greatest adsorption capacity and can create the thickest adsorption film (28 layers), which is in line with its anti-wear and friction-reducing properties when applied to soybean oil. When comparing DNS-3 and DNS-2 with large particle sizes, the latter has a substantially smaller equilibrium adsorption mass. A dense tribo-film with high shear strength is formed by DNS-2 through friction shear sintering, which raises the friction coefficient. As a result, DNS-2 has remarkable anti-wear capabilities.

Conclusions

Utilizing a four-ball wear and friction tester and a QCMD, the tribological characteristics and adsorption behavior of four distinct types of surface capped ZnO nanoparticles were investigated as nano-additives in soybean oil, with respect to particle size and the polarity of their surface functional groups. The following are the results.

- To create an adsorption layer on rubbed metal surfaces, organic species with different functional groups can be added to the surface of ZnO nanoparticles. The anti-wear and load-carrying capacities of the basic stock can be improved by adding this layer.
- According to their particle size and surface functional group polarity, the ZnO nano-additives that were examined engage in competitive adsorption on rubbed steel surfaces with the base stock. DNS-2, which has larger particles compared to DNS-3, has a higher equilibrium adsorption mass. Additionally, DNS-2 may produce a tribo-film with excellent strength and resistance to wear in soybean oil by shear sintering.
- According to the polarity of their surface functional groups, the average adsorption mass, adsorption rate, and adsorption layer number are ranked in the following order: DNS-3 > RNS-D > RNS-E. Both the coefficient of friction and the diameter of the wear scar are decreased by the viscoelastic adsorption films that are created as-is, instead of by the shear sintering tribo-films. Among the nano-additives examined, RNS-E with a strongly polar epoxy group exhibited the highest equilibrium adsorption mass and adsorption rate, which is in good agreement with its target tribological characteristics in soybean oil. This brings to mind the possibility that grafting organic species with high polarities onto ZnO nanoparticles could improve their tribological characteristics and increase their adsorption on rubbed metal surfaces.

Acknowledgements

None.

Conflict of Interest

None.

References

Investigation on the Impact of Zinc Oxide Nanoparticles with Varied Surface Modifications in Soybean Oil on Tribological Properties

Mohan et al.


