The tribological properties of lanthanum borate nanoparticles with different morphologies as lubricant additive in rapeseed oil

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Abstract. Sheet-like, Petal-like and Ball-like lanthanum borate nanoparticles were prepared by hydrothermal method (abbreviated as SLBN, PLBN and BLBN, respectively). The morphologies in rapeseed oil (abbreviated as RO) were characterized by scanning electron microscope (SEM). The antwear and friction-reducing performances of lanthanum borate nanoparticles in rapeseed oil were evaluated on a four-ball tribo-tester. Moreover, the worn steel ball surface was investigated by SEM, X-ray photoelectron spectroscopy (XPS) and Surface Profiler. The result shows that PLBN and SLBN have a thickness of 10nm and 30nm, which exhibits excellent dispersing ability in rapeseed oil, and BLBN have a diameter of 50-120nm. Furthermore, PLBN show a better friction-reducing and antiwear performance. Meanwhile, 2D appearance indicated the worn steel ball lubricated with RO+SLBN have the more shallow and narrow scratches, which consistent with 3D topography. The excellent friction-reducing and antiwear performances attribute to tribochemical film, which contains B_2O_3 and La_2O_3.

1. Introduction

For industrial applications to reduce friction and resist wear, mineral oil-based lubricant is one of the most conventional choice. However, as environmental protection has been given priority to, the toxicity and non-biodegradable nature of mineral oil-based lubricant can not be ignored. Therefore, it is critical to develop biodegradable lubricants to substitute mineral oil-based lubricants. Vegetable oils is one of reliable substitutes for mineral oil because they are nontoxic materials and can be degraded by bacteria. Generally, vegetable oils show excellent tribological performances owing to their polar functional groups and the presence of long fatty acid chain. Literatures[2, 6, 8] suggest that polar functional groups of vegetable oils play a key role in maintaining excellent boundary lubricating properties by strong physical and chemical adsorption on the metal surface in contact regions. Furthermore, long fatty acid chains followed with polar functional groups swing normally as rub happen between metal in vegetable oils[1], offering continuous lubrications.

Generally, the antiwear and friction-reducing performances of lubricants can be improved by lubricant additives. However, chlorine and phosphorus compounds that are extensively used as lubricant additives have been restricted for environmental protection issue. In recent years, researchers have achieved progresses on applications of environmentally friendly nanoparticles in the field of lubricant. Boron nitride nanoparticles show excellent tribological performances owing to rolling between metal
surfaces[7]. Furthermore, lanthanum borate nanoparticles tend to deposit on the worn surface and then form a protective film, which contains FeO, B₂O₃ and La₂O₃[5, 9].

Literatures suggest friction-reducing and antiwear performances are dependent on the characteristics of nanoparticles, such as shape, size, concentration and amphiphilicity[3, 5, 7]. Therefore, it is significant that unveiling how shape, size and structure of nanoparticles effect tribological performances of lubricant. According to our previous work[4], lanthanum borate nanoparticles have been verified to have excellent friction-reducing and antiwear performances in rapeseed oil. In this article, we focus on different morphologies of lanthanum borate nanoparticles, which used as lubricant additives in rapeseed oils, to explore the effect of morphology of nanoparticles on tribological performances.

2. Experimental Procedure

2.1. Preparation of the different morphology of lanthanum borate nanoparticles.

2.58g of La(NO₃)₃·6H₂O and 0.263g of (1.0wt%) stearic acid were well dissolved into 30mL anhydrous ethanol under adequately stirring, which marked as A. In addition, 3.42g of Na₂B₄O₇·10H₂O were well dissolved in 30mL distilled water, which was marked as B. Then, solution A was added dropwise into solution B under agitation at room temperature. The pH values of mixed solution were adjusted to 6.5 with diluted hydrogen nitrate solution after solution A is completely dropped to the solution B. Then, the resultant mixture was kept on stirring for 1h and transfer into a 100mL Teflon-lined stainless-steel autoclave filled with anhydrous ethanol up to 80% of total volume, which was sealed and treated hydrothermally at 180°C for 24h. Thereafter, the treated mixture was cooled to room temperatures naturally and filtered to obtain the precipitates, which were then washed for three times with distilled water and anhydrous ethanol, followed by drying at 80°C for 4h in drying oven to obtain the Sheet-like lanthanum borate nanoparticles (abbreviated as SLBN).

For comparison, Petal-like lanthanum borate nanoparticles (abbreviated as PLBN) and Ball-like lanthanum borate nanoparticles (abbreviated as BLBN) are also prepared in the same procedure under 4 hours reaction time and 48 hours reaction time.

2.2. Friction and Wear tests

Firstly, 0.1%wt mass percentage of different morphologies of nanoparticles were dispersed in anhydrous ethanol and resultant solution was added dropwise into rapeseed oil by separating funnel under adequately stirring at 120°C. Then, resultant solution was dispersed ultrasonically at 60°C for 1h. The friction coefficient (COF) and average wear scar diameter (WSD) of rapeseed oil (abbreviated as RO), RO+SLBN, RO+PLBN and RO+BLBN were evaluated on a four-ball tribo-tester at room temperature, 1200 rpm and 392N for 30 min. GCr15 bearing steel balls were used for tests, which are 12.7mm in diameter, 59-61 HRC in hardness and Ra 0.040μm in surface roughness. The friction coefficient and the wear scar diameters reflect friction-reducing and antiwear performances of different morphology of nanoparticles respectively.

2.3. Characterization of nanoparticles and analysis of worn surfaces

Three different morphologies of nanoparticles were characterized by field emission scanning electron microscope (SEM). Then, the worn steel ball surface was characterized by SEM. The 3D topography and the line roughness of wear scar was obtained by RTEC Up Dual Model. Chemical state of elements on the worn steel ball surfaces were characterized by Thermo ESCALab-250 X-ray photoelectron spectroscope (XPS), where the binding energy of the tested elements was measured at a pass energy of 29.4 eV and a resolution of ±0.3 eV, with the Al Kα radiation as the excitation source.
3. Result and Discussion

3.1. Characterization of Ball-like, Petal-like and Sheet-like nanoparticles.
The morphologies of lanthanum borate nanoparticles are presented in Figure 1, which shows SLBN with a length of 100-300nm and a thickness of 30nm, PLBN with a length of 150-300nm and a thickness of 10nm and BLBN with a diameter of 50-120nm.

![Figure 1. SEM and EDS of different morphology of nanoparticles (a)SLBN (b)PLBN (c)BLBN.](image)

3.2. Tribological properties
It can be observed that COFs of RO+BLBN, RO+PLBN and RO+SLBN are less than that of RO in figure 2. In addition, COFs of RO+SLBN increase fiercely at 294s and 690s from 0.07 to 0.1, indicating adsorption film was repeatedly broken and regenerated as temperature increase. From then on, COFs of RO+SLBN drop down to 0.07, finally reaching steady state. Figure 3 shows the average COFs of RO+SLBN, RO+PLBN and RO+BLBN are reduced by 18.68%, 19.07% and 12.78%, respectively. When no additives are used, generally, polar functional groups of fatty acid adhere to metal surface and long fatty acid chain slip well, reducing friction between surface metals. Thus, the tribological performances of friction pair principally depend on surface roughness and lubricant. When nanoparticles are used, direct contact between surface metals translates into contact between surface metals and nanoparticles. The friction results show PLBN has best friction-reduction performances. The potential reason is that the flake nanoparticles more easily adsorb on the surface than the spherical nanoparticles, filling the inter-asperity valleys gap of metal surface and forming easily shearable nanoparticle layer, thus it aids in friction reduction and antiwear performances during tests. Moreover, the smaller thickness of nanoparticles and the larger specific area of nanoparticle contribute to their strong adsorption capacity and chemical activity. Hence, the flat shape and small size of PLBN make it easier to be laid flat on the direct tribological contact zone and form hard oxide layer subsequently under high temperature and high pressure.
Figure 2. Friction coefficients of RO, RO+SLBN, RO+PLBN and RO+BLBN.

Figure 3. Average friction coefficient of RO, RO+SLBN, RO+PLBN, RO+BLBN.

Figure 4 shows that WSD of rapeseed oil is reduced by 7.34%, 18.67% and 10.12% when SLBN, PLBN, and BLBN are added respectively. In addition, PLBN have a better antiwear performance compared to BLBN, SLBN and RO. In this article, flake nanoparticles have better friction-reducing performances than spherical nanoparticles. However, it is interesting that SLBN show a poorer antiwear performance than BLBN, which show better anti-friction performances than BLBN previously. Antiwear performances depend not only on the shape of the nanoparticles, but also on the size of the nanoparticles.
3.3. Analysis of worn surfaces

Figure 5 shows that there are some obvious furrows on the steel ball lubricated with RO due to the abrasive wear. Compared to steel ball lubricated with RO, the steel ball lubricated with RO+BLBN, RO+PLBN and RO+SLBN show a smoother worn surface and less wear. Figure 6 shows that there are deeper furrows and wider scratches on the worn steel ball surfaces lubricated with RO than that of RO+SLBN, RO+PLBN and RO+BLBN. Furthermore, figure 7 demonstrates that the wear scar depth on the worn steel ball surfaces lubricated with nanoparticles is significantly less than RO. It is worth mentioning that the severe depression in figure 6 is related to damage in sample preparation procedure.
Figure 6. The three-dimensional topography of worn steel surface 
(a)RO (b)RO+SLBN (c)RO+PLBN (d)RO+BLBN.

In figure 11 (a), the binding energy of 529.3eV and 530.9eV are the O1s peak, indicating the present of metal oxides and hydroxyl group. In figure 11 (b), the C1s peak at a binding energy of 284.5eV, 286.4eV and 288.1eV, respectively, refer to -C-H-, -C-O- and -COO-, which adheres to the worn steel surfaces. In figure 11 (c), the binding energy of 710.4eV in XPS spectra of Fe2p suggests that the worn steel surface covered with iron oxides. This result verifies that fatty acids and fatty acid glycerides in vegetable oils adsorb on the worn steel surface for reducing friction. Figure 8 (a-c) shows that the B1s peaks at a binding energy of 193.3eV, 192.7eV and 193.3eV refer to boron oxidized product (B2O3). Figure 8 (d-f) show that the La3d peaks at a binding energy of 834.9eV corresponding to La2O3. Obviously, nanoparticles react with the metal surface and generate a tribochemical film on the metal surface under the combined action of shear and heat. The tribochemical film containing B2O3 and La2O3 play a significant role in antiwear performances. The XPS spectra of B1s show an obvious difference at a binding energy of 193eV. The B1s peak at a binding energy of 193eV in RO+SLBN show a greater intensity than that in RO+PLBN and RO+BLBN, indicating more relative content of boron, which attributes to a larger contact area between nanoparticles and the worn steel surface. Therefore, the morphology of nanoparticles has a significant effect on tribochemical reaction on steel ball surface. In this article, the flake nanoparticle has a greater chance of reacting with worn steel surface than spherical nanoparticles.
Figure 7. The line roughness perpendicular to the direction of the wear scar of steel ball surface (a) RO (b) RO+SLBN (c) RO+PLBN (d) RO+BLBN.

Figure 8. The XPS spectra of B1s and La3d on the worn steel surface lubricated with RO+SLBN, RO+PLBN and RO+BLBN, respectively (a) B1s, RO+SLBN (b) B1s, RO+PLBN (c) B1s, RO+BLBN (d) La3d, RO+SLBN (e) La3d, PLBN (f) La3d, BLBN.
4. Conclusion
Sheet-like nanoparticles, Petal-like nanoparticles and Ball-like nanoparticles were prepared by the hydrothermal method. Compared to RO, the average COFs of RO+SLBN, RO+PLBN and RO+BLBN are reduced by 18.68%, 19.07% and 12.78%, respectively. The WSD of rapeseed oil is reduce by 7.34%, 18.67% and 10.12% when SLBN, PLBN and BLBN are added respectively. Therefore, PLBN show best friction-reducing and antiwear performances.

Analysis of worn surfaces show that polar functional groups, such as -C-O- and -COO- adsorb on the worn steel surface and nanoparticles react with the metal surface and generate a tribochemical film on the metal surface. Furthermore, flake nanoparticles have more chance to reacting with worn steel surface and generate a tribochemical film than spherical nanoparticles.

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