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TRIBOLOGICAL PROPERTIES OF Sn-BENZOTRIAZOLE (BTA) COMPOSITE

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Abstract-This paper is to study the synthesis of Sn-benzotriazole (Sn-BTA) composite nanooil by chemical reduction and its tribological properties. The Sn-BTA composite nanoparticles are produced through the reaction of tin (II) 2-ethylhexanoate, 1, 10-phenanthroline, sodium borohydride and BTA in anhydrous methanol solution. BTA functions as stabilizer of Sn nanoparticles and protector of anti-oxidation of Sn nanoparticles in various concentrations. Tribological experiments are conducted by using the pin-on-disk tester to observe the wear scar diameter, friction coefficient, and morphology of worn surface. In order to find out new green oil, investigation of the effects of epoxidized soybean oil for tribological characteristics is made. Their anti-wear and anti-friction performances are found. Finally, TEM, OM, SEM and EDX are used to interpret the possible lubricating mechanisms of the anti- friction and the anti-wear functions. The test results show that the Sn-BTA nanoparticle used as an additive in liquid paraffin oil and epoxidized soybean oil at an appropriate concentration exhibit better tribological properties than those of pure paraffin oil. Compared with the pure liquid paraffin oil, the friction coefficient of the Sn-BTAadded paraffin oil is decreased by approximately 36 %, and compared with the pure liquid epoxidized soybean oil, the friction coefficient of the Sn-BTA added epoxidized soybean oil was decreased by approximately 31 %, with an additive concentration of 0.15 wt.%.

Keywords-Chemical reduction, Composite particles, Tribological, anti-oxidation, Epoxidized soybean oil.

I. INTRODUCTION

There is a rapid increase in the need of adding lubricant to mechanical parts. Sulfur, chloride, phosphorus and nitrogen compounds have been taken as traditional additives because they could form sulfide, chloride or phosphide layer, which is easy for cutting on metallic surface,and could prevent serious wear.Graphite,molybdenum disulphide and PTFE often function as solid additives because they also possess satisfactory properties [1]. Nevertheless,they have defects that will easily become oxidized,deposited and corrosive[2-4].

In recent years, the studies about nanomaterials functioning as lubricant additives generally indicated that they owned excellent features of wear decrease and anti-wear functions comparing to traditional solid additives, and could enhance the load performance of lubricant. There were also other studies indicating that nanoparticles of soft materials could repair the worn surface. All these studies show that using nanoparticles as lubricant additives has very bright future. However, to metallic nanoparticles, which are vulnerable to oxidation, oxides can be easily formed before modification, and will decrease the tribological properties. But composite nanoparticles, when serving as lubricant additives, can prevent nanoparticles from forming oxides.

Excellent physical and chemical properties of nanoparticles have been frequently discussed in recent years. For example, X. Tao etals. used diamond nanoparticles as additives, and found that they could effectively reduce friction and wear, and could enhance loading bearing capacity[5-10]. Z. Zhang etals used Mo-S nanoparticles as lubricant additives, and DDP for surface modification. When it was compared with T202 commercial additive (with main ingredient ZnDDP) added with pure paraffin oil, four-ball tribotester was used to do a test [11-12]. The acquired additive of Mo-S nanoparticles had better anti-extreme pressure than other lubricant additives. The rolling effect of spherical nanoparticles reduced the friction between two machines during operation, and also decreased the vibration and noise caused, presenting excellent performance of the lubricant additives.

Furthermore, developing the green energy of bio-lubricant is currently an essential task to protect the earth. And there have been some studies about using soybean oil to make different kinds of lubricants. Nevertheless, it has major defects of low oxidation stability and poor low-temperature fluidity[14]. Fortunately, composite metallic nanoparticles of soybean oil being chemically modified can improve its oxidation stability and low temperature fluidity, so that it can be provided to make the base oil of lubricant so as to make good bio-lubricant products. Since its molecules are in more even size, it can be easily adhered to the metallic surface of engine to enhance its lubricating effect. As its viscosity index is greater, under the situation of wide range of temperature, its viscosity change is smaller, which is suitable for achieving operation effect. Besides, its volatility is low, and its loss rate is small, thus reducing the operation cost. It does not produce colloidal, precipitated substance or residual to affect the lubrication of oil. Its flash point is quite high, and its operation safety is good. And it is recyclable, biologically decomposable and non-toxic. Above all, its cost is cheap. Although its cost is slightly higher than petroleum products, its cost is still lower than the expensive synthetic oil products.

There have been studies about copper and tin metallic nanoparticles made in recent years. Both nanocopper and nanotin additives belong to soft metals, which can have the

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functions of filling, enhancing anti-extreme pressure of lubricant, reducing friction and decreasing wear. However, once copper and tin nanoparticles contact with air, oxidation happens. Then the mechanical and chemical properties of additives are changed, the tribological properties of lubricant are decreased, and the lubricating function is made to become ineffective in advance, resulting in damage of machines. Composite metallic nanoparticles can improve its oxidation stability and low temperature fluidity, and also can improve the defect of decreased tribological properties in lubricant.

Sn-benzotriazole (Sn-BTA) composite nanoparticle is the target to be explored in the study. Under the same working conditions and different added amounts of particles, and comparing to paraffin-base oil and epoxidized soybean oil, the study analyzes the decrease of friction, reduction of wear and extreme pressure nature, and then finds out how lubricants added with composite metallic nanoparticles, with lubricant additive being under an extreme operation environment, can improve the defect of decreased tribological properties of lubricant.

II. EXPERIMENTAL DETAIL

According to ASTM G99 standard, under the same test conditions, pin-on-disk friction and wear tester is used to study the friction properties of Sn-BTA composite nanoparticle when functioning as lubricant additive. The schematic diagram of its mechanism is shown is Figure 1. It makes a fixed steel ball rotate beneath a disk and on a sample to create friction.

The sample beneath the disk is made by bearing steel (composition of JIS G4805-1999 SUJ2 steel and HRC58-65; 0.9~1.1% of C, 0.15~0.35% of Si, < 0.5% of Mn, < 0.025% of P, < 0.025% of S, 0.9~1.2% of Cr), with diameter 3.158mm and height 8mm. The steel ball used in the study is made by bearing steel GCr15 and HRC59-61, with height 6.35mm. Both the steel ball and the sample beneath the disk have been polished, making the surface roughness of the steel ball reach Ra=0.05μm, and the surface roughness of the sample beneath the disk reach Ra=1.0μm. The experiment is carried out under a load 2.5kg. The additive concentrations are 0.01 wt.%, 0.05 wt.%, 0.1 wt.%, 0.15 wt.% and 0.2 wt.%. The steel ball rotates under room temperature at a fixed sliding speed 0.8 m/s for 3,600 seconds.

In the wearing process, since Sn-BTA composite nanoparticles deposit on the surface and fill up the surface asperities under an environment with a high temperature produced from friction, the analysis result of elements shows that Sn exists. Figure 2 shows the deposition process of Sn-BTA composite nanoparticles undergone between the asperities.

Fig. 1.Schematic diagram of wear test mechanism.

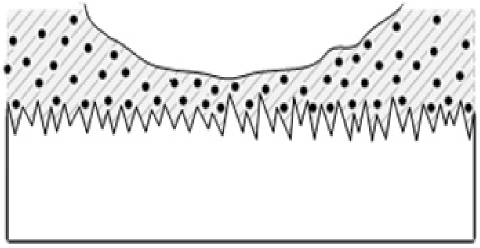


Fig. 2. Schematic diagram of Sn-BTA composite nanoparticles deposited on wear surface.

$$\begin{aligned} & L_2 \le f_2(x) \le \varepsilon_2 \\ & x \in M \end{aligned} \qquad (3)$$

III. RESULTS AND DISCUSSION

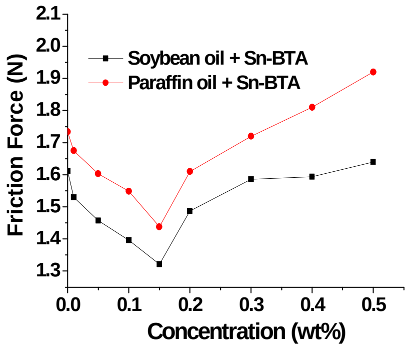


Fig. 3.Friction force and concentration of paraffin oil and Sn-BTA added epoxidized soybean oil.

In the experiment, friction and wear tester tests the friction force of Sn-BTA added liquid paraffin oil and epoxidized soybean oil, as shown in Figure 3. In the figure, the curve shows that the friction forces of Sn-BTA added epoxidized soybean oils are all smaller than that of Sn-BTA added paraffin oil. With the increase of additive, friction force decreases gradually. The epoxidized soybean oil added with 0.15wt.% Sn-BTA has the lowest friction force 1.3N. As the additive is increased and 0.15wt.% Sn-BTA is added, friction force gradually increases from 1.3N to about 1.6N, far more lower than the friction force 1.9N of Sn-BTA added paraffin oil by as much as 18%. After addition of 0.15wt.% Sn-BTA, friction force gradually increases from 1.3N to about 1.6N. It is thus known that adding too much Sn-BTA particles would obstruct friction of two objects and reduce the rolling effect of spherical nanoparticles.

As shown in Figure 4, after analysis by BTA infrared spectroscopy, it is found that when spectrum is between 3300cm-1 and 1250cm-1, there is absorption value, being the stretching band of N-H bond and C-N bond on BTA amine; when spectrum is between 2900cm-1 and 3100cm-1, the absorption value is not so strong; when spectrum is at about 1400cm-1, there is also absorption value, being the stretching band and bending band of C-H bond in aryl, as well as vibration band of C-C bond. After comparison is made with Sn-BTZ infrared spectra on the curve of Figure 5, it is found that the original stretching band of N-H bond disappears from the infrared spectrum. It is judged that the bonding between Sn and BTA is at the positions of the original C-H bond and delocalized electrons in the benzene ring. After verification is made by Fourier transform infrared spectroscopy (FTIR), the bonding way of Sn-BTA composite nanoparticles, as synthesized in the experiment, is confirmed, and Sn nanoparticles are confirmed to have BTA covered on the surface.

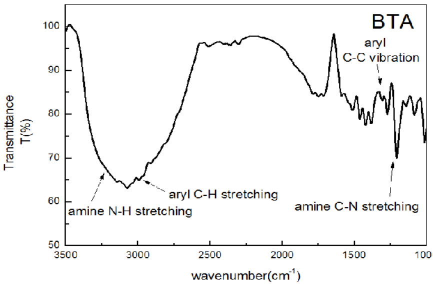


Fig. 4.FTIR spectra of BTA.

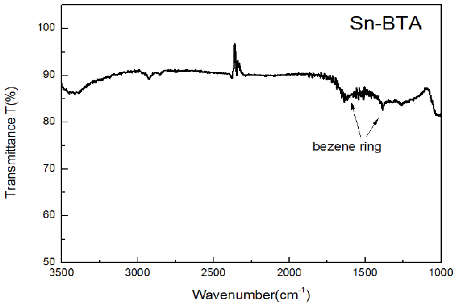


Fig. 5.FTIR spectra of Sn-BTA

As shown in the images under transmission electron microscopy (TEM) in Figure 6, the spherical Sn-BTZ composite nanoparticles have the function of protecting tin from being oxidized; and rolling of spheres can decrease friction force produced from operation of two machines, and also reduce vibration and noise created from running of two machines. Table 1 shows that the measured surface roughness, value after addition of Sn-BTA, tremendously falls by 36.7%, and the greatest decrease by 53.4% occurs after the amount of 0.15wt.% is added.

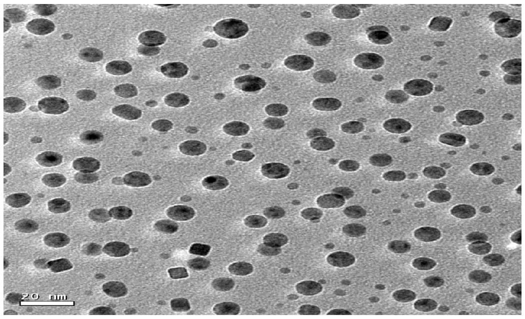


Fig. 6 Spherical Sn-BTA composite nanoparticles under TEM

Wear scar diameters are shown in Figure 7. The curve in the figure shows that Sn-BTA added epoxidized soybean oil and Sn-BTA added liquid paraffin oil have their friction forces and wear scar diameters reduced gradually with the increase of additive. In the figure the most ideal Sn-BTA oncentration is 0.15wt.%. After it is added to the above two oils, thelowest friction force is achieved. And epoxidized soybean oil added with Sn-BTA at an optimal concentration 0.15wt.% can achieve the smallest wear scare diameter 0.29 mm. and Sn-BTA added epoxidized soybean oil.

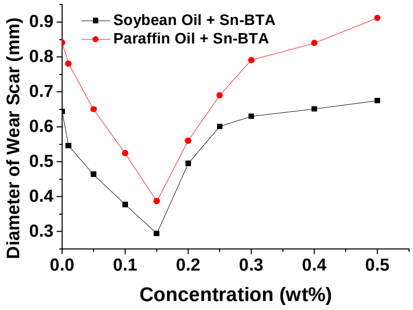
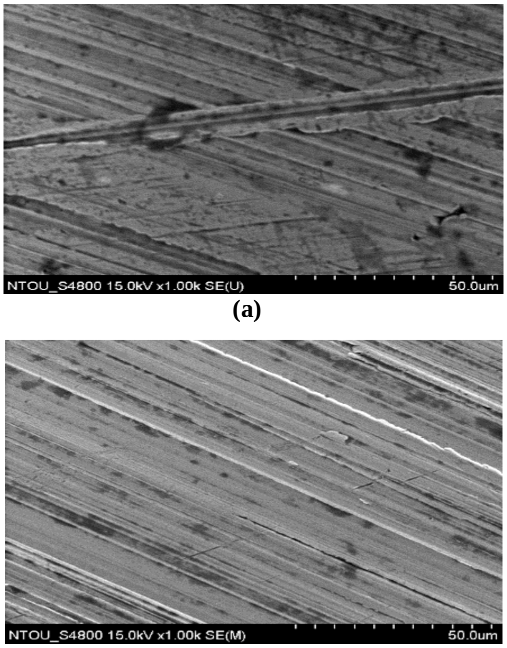


Fig.7. Wear scar of Sn-BTA added paraffin oil



(a)

(b)

Fig. 8. SEM images of worn surface using (a) Pure epoxidized soybean oil (b) 0.15wt.% Sn-BTA added epoxidized soybean oil

Figure 8 shows the friction surface formed by two different lubricants. Figure 6(a) shows the friction surface formed after taking pure epoxidized soybean oil as lubricant. The surface is rough, and is distributed with thick and deep grooves and holes. Besides, peel wear, extrusion wear and adhesion wear are caused. Figure 6(b) shows the friction surface formed after taking 0.15wt.% Sn-BTA added epoxidized soybean oil as lubricant. The surface appears to be smooth, and the grooves are shallow. There are fine scratches, but filled up by Sn-BTA nanoparticles.

As shown in Table 1, experiment of wear is made for epoxidized soybean oil without addition of nanoparticles. Surface roughness of wear surface is measured before and after the experiment. The results show that the trend of slight fall of surface roughness of epoxidized soybean oil is decreased by 9.1%. Then an experiment of wear is made for Sn-BTA added epoxidized soybean oil. Again, surface roughness is measured before and after the experiment. After fixed amounts are added, the measured results of surface roughness after addition show an obvious trend of decrease. At the added amounts of 0.01wt.% and 0.05wt.%, the measured results of surface roughness are reduced by 14.5% and 18.1% respectively. It is speculated that the added amount of Sn-BTA composite nanoparticles is insufficient, so that there are insufficient particles to conduct repeated polishing, filling and deposition on the wear surface, thus failing to reduce the surface roughness value to a great extent.

TABLEI.TESTDATAOFROUGHNESS ONWEARSURFACE BY EPOXIDIZEDSOYBEAN OIL.

Sn-BTA added (wt%)	Before wear Ra(μm)	After wear Ra(μm)	Increase / Decrease (%)
0	1.589	1.445	-9.1
0.01	1.603	1.371	-14.5
0.02	1.708	1.442	-15.6
0.05	1.634	1.339	-18.1
0.10	1.688	1.069	-36.7
0.15	1.714	0.799	-53.4
0.20	1.727	1.038	-39.9
0.50	1.692	1.494	-11.6

When the amount of additive increases to 0.10wt.%, since the added amount is increased by 2 times, there are sufficient particles to conduct repeated polishing, filling and deposition on the wear surface, thus making the measured value of surface roughness immensely decrease by 36.7%. And the maximum decrease of 53.4% happens at the added amount of 0.15wt.%. It is speculated that the particle this addition percentage can obtain the best operation efficiency, and can repeatedly carry out polishing, filling and deposition on wear surface. However, when the added amount gradually increases from 0.15wt.% to 0.20wt.% and 0.50wt.%, the roughness on wear surface contrarily does not increase to a great extent, but falls by 39.9% and 11.6% respectively. As for its reason, it is speculated that excessive addition of Sn-BTZ composite nanoparticles makes particles have flocculation in epoxidized soybean lubricant, and let them greatly agglomerated. Therefore, the nano effects of small-size effect and surface effect cannot work. As a result, it fails to conduct polishing, filling and deposition on the surface at higher efficiency.

As known clearly from the results in TABLE 1, additive at 0.15wt.% achieves the best performance. After different functions have effectively played their roles, surface roughness decreases to the greatest extent. According to the results of initial tribological experiment, 0.15wt.% is the optimal addition percentage for Sn-BTZ added composite nanoparticles. It achieves the best anti-wear and friction decrease effects under the same conditions. Comparing to paraffin-base oil, friction force decreases by 17%, and wear scar diameter decreases by 53.9%. Comparing to epoxidized soybean oil, friction force decreases by 19.2%, and wear scar diameter decreases by 54.3%. This result is the best comparing to Sn-BTA added composite nanoparticles at other addition percentage. Therefore, after adding the amount 0.15wt.% to paraffin-base oil and epoxidized soybean oil, both paraffin-base oil and epoxidized soybean oil take extreme tests of lubricants under different loads and rotational speeds.。 The paper evaluates, with the optimal addition amount adopted, whether the tribological properties of paraffin-base oil and epoxidized soybean oil have been increased tremendously.

CONCLUSION

From the above experimental data, the following conclusions are drawn:

1. Sn-benzotriazole(BTA), a spherical composite particle synthesized by chemical reduction, has the features of protecting tin and not letting it be oxidized. Its better low-temperature fluidity and rolling of spheres reduces the friction force during operation of two machines, decreases the wear in times of operation of two machines, and meanwhile reduces vibration and noise, presenting the excellent performance of lubricant additive.
2. With the increase of additive, the friction forces and wear scar diameters of the Sn-BTA added base oil and epoxidized soybean oil decrease, but the optimal concentration is 0.15wt.%. It refers that the most ideal Sn-BTA concentration is 0.15wt.% as it can create the smallest wear scar diameter. Besides, the liquid paraffin oil and epoxidized soybean oil added with 0.15wt.% Sn-BTA also achieves the least friction force. After addition, the measured value of surface roughness tremendously decreases by 36.7%, and the maximum decrease is around 53.4%.
3. Sn-BTA's added amount of 0.15wt.% can give the best performance. After different functions have effectively played their roles, surface roughness has the greatest decrease, proving that Sn-BTA particles can carry out repeated polishing, filling and deposition on the surface by wear machines, and make surface roughness decrease to a great extent.

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