Nanolubricants developed from tiny CuO nanoparticles

S.M. Alves *, V.S. Mello, E.A. Faria, A.P.P. Camargo

Grupo de estudos de Tribologia e integridade estrutural, Universidade Federal do Rio Grande do Norte, Avenida Senador Salgado Filho, 3000, 59078-970
Natal, RN, Brazil

ARTICLE INFO

Article history:
Received 31 August 2015
Received in revised form 23 December 2015
Accepted 29 January 2016

Keywords:
Tiny CuO nanoparticles
PAO oil
Boundary lubrication

ABSTRACT

This paper reports the use of tiny CuO nanoparticles as EP additives in the synthetic oil, developing nanolubricants with low concentrations of this oxide. The nanoparticles were synthesized by hydrothermal microwave technique, and their average size was 5 nm. After that, the nanoparticles were covered with oleic acid and added three different concentrations in PAO oil (0.1, 0.25 and 0.5 wt%) using Toulene as the dispersant. The tribological performance of these oils was evaluated in HFRR tribometer under boundary lubrication conditions. The results showed that it is possible to reduce the friction coefficient and wear using tiny nanoparticle as well as decrease the percentage of CuO addition in lubricating oil. Moreover, tiny copper oxide reveals potential use lubricant applications.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Recently, the applications of metal nanoparticles (NNP) as extreme pressure and antiwear additives in lubrication systems have been studied. They can reduce friction and surface damage caused by high pressures and temperatures. Some researchers have reported that the addition of the NNP’s in lubricants promotes improvements in tribological properties besides reducing lubricants environmental impacts. However, their friction reduction antiwear performance depends on some factors such as size, shape and concentration of nanoparticles as well as their actuation mechanism [1–3]. Nanoparticles concentration is a fundamental issue because they can act negatively when there is an excess of nanoparticles. Wu et al. [4] identified that low concentration (0.05–2.97% by weight) is sufficient to improve the tribological properties of the lubricant. Several authors have investigated the role of nanoparticles concentration in reducing friction. Battez et al. [5] conducted studies with low amount of NNP (0.5–2.1% by weight) and found low friction coefficient with 1% concentration for CuO (30–50 nm). However, Jatti and Singh [6] observed the lowest friction coefficient in concentration 1.5% CuO (30–40 nm). The authors Ma et al. [7] and Battez et al. [5] obtained a lower friction coefficient for the ZrO2 (100 nm and 20–30 nm, respectively) in the lower concentration equal to 0.5%. Also, Rabaso et al. [8] verified lower coefficient with 1% MoS2. Luo et al. [9] achieved that 0.1% lower coefficient of nanocomposite Al2O3/TiO2 (75 nm) in the lubricating oil. Kolodziejczyk et al. [10] reduced the coefficient with 5% Pd nanoparticles in paraffin oil compared to pure oil. Peng et al. [11], in their research, demonstrated that 0.2% of diamond nanoparticles (110 nm) were sufficient to reduce low coefficient. The size of the nanoparticle is another factor that needs attention with antiwear additives in oils, which may affect the type of nanoparticles action mechanisms in lubricants. Numerous researchers used nanoparticles as oil additives, and commonly they present a size between 20 and 80 nm diameter of copper oxide, as mentioned before. According to Hwang et al. [12] the lubrication performance improved with decreasing size of NNP suspended in mineral oil.

Based on literature research, some mechanisms whereby nanoparticles added to the PAO oil could act: (1) smaller nanoparticles can interact with the surfaces of the friction pairs to form a surface protective film [13]; (2) small spherical nanoparticles create a rolling effect between surfaces [3]; (3) filling valleys, promoting a protective film formation on the surface [14], and (4) nanoparticles are deposited on the surface forming a physical tribofilm that compensates for the loss of mass, this effect is called “mending effect” [15], and (5) may be tribo-sintered to the surface [5]. The combination of these effects results in the good friction and wear properties of nanoparticles in base oil.

This study examined the synthesis and tribological properties of nanolubricants with tiny CuO nanoparticles (around 5 nm) at small percentage of the additive. The friction and wear experiments were performed to evaluate the friction reduction and antiwear abilities of these tiny nanoparticles, and their friction reduction mechanism. In addition, more investigations were performed using transmission electron microscope (TEM), scanning
electron microscopy (SEM), and Raman spectroscopy to evaluate the effect of concentration in the mechanisms of lubrication and wear with these tiny nanoparticles.

2. Experimental and methods

2.1. Synthesis and characterization of nanoparticles

CuO nanoparticles were synthesized using the microwave technique with alcoholic solution of copper acetate (2 mol of copper acetate monohydrate was dissolved in 40 mL of ethanol) and alcoholic solution of sodium hydroxide (8 mol of NaOH dissolved in 40 mL of ethanol). In Teflon vessel 10 mL of each solution was mixed and then the resultant solution was thermally treated using a microwave oven. The hydrothermal reaction was performed under 99 W for 140 s with ON/OFF pulse of 20 and 10 s, the pulse was repeated nine times in order to keep the solution at temperature of 80°C.

After this procedure, solutions were cooled to 15°C for 5 min. The nanoparticles were separated from these suspensions by centrifuging at 3600 rpm for 5 min. The nanoparticles were washed several times with hot water and ethanol. Then, they were dried at 60°C for 2 h or until complete evaporation of ethanol. The synthesis was performed in triplicate.

The nanoparticles surfaces were modified with oleic acid to minimize the agglomeration. The addition of oleic acid could improve the particle size distribution by the formed protective layer on its surface [16], avoiding the increase of size that can be negative effect on lubrication. Twenty milliliters of ethanol was added into a beaker containing 0.01 g of oleic acid and 0.2 g of CuO nanoparticles. Then the solution was kept at 60°C under stirring for 2 h. After the reaction was complete, the resultant was centrifuged for 10 min, and dried for 2 h or until complete ethanol evaporation.

The crystal structure of the CuO nanoparticles was analyzed by X-ray diffraction (XRD). This analysis was carried out using XDR-6000 diffractometer equipped with graphite-monochromatized CuKα radiation, operating at 30 kV. The crystallite size was calculated according to Scherrer’s equation [17]:

\[
D_{hkl} = \frac{k \lambda}{\beta \cos \theta}
\]

where \(D_{hkl}\) is the crystallite size, \(k\) is the sphere shape factor (0.89), \(\theta\) is the angle of the diffraction, \(\beta\) is the full-width at half-maximum (FWHM) of the peak and \(\lambda\) is the wavelength of X-ray (1.54056 Å).

In addition, JEOL-JEM 2100 transmission electron microscope (TEM) was employed to obtain the morphology and size of the nanoparticles. For TEM analysis, CuO was dispersed in a few milliliters of ethanol in an ultrasonic bath. The NNP size was determined following the methodology described by [18]. This methodology measured N nanoparticles diameter from TEM images using the Imag-J software.

Table 1
Composition of nanolubricants (oil, nanoparticle and dispersant).

<table>
<thead>
<tr>
<th>Concentration %</th>
<th>NNP (g)</th>
<th>Oil (mL)</th>
<th>Toluene (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.008</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>0.25</td>
<td>0.02</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>0.5</td>
<td>0.04</td>
<td>8</td>
<td>10</td>
</tr>
</tbody>
</table>

2.2. Nanolubricants preparation

In order to improve the nanoparticles dispersion, Toluene (solvent) was employed to disperse them in synthetic oil (Poly-alphaolefin-PAO, 88.21 cSt at 40°C and 150 IV). The nanolubricants were prepared with 0.1%, 0.25% and 0.5% by weight of nanoparticles. The mixing conditions for the nanolubricants are shown in Table 1. Firstly NNP were added to toluene and then to PAO, the mixture kept at 20°C under stirring for 6 h. After that, the solution was dried at 70°C until complete evaporation of the toluene. The analysis of dispersion of nanoparticles in oil was done by visual way and Ultra-Violet (UV) Visible Spectrophotometer (SHIMADZU UV-1650PC). The absorbance level of visible light is proportional to the dispersion of nanoparticles in the oil.

2.3. Tribological test

The friction reduction and antiwear abilities of nanolubricants were evaluated using the HFRR, as shown schematically in Fig. 1. It consists of a ball-on-disc test to measure the friction and wear under boundary lubrication conditions using a highly stressed ball against a disc. The description of tribological pair is described in Table 2, both ball and disc were made of AISI 52100 steel. The discs were polished in order to minimize the roughness effects on nanoparticles action.

The hard steel ball slides against the soft steel disc with a 1.00 ± 0.02 mm stroke length at a frequency of 20 Hz and sliding speed of 0.01 m/s for 60 min. The ball and disc in contact are fully submerged in 2.0 ± 0.2 mL of lubricant at normal load of 10 ± 0.01 N. The tests were performed in triplicate.

The lubricant temperature was kept at 50±1°C. This temperature was chosen to minimize the viscous effects of lubricant and to enhance the nanoparticles action, and because it is a little below the maximum operation temperature of HFRR-60°C. The contact pressure was 1.4 GPa, characterizing a boundary lubrication regime. The friction coefficient was measured by a

Table 2
Physical characteristics of tribological pair.

<table>
<thead>
<tr>
<th></th>
<th>Ball</th>
<th>Disc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (HV)</td>
<td>(570–750)</td>
<td>(190–210)</td>
</tr>
<tr>
<td>Dimensions</td>
<td>Diameter=6.0 mm</td>
<td>Diameter=10.0 mm</td>
</tr>
<tr>
<td>Roughness – Ra (µm)</td>
<td>0.05</td>
<td>0.008</td>
</tr>
</tbody>
</table>
piezoelectric force transducer. The contact resistance (Ω) between rubbing specimens was measured by electrical contact resistance technique (ECR). This resistance can be used to study the film formation process of the nonconductive chemical film of lubricating oil additives [3]. The samples (balls and discs) had been cleaned with ethyl alcohol and acetone and then dried before the tests.

Some instruments were used to examine the action of lubricant on discs surface for more detailed analysis of the tribological properties. The morphology of worn surface and film formation process of the nonconductive chemical film of lubricating oil additives [3]. The samples (balls and discs) had been cleaned with ethyl alcohol and acetone and then dried before the tests.

Some instruments were used to examine the action of lubricant on discs surface for more detailed analysis of the tribological properties. The morphology of worn surface and film formation was evaluated with (Jeol-JSM-6010LA) scanning electron microscope (SEM). The energy dispersion of X-rays (EDX) and Raman spectroscopy (JEOL-JEM 2100) was employed to analyze the chemical composition on the rubbing surfaces.

3. Results and discussion

3.1. Characterization of the CuO nanoparticles and nanolubricants stability

Fig 2 shows the XRD patterns of the synthesized CuO nanoparticles. All the diffraction peaks in this patterns are indexed to the cupric oxide (CuO), indicating that the products obtained are only CuO. The characteristic peak of CuO has an angulation of 38.44°, agreeing with the limits of its characterization from 35.7° to 38.5° [19]. From the XRD patterns is also possible to obtain the average crystallite size by Scherrer equation, which was 5.0 nm. Also, the formation of a single phase with high purity and crystallinity was observed due to narrow and intense peaks seen in the XRD patterns [20]. As verified by Jamil et al. [20] the treatment and manipulation of the microwave parameters synthesis have the ability to control the nanoparticle formation.

Morphology of the CuO nanoparticle was investigated with TEM images as shown in Fig. 3a–c, with different magnifications. The NNP is well dispersed and near spherical. The corresponding particle size distribution (Fig. 3b) indicates that the average diameter of CuO is about 4.3 nm. Despite the large uncertainty associated with the standard deviation of the distribution, the mean diameter value is consistent with the average crystallite size obtained by XRD analysis. This result suggests that crystal size of the nanoparticle is comparable to the physical size.

Therefore, it was concluded that hydrothermal microwave technique is efficient to produce tiny, crystalline and spherical oxide nanoparticle, as desired for lubrication applications.

The dispersion of nanoparticles in the lubricant can be characterized using UV–vis absorption spectroscopy. Generally, higher absorbance indicates better dispersion and solubility of the nanoparticles in solution. Absorbance values recorded a wavelength of about 240–300 nm characterizing the CuO nanoparticle, as reported in [21,22]. Fig. 4b shows that the highest absorbance peak of the CuO in oil solution with 0.1% of concentration was recorded at a wavelength of 270 nm. This highest absorbance (3.5 abs) and the unique peak at wavelength of 250 nm indicate the good dispersion CuO in lubricant oil. As the nanolubricants with 0.25 and 0.50% are dark, it was necessary to dilute them before UV–vis analysis, and the spectra of diluted solutions were similar to 0.1% because of this, just one absorbance curve was plotted in Fig. 4b. In addition to UV–vis analysis, the photographs of the CuO nanolubricants, for three concentrations are shown in Fig. 4a. The nanolubricants are kept for 30 days after preparation. Visualization of the samples gives clearly the good dispersion of CuO nanoparticles, without sedimentation after the storage time.

The good dispersion has been ensured by superficial modification with oleic acid and the use of dispersant agent (Toluene), bad dispersion promotes agglomeration of nanoparticles, increasing their size. These agglomerated nanoparticles can act as third body and to cancel the beneficial effect of CuO on friction and wear reduction.

3.2. Tribological properties of CuO nanoparticles

The results on wear scar diameter (WSD) of ball are shown in Fig. 5 (images of WSD obtained from optical microscope), as well as average friction coefficient (COF) and WSD are summarized in Table 3. From Table 3, the addition of CuO tiny nanoparticles provides a little reduction in friction coefficient in comparison to pure lubricant; however, the wear scar diameter of ball decreased by about 15% when compared to pure oil and nanolubricant with 0.10%. Thus, it is possible to conclude that tiny nanoparticle dispersed in PAO at lower concentration has more effect on wear than friction reduction. Besides the WSD values, Fig. 5 shows that scar for 0.10% is more smoother and has less depth than other concentrations. This observation will be proved with morphological analysis of wear (SEM images). For all concentrations a positive effect of nanoparticles on lubrication was observed. The reductions are large when the additive concentration is 0.1 wt%.

Fig. 6 shows the friction behaviour during test, and it reveals the interesting aspect of nanoparticle action. Friction variations of nanolubricants as a function of nanoparticles content are related to size and deposition of nanoparticles on wear surfaces. Battez et al. [5] verified the best concentration for CuO in PAO was 1 wt%, the nanoparticle size was 30–50 nm. They evaluated a concentration range from 0.5 to 2.0 wt%. On the other hand, Jatti and Singh [6] concluded that coefficient of friction decreased with rising percentage of CuO nanoparticle (30–40 nm) concentration. However, this trend continued only up to a concentration of 1 wt%. Therefore, in this work showed if tiny CuO NNP (around 5 nm) is used as the lubricant additive, lower concentration (0.1 wt%) gives lower friction coefficient. Tiny size promotes different behaviour in relation to concentration, and it is interesting because a minimum concentration of nanoparticles was enough to reduce the friction, decreasing costs with additives.

Three stages of friction reduction are observed in Fig. 6, and they are correlated with nanoparticle concentration, indicating different lubrication mechanisms: (1) increase of friction due to polish effect caused by rolling of copper oxide nanoparticle on surface [23]; this mechanism promotes a decrease of COF after
500 s; (2) with asperities reduction, the nanoparticles fill valleys and micro-grooves on surface by sliding; this promotes that a smoother surface can be seen from 1500 to 2500 s\cite{14,22}; (3) CuO NNP is deposited on friction surface forming the tribofilm that compensates the loss of mass, which has been called “mending effect” \cite{15}. This mechanism was observed after the 2500 s for nanolubricant with 0.1 wt% of CuO.

Fig. 7 shows film percentage formation during HFRR test measured by ECR sensor. The film percentage is a good indicator of the contact situation for both specimens during the friction test process; since that, the films cover the rubbing surfaces, and it affects the roughness and structure of the surface \cite{24}. In addition, ECR is a measure of current flow between surfaces in contact. Metallic contact shows lower electrical resistance while a thin layer between metallic surfaces provokes the increase in resistance.

The film formation is strongly influenced by nanoparticle concentration. From test with nanolubricants and pure PAO (Fig. 7), it was observed that the film formation takes some time to be developed (about 750 s) and, in this time friction coefficient is unstable showing running-in (Fig. 6). After this time, different behaviours were observed for nanolubricant. PAO film formation showed high fluctuations until 1500 s. Probably this fact has occurred because the debris that comes off of the bodies in contact during the running-in stage hampers film formation because the adhesion of layer lubricant is not strong, and it was removed because of the motion of the ball. From 1500 s, nanolubricant 0.5% and PAO pure presented similar behaviour of film formation. On the other hand, 0.1% and 0.25% of CuO improved the surface covering, by filling of grooves. As mentioned before, the percentage of the film is a measure of electrical resistance between the metallic surfaces, both the lubricant oil and the nanoparticles are insulating materials that increase the value of electrical resistance, but it does not necessarily decrease the friction in same proportion. Due to this fact, even film formation was different the nanolubricant presented similar COF until 2500 s. However, from 2500 s 0.1 a tribofilm formation was observed to 0.1% of CuO, which promoted
a decrease in COF. The film formation behaviour corresponds to friction coefficient stages described above.

Fig. 8 highlights how the increase of nanoparticle concentration in the base oil enhances deposition on wear surfaces. Lower CuO concentration improved the tribological behaviour of suspension. This result did not correspond with Battez et al. [5], in their experiment they verified that higher CuO concentration improved the tribological behaviour of suspensions. Considering that size of CuO nanoparticle of this present work is 10 times lower than the one used by Battez et al. [5], it can conclude that tiny nanoparticles promote a different tribological behaviour in function of NNP concentration.

The worn surface morphology depends on concentration (Fig. 8). The smoother surface was observed to disc lubricated with 0.1% nanolubricant due to nanoparticle film formed, and the wear mechanism of tribo-sintering could be observed for this condition. On the other hand, the reciprocating sliding with more amount of CuO (0.5%) increased the surface damage drastically (wear) in comparison with pure oil. Deformation of the surface is also increased with increasing NNP concentration. Surface morphologies of the worn scar of 0.25 and 0.50% show that layers of debris from the surfaces have been extruded out from the contact interface in the sliding direction. It is seen that the surface at 0.5% has been plastically deformed and elongated with more wear debris; this indicates that the wear for this concentration can be

<table>
<thead>
<tr>
<th>Concentration (wt%)</th>
<th>Average friction coefficient</th>
<th>WSD (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.124 ± 0.0184</td>
<td>417 ± 0.631</td>
</tr>
<tr>
<td>0.10</td>
<td>0.104 ± 0.0054</td>
<td>356 ± 0.385</td>
</tr>
<tr>
<td>0.25</td>
<td>0.112 ± 0.0053</td>
<td>363 ± 0.560</td>
</tr>
<tr>
<td>0.50</td>
<td>0.114 ± 0.0037</td>
<td>388 ± 0.205</td>
</tr>
</tbody>
</table>

Table 3
Friction coefficient and wear scar diameter summarized.

Fig. 4. Dispersion results: (a) visual analysis, and (b) UV–vis spectrum.

Fig. 5. Wear scar diameter of ball after tribological tests (optical microscopy with 100x magnification).
categorized as adhesive wear. The higher wear was observed for worn surface lubricated with pure oil and nanolubricant with 0.5 wt% of CuO.

The EDX analyzer was employed to examine the presence of nanoparticle elements on worn surfaces. The analyzed result of oxygen and copper elements is shown in Fig. 8 for four points in each SEM image. Only for pure PAO the EDX results correspond to the chemical composition of role analyzed surface. The variation of the copper amount present on worn surface demonstrates that CuO deposition occurs for all nanolubricants, but it is not uniform. Comparing nanolubricant 0.25% and 0.5%, therefore the second has more nanoparticles in its composition the deposition on surface is lower than the first, this suggests that part of CuO remained dispersed in PAO or become a third body. In addition, higher concentration of nanoparticles was observed for surface less uniform (see 0.25 and 0.50% SEM images). In case of 0.25% more grooves are observed, these allowed the deposition of nanoparticles. For 0.50%, the SEM images and the EDX analysis indicate the presence of a thick of nanoparticles adhered to the surface. The uniform deposition of nanoparticles on worn surface can decrease the shearing stress, and hence reduce friction and wear. Low CuO concentration (0.1%) has a self-repairing effect on the rubbed surface even with lower percentual of CuO on worn surface. In order to clarify the lubricant layer formation, Raman spectroscopy was performed to investigate film formation once EDX identifies only chemical elements and not compounds. Raman spectra of the worn surface can be seen in Fig. 9.

The monoclinic copper oxide (CuO) in nanolubricant produced three peaks, corresponding three (Ag2+Bg) modes in Raman active (Ag-213; Bg1-286 and 402; Bg2-653). These results corroborated with [25–28], although small variations in wavelength can be observed, this occurs due to the effect of smaller particle size on the force constants and vibrational amplitudes of closer neighbor bonds. Raman peaks are closely related to film formation on disc surface. Also, for the concentration of 0.1% the Raman peaks near 1318 cm⁻¹ corresponds to vibration and distortion of the CH₂–CH₂ bonds. These results confirm the CuO tribofilm formation on disc surface. This film is formed because the nanoparticles are compacted on the contact surface under boundary lubrication conditions (high contact pressure and temperatures) [5,29,30].

Therefore, the mechanism by which nanoparticles reduce friction and wear can be explained for spherical nanoparticles deposited onto the surface result in effective rolling friction, mainly in beginning the test. After some time of friction, the surface roughness increased, and nanoparticles deposited on the rubbing surface and embed into the micro-grooves. Also, a protective film is formed when nanoparticles are compacted on the contact surface at a higher temperature during friction [5,29,31]. According to Battez et al. [5], the film formation can follow three
different processes: melting of nanoparticles on the rubbing surface, reaction of them with active surface and their tribo-sintering on the surface. The first two processes are not feasible because the melting point of CuO is 1326 °C and electropositive nature of metal oxide nanoparticle and metallic surface. The third process is the most suitable and verified by some researchers [29–33]. When

![SEM images of the rubbed surface lubricated with different NNP concentration: a) 0.1 wt%; b) 0.25 wt%; c) 0.50 wt% and e) 0 wt% (pure oil).](image)

<table>
<thead>
<tr>
<th>Point</th>
<th>Fe</th>
<th>O</th>
<th>Cu</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>92.74</td>
<td>--</td>
<td>0.12</td>
<td>7.14</td>
</tr>
<tr>
<td>002</td>
<td>94.52</td>
<td>2.30</td>
<td>0.41</td>
<td>2.77</td>
</tr>
<tr>
<td>003</td>
<td>94.89</td>
<td>2.31</td>
<td>0.56</td>
<td>2.24</td>
</tr>
<tr>
<td>004</td>
<td>96.71</td>
<td>--</td>
<td>0.20</td>
<td>3.09</td>
</tr>
</tbody>
</table>

0.1 wt

<table>
<thead>
<tr>
<th>Point</th>
<th>Fe</th>
<th>O</th>
<th>Cu</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>78.10</td>
<td>9.61</td>
<td>1.34</td>
<td>10.98</td>
</tr>
<tr>
<td>002</td>
<td>90.72</td>
<td>2.65</td>
<td>2.69</td>
<td>3.94</td>
</tr>
<tr>
<td>003</td>
<td>95.82</td>
<td>1.38</td>
<td>1.01</td>
<td>1.79</td>
</tr>
<tr>
<td>004</td>
<td>93.04</td>
<td>4.45</td>
<td>1.26</td>
<td>1.25</td>
</tr>
</tbody>
</table>

0.25 wt

<table>
<thead>
<tr>
<th>Point</th>
<th>Fe</th>
<th>O</th>
<th>Cu</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>96.28</td>
<td>1.08</td>
<td>0.59</td>
<td>2.05</td>
</tr>
<tr>
<td>002</td>
<td>93.12</td>
<td>3.02</td>
<td>1.44</td>
<td>2.42</td>
</tr>
<tr>
<td>003</td>
<td>95.54</td>
<td>1.73</td>
<td>0.43</td>
<td>2.30</td>
</tr>
<tr>
<td>004</td>
<td>89.79</td>
<td>7.06</td>
<td>0.78</td>
<td>2.37</td>
</tr>
</tbody>
</table>

0.5 wt

<table>
<thead>
<tr>
<th>element</th>
<th>Fe</th>
<th>O</th>
<th>Cu</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>%wt</td>
<td>92.45</td>
<td>4.56</td>
<td>--</td>
<td>2.99</td>
</tr>
</tbody>
</table>
very fine metallic particles are employed under high compressive pressure, the sintering process starts as soon as the temperature increases above room temperature [32,33].

4. Conclusions

The effect of tiny CuO addition and its different concentration on the tribological properties of PAO was investigated. On the basis of results presented above, it can be concluded that:

- Spherical tiny CuO nanoparticles were successfully synthesized via a hydrothermal microwave method and modified by oleic acid and well dispersed in PAO, for lubrication application.
- All nanoparticle concentration exhibited friction and wear reduction compared to the base oil. Best results were obtained for nanolubricants with 0.1 wt% of CuO nanoparticles. The concentration of 0.25% and 0.5% showed same friction reduction behaviour. However, the tiny CuO nanoparticles are more effective on wear than friction reduction.
- CuO nanoparticles at 0.1\% exhibit better antiewear performance compared with other concentrations. The antiewear mechanism was produced by tribo-sintering of CuO nanoparticles on the wear surfaces, reducing metal-to-metal contact and making a smoother surface.
- So CuO tiny nanoparticles reveal large potential in lubrication, using low concentration and reducing costs.

Acknowledgments

The authors wish to express thanks to Laboratory of surface engineering of USP to support this research.

References

[37] Alves SM, Barros BS, Trajano MF, Ribeiro KSB, Moura E. Tribological behaviour of vegetable oil-based lubricants with nanoparticles of oxides in boundary
triboint.2013.03.027.
international improving the AW/EP ability of chemically modified palm oil by
org/10.1016/j.triboint.2015.03.035.
[29] Song X, Zheng S, Zhang J, Li W, Chen Q, Cao B. Synthesis of monodispersed
ZnAl2O4 nanoparticles and their tribology properties as lubricant additives.
suspension under extreme pressure conditions. Wear 2007;263:1568–74.
http://dx.doi.org/10.1016/j.wear.2007.01.093.
http://dx.doi.org/10.1016/j.wear.2007.09.009.
[32] Zhou YH, Harmelin MJ, Bigot J. Sintering behaviour of ultra-fine Fe, Ni, and Fe–
[33] Kato H, Komai K. Tribofilm formation and mild wear by tribo-sintering of
nanometer-sized oxide particles on rubbing steel surfaces. Wear