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Bismuth nanoparticles synthesized by laser ablation in lubricant oils for tribological tests

M. Flores-Castañeda [a,b,*], E. Camps [b], M. Camacho-López [a], S. Muhl [c], E. García [c,d], M. Figueroa [c,d]

[a] Universidad Autónoma del Estado de México, Av. Instituto Literario No. 100, Oriente Col. Centro, Toluca, Estado de México C.P. 50000, México
[b] Instituto Nacional de Investigaciones Nucleares, Carretera México-Toluca s/n, La Marquesa, Ocoyoacac, Edo. de México C.P. 52750, México
[c] Instituto de Investigación en Materiales (UNAM), Circuito Exterior, Ciudad Universitaria, Coyoacán, 04510 México, D.F., México
[d] Instituto Politécnico Nacional, Av. Luis Enrique Erro S/N, Unidad Profesional Adolfo López Mateos, Zacatenco, Delegación Gustavo A. Madero, C.P. 07738 México, D.F., México

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ABSTRACT

The improvement of the tribological properties of mineral base oils through the addition of bismuth nanoparticles as an additive, together with the idea of obtaining lubricants free of heavy metals, was evaluated. Bismuth nanoparticles were produced directly in the heavy and light viscosity mineral base oils (BS900 and BS6500) using the technique of laser ablation of solids immersed in liquids. Transmission electron microscopy measurements showed the presence of pure bismuth nanoparticles. Small Angle X-ray Scattering (SAXS) measurements showed that the average size of the nanoparticles was between 7 and 65 nm depending on the experimental conditions used. The tribological properties of the base oil with the bismuth nanoparticles additives were evaluated using a four-ball tester. Tests were performed using the base oil with and without Bi nanoparticles. It was observed that the coefficient of friction of the oil decrease with an increasing concentration of the nanoparticles. The results also showed that the wear rate was reduced when the Bi nanoparticle additives were used.

1. Introduction

The majority of lubricant base oils are produced from refining of crude oil. The reasons for the predominance of refined petroleum base oils are because of their performance, availability and price. In general, large scale oil refining operations produce base oils with excellent characteristics in a variety of modern lubricant formulations at economic prices.

Modern lubricants are produced from a range of the base oils with chemical additives. The base oil has several functions but it is primarily the lubricant which provides the fluid layer to separate moving surfaces. It also removes heat and wear debris whilst minimizing friction. Many properties of the lubricant can be enhanced or created by the addition of special chemical additives to the base fluid. For example, stability to oxidation and degradation in engine oil is improved by the addition of antioxidants, whilst extreme pressure (EP) and anti-wear properties needed in gear lubrication are created by the addition of different additives. The base oil acts as the carrier for these additives and therefore must be able to maintain them in solution, or suspension, under all normal working conditions [1].

In recent years, many of the studies of the use of nanomaterials additives in lubricating oils has drawn attention to how the physico-chemical properties of the additives can directly contribute to the improvement of tribological properties of the lubricants, such as anti-wear, reducing friction, operation under extreme pressure and thermal stability [2–4].

Some of the lubricant additives that have been studied include nanoparticles of metals [5,6], metal oxides [7,8], metal sulfides [9,10], rare earth compounds [11], etc. In many of these cases significant improvements to the tribological properties of the lubricants have been obtained. However, some of these nanomaterials contain sulfur or phosphorus compounds, or even involve the incorporation of heavy metals that are potentially harmful to humans and the environment. In the present investigation the incorporation of nanoparticles of bismuth as an additive offers an ecological alternative, as this element is known to have low toxicity and is considered a good Green alternative.

Nanoparticle additives to lubricants present several major advantages compared to the organic molecules that are currently used, for example their small size allows them to easily enter the contact area. They are often efficient at ambient temperature and

* Corresponding author at: Instituto Nacional de Investigaciones Nucleares, Carretera México-Toluca s/n, La Marquesa, Ocoyoacac, Edo. de México C.P. 52750, México.

E-mail address: mar.floc@hotmail.com (M. Flores-Castañeda).

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therefore no induction period is necessary to obtain good tribological results [12].

Another effective way to use nanoparticles for tribological improvement is by embedding them inside a coating. The nanoparticles can enhance the tribological performance of the coating itself but the nanoparticles can also be released during the wear of the coating in use and in this way act as a solid lubricant.

The ablation laser of solids in liquids is a relatively new and simple technique for the formation of nanoparticles in the desired medium, for their direct application. Several investigations are using this method for obtaining different nanoparticles, for a number of applications like biological [13], photocatalytic [14], mechanical [15], etc. The method has many advantages that could be applicable to almost an unlimited variety of solid and liquid materials. In our investigation this technique allowed obtaining colloids that were directly used in the tribological tests.

2. Experimental

The bismuth nanoparticles were made using the technique of laser ablation of a solid immersed in a liquid. With this technique the nanoparticles are directly dispersed in the liquid and the colloid that is obtaining that can be directly used in tribological tests. The experimental set up was designed and constructed similar to that reported in the literature [16]. In the present experiment we used a Nd:YAG laser with a wavelength of 1064 nm, giving 28 ns pulses with a repetition frequency of 10 Hz and a maximum output energy of 135 mJ. A 99.99% purity bismuth metallic target was placed at the bottom of a glass container and immersed in the liquid media. In this case the liquid used was one of two types of base oils, called light and heavy base oils (BS6500 and BS900, respectively). These oils are the starting material used by the lubrication industry for fabrication of different types of lubricant oils and are free of the additives. Some of the characteristics of the two types of oil are given in Table 1.

The laser was directed onto the target surface with the help of a mirror and a focusing lens. The laser beam traveled through approximately 3 mm of the liquid media to hit the target surface. The laser induced plasma rapidly condensed in the liquid with the formation of the nanoparticles in the liquid. During the ablation process the container was rotated in order to avoid localized drilling of the Bi target. We found we could control the size of the nanoparticles in the liquid by varying the target to focusing lens distance.

The morphology of bismuth nanoparticles was studied by transmission electron microscopy (TEM) using a JEOL JEM-2010Ex at 200 kV. In order to carry out the measurements in the TEM, a small sample of the nanoparticles previously transferred to the water was analyzed. The process to transfer nanoparticles to the water consisted of placing a small amount of water (10 mL) in a beaker and add 1.5 mL of oil with nanoparticles, placing the beaker on a hot grill with a magnetic stirrer and warming no more than 80 °C by a 30–40 min, with occasional agitation. This procedure ensures that some of the nanoparticles that were present in the oil were transferred to the water, so that once the water and the oil are well separated, it is possible to use a syringe to take sample of the water which includes the nanoparticles. Then a few drops of this water was deposited onto a copper grid coated with a carbon film, in order to be analyzed in the TEM. With this, it is expected that the same type of nanoparticles embedded in the oil are present in the water colloid, at least the size is not altered, as it can be seen in the results shown in Fig. 2b where the size of the nanoparticles determined by TEM are very close to those obtained from the SAXS measurements directly from the oil colloid of the same sample.

The concentration of nanoparticles in the oils was determined by weighing the target before and after the ablation, the difference of weight is attributed to the amount of material removed from the target and deposited in the oil during the ablation process, the possible error in the measurement is a systematic error present in all the samples, and with this measurement we can observe the trend in the tribological tests as a function of the concentration. The concentration could be varied by changing the ablation time and/or the energy density deposited on the target.

The particle size distribution obtained by TEM corresponded to the analysis of a relatively small number of nanoparticles in the area of observation. Therefore, to obtain a somewhat more representative average particle size the distribution of the particle size was also measured by Small Angle X-ray Scattering (SAXS) using

Table 1
General properties of liquid media.

	BS900 (heavy base oil)	BS6500 (light base oil)
Density	0.91 g/mL	0.89 g/mL
Flashpoint	300 °C	248 °C
Viscosity at 40 °C	544 cST	168.2 cST
Viscosity at 100 °C	31.3 cST	15.04 cST
Viscosity index	86	88

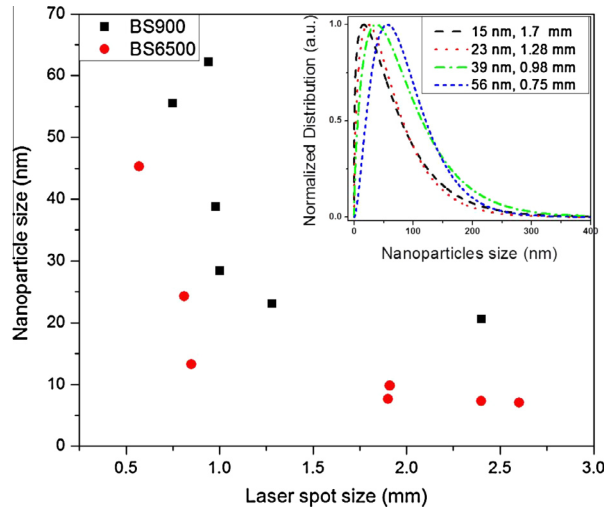

Fig. 1. The size of the nanoparticles (measured by SAXS) as a function of the laser spot size. The inset indicates the size distribution of nanoparticles in the heavy base oil samples, obtained using different spot sizes.

an Ultima IV X-ray diffractometer, Rigaku in the transmission SAXS mode. The data obtained was analyzed supposing the presence of spherical nanoparticles. The fitting procedure was carried out using the nanosolver program.

The tribological tests (measurement of the friction coefficient and wear scar diameter) using the oil with or without Bi nanoparticles were carried out in a four ball test machine. The four 1/2″ AISI 52100 steel balls are in contact through a thin oil layer and during the rotation of the upper ball sliding wear occurs on the three lower balls. The friction coefficient was measured using a torque sensor and the wear rate was estimated from the size of the wear marks on the three lower balls for the 40 kgF applied force. The measurements were carried out at 75 °C, at 392 N of load, 1200 RPM and 30 min accord to the international norm ASTM D4172-94 for lubricants oils. Each test was performed with a new set of balls and a fresh oil sample; at least 3 tests were carried out for each experimental condition.

3. Results and discussion

3.1. Nanoparticle characterization

The difference in the nanoparticle sizes in the samples was mainly due to the variation of the distance between the focusing lens and the bismuth target. As the distance between the focusing lens and the target was increased the area (or spot size) where the laser deposited its energy also increases and therefore the energy density deposited in the target diminished. The reduction of this energy density produced a reduction in the nanoparticle size. The observed overall behavior is shown in Fig. 1.

In general, for the different samples from both oils the most probable sizes were from 7 to 65 nm. Fig. 1 inset shows the distribution of nanoparticle sizes obtained from the SAXS measurements for some heavy base oil samples synthesized varying the distance from the focusing lens to the bismuth target (indicated in the box) with which were obtained different spots. In this plot we indicate the value of the most probable size for these samples, followed by the spot size.

The size and morphology of the nanoparticles was observed by TEM. A typical TEM image of bismuth nanoparticle is shown in the inset (b) of Fig. 2. It can be seen that the bismuth nanoparticles had a wide size distribution and an average particle diameter of 5–9 nm which agrees well with the size obtained from the SAXS measurements of 7.6 nm (lower graph of the inset (b). The particles appeared to have a spherical shape, which can be due to the fact that thermodynamically is more favorable the formation of spherical nanoparticles, the ablation technique can form small droplets of molten bismuth into the oil which take a spherical shape due

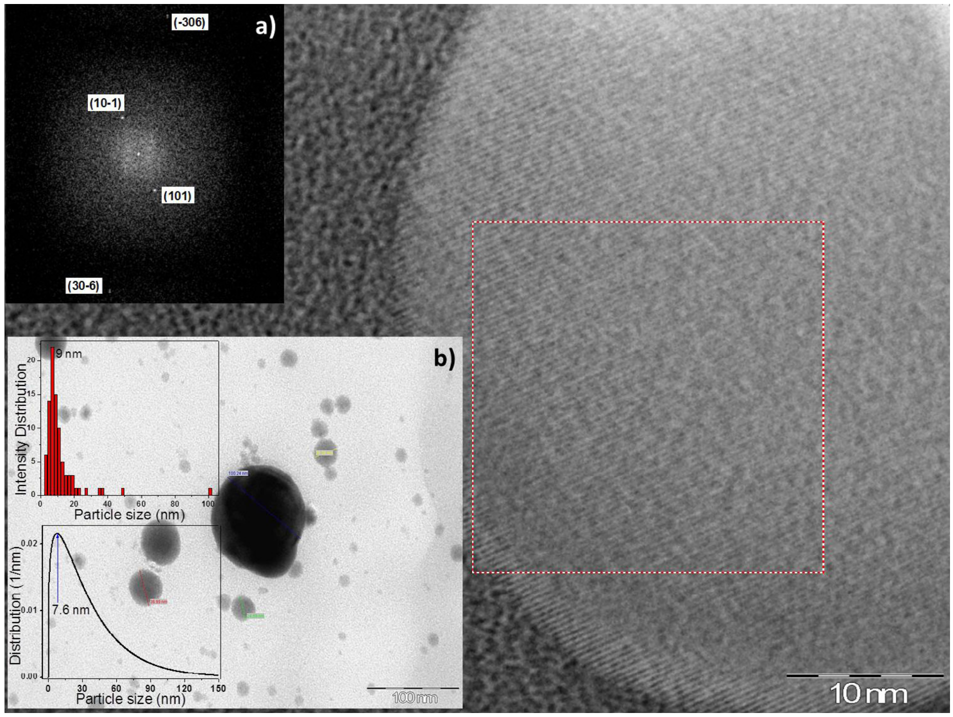

Fig. 2. HRTEM image of a bismuth nanoparticle, obtained in heavy base oil (BS900). Inset (a) shows the FFT and the crystallographic planes. Inset (b) shows the TEM image of isolated nanoparticles with their size distribution (upper graph) compared with the size distribution obtained by SAXS (lower graph).

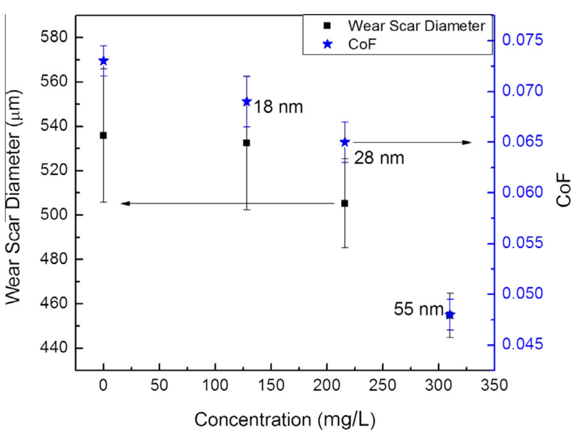

Fig. 3. Wear scar diameter and coefficient of friction as a function of the concentration of nanoparticles, for the heavy base oil samples. The average nanoparticle sizes for each concentration are indicated.

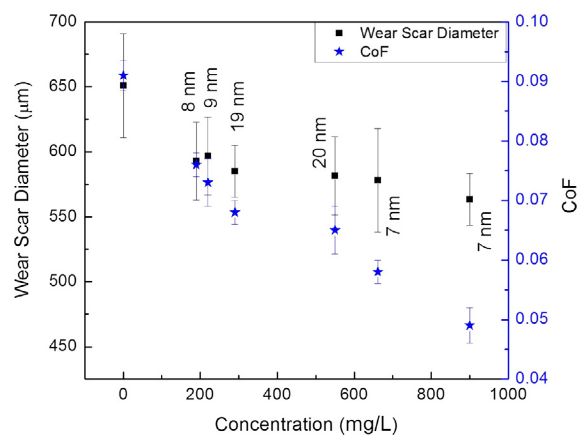

Fig. 4. Wear scar diameter and coefficient of friction as a function of the concentration of nanoparticles, for the light base oil samples. The average nanoparticle sizes for each concentration are indicated.

to the rapid cooling [17]. In the HRTEM image, Fig. 2, we can observe the presence of metallic bismuth particles with a (101) orientated rhombohedral structure with an interplanar distance of 3.7 Å; the nanoparticle was from a sample prepared with the heavy base oil BS900. The study of the High resolution TEM images, show the presence of only metallic bismuth. The inset (a) in Fig. 2 shows the Fourier transform of the (101) and (−306) planes corresponding to the squared area. The same analysis was carried out for the case of the light base oil and here we observed nanoparticles with a (123) orientation with an interplanar distance of 3.25 Å; this also corresponds to rhombohedral metallic bismuth.

3.2. Tribological tests

The bismuth nanoparticles obtained by the laser ablation of solids in liquids technique gave good quality colloids which could be used directly as lubricants. In the four-ball tests the relationship between the wear scar diameter (WSD) and friction coefficient (CoF) as a function of the nanoparticle concentration was measured. The average values of WSD and CoF of heavy base oil without nanoparticles were 535 µm and 0.074 respectively. For the case of the light base oil without nanoparticles, the WSD and the CoF were 651 µm and 0.09, respectively.

The transmission of the laser light in the heavy base oil is more difficult since it is significantly darker in color than the light base oil. Due to this, the maximum concentration achieved in the heavy base oil was lower than in the light base oil. However, for both oils the trend was similar, the WSD and CoF decreased as the concentration was increased. These results are shown in Figs. 3 and 4. In these figures we also indicate the nanoparticle sizes of each sample. It can be seen in Fig. 3, that the size of the nanoparticles varied

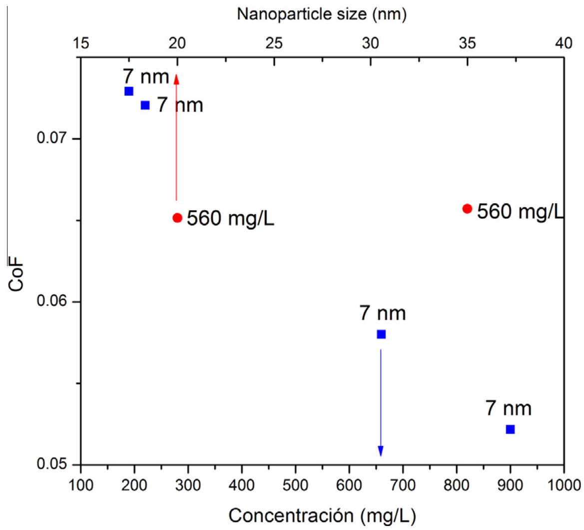

Fig. 5. CoF as a function of the concentration and the nanoparticle size.

and increased with increasing concentration. This was due to the fact that in the heavy base oil a higher energy density was needed to increase the concentration. This was achieved by reducing the spot size of the laser beam and as shown in Fig. 1 the nanoparticle size therefore tended to increase. In the case of the light base oil, the experimental conditions were maintained almost constant and in order to change the concentration only the ablation time was increased. Nevertheless it was found that the nanoparticle size could not be kept strictly constant. In general the light-oil nanoparticles were smaller than in the case of the heavy base oil. Unfortunately, the influence of the size of the nanoparticles in this experiment could not be studied independently to the concentration. However, if we assume that the tribological performance of the two oils depend on the concentration and nanoparticles size in the same way, then the results shown in Fig. 4 means that it is reasonable to conclude that within the size range used in this study, the WSD and CoF are determined by the concentration rather than the size of the nanoparticles. For a maximum concentration of the bismuth nanoparticles in the heavy base oil of 310 mg/L the WSD decrease to 454 μm and the CoF decrease to 0.048 (see Fig. 3), in the light base oil the maximum concentration was 900 mg/L and the WSD decrease to 563 μm and the CoF to 0.049 (see Fig. 4).

Fig. 5 shows that when the nanoparticles size is kept constant and the concentration is increased the friction coefficient decreases (square points). However when the concentration is kept constant and the nanoparticle size is changed, the friction coefficient did not show a meaningful variation (circular points).

Some authors have reported that metal nanoparticles can form an efficient metal film on the contacting zones, that may disappear when the load is removed [18,6]. However, energy dispersive spectroscopy (EDS) analysis in the zones of contact only steel components were observed, and no signals related to bismuth were observed. This indicates that no chemical reaction occurred between bismuth nanoparticles and the rubbing surfaces. The interaction between the bismuth film and the rubbing surfaces appears to be weak so that the metal film is easily released from the rubbing surfaces. We suppose that the good tribological performance of bismuth nanoparticles might be attributed to the formation of an instant metallic tribo-film that disappears when the load is removed [6].

4. Conclusions

Laser ablation of solids in liquids can produce good quality stable colloids of bismuth nanoparticles in base oils and these exhibit good dispersion with particle sizes in the range of 3–65 nm.

Bismuth nanoparticle additives can act effectively to improve the lubricant characteristics of base mineral oils. All of the nanoparticle suspensions produced a reduction of friction and wear compared to the base oil without additives. In the light base oil the presence of nanoparticles lowered the coefficient of friction from 0.091 to 0.052 (for a concentration of 900 mg/L) and in the heavy base oil from 0.074 to 0.047 (for a concentration of 310 mg/L).

The mechanism of wear rate reduction by the bismuth nanoparticle additives was considered to be produced by the tribo-sintering of the nanoparticles on the rubbing surfaces reducing the metal-to-metal contact and acting as a low friction load-bearing film.

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