Bismuth (III) sulfide as additive: towards better lubricity without toxicity

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Abstract

Purpose – The purpose of this study is to design a fluid formulation with good lubricant properties by using an environmentally friendly additive for: high and low contact pressure conditions and steel/steel and polymer/steel systems.

Design/methodology/approach – Bismuth (III) sulfide (Bi_2S_3, "green chemistry" synthesis) is added to a commercial vinyl-terminated silicone fluid (PDMS-Vi) to obtain different weight-per cent mixtures. Tribological performance of formulations is studied from Reichert's tests (steel/steel system) and block on ring tests (polymer/steel). The results are compared with formulations prepared with commercial bismuth (III) sulfide (Bi_2S_3), molybdenum (IV) sulfide (MoS_2) and graphite.

Findings – An orthorhombic crystal lattice (XRD) and a high-purity product (XRF) are evidenced for synthesized Bi_2S_3. Lubricant properties increase when the weight-per cent of the synthesized Bi_2S_3 increases in formulations. The wear area decreases up to 90 per cent according to Reichert's tests. The synthesized Bi_2S_3 shows a better tribological behavior when compared to commercial Bi_2S_3, MoS_2 and graphite.

Originality/value – Replacement of lead derivatives by an environmentally friendly lubricant in extreme pressure (EP) formulations and excellent performance compared to commercially used additives are achieved.

Keywords Additives, Lubricity, Bismuth (III) sulfide, Poly(dimethylsiloxane), Reichert's test

Paper type Research paper

Introduction

Any technological industry suffers great economical losses caused by wear and mechanical failures. Lubricity refers to the use of a material (lubricant) that allows movement from one surface to another by enhancing smoothness between them (Zhao *et al.*, 1990; Kalin and Vižintin, 2006). Lubricants are usually liquid or semi-liquid materials, a combination of both or solids (like grease) (Lansdown, 2003).

Silicone fluids have unique properties and almost no chemical reactivity (Lötters *et al.*, 1997). In addition, they have a very low viscosity coefficient at low temperatures that justifies their use as lubricants, in rubbers and resins formulations, for dispersion of metal particles (Stevenson *et al.*, 2001) and as hydraulic fluids. Moreover, they have a unique viscosity coeficient at low temperature, which is an appreciated characteristic for lubricity purposes. A major drawback is their extremely poor performance under marginal lubricity conditions, especially for steel surfaces. In such conditions, the use of silicone fluids leads to poor lubricity, high friction, galling and seizing (Gu *et al.*, 2009).

Extreme-pressure additives (EPAs) are added to lubricant formulations to withstand conditions of high loads, temperatures and sliding speeds. EPAs provide a low friction or anti-wear interface, which allows an efficient contact between metallic devices (Wu *et al.*, 2007). Lead (Pb) additives are the most popular, although their use is not recommended owing to their high toxicity (Didziulis and Fleischauer, 1991; Hewstone, 1994; Bartz, 1998; Goyer, 1993). Bismuth (Bi) and its derivatives appear as a very interesting alternative, because of their good lubricity properties and enviorment-friendly behavior (Rohr,

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2002). Moreover, Bi is used in greases and extreme pressure (EP) lubricants instead of Pb because its addition enhanced their properties (Hart *et al.*, 2009; Wan *et al.*, 2000). Particularly, bismuth (III) sufide (Bi_2S_3) is known to have lubricious properties, forming a stable tribolayer on lubricated interfaces of metal–oil–metal (Gonzalez-Rodriguez *et al.*, 2016).

In this work, Bi_2S_3 nanoparticles (synthesized by a "green chemistry" procedure) (Zhao *et al.*, 2004; Panigrahi and Pathak, 2013; Li *et al.*, 2013) were used to produce an EP lubricant fluid. Its performance was studied over high alloy steel and analyzed by suitable tests. Results were compared with those obtained by using other well-known additives: graphite and molybdenum (IV) sulfide (MoS_2).

Materials and methods

Materials

Commercial vinyl-terminated poly(dimethylsiloxane) (PDMS-Vi) (500 cS, United Chemical Technologies, INC., Philadelphia, USA) was used as the fluid. Bismuth nitrate ($Bi(NO_3)_3.5H_2O$, Sigma-Aldrich, Missouri, USA, 98 per cent purity), thiourea (CH_4N_2S, Sigma-Aldrich Missouri, USA, 99 per cent purity) and distilled water were used as starting materials for the synthesis of Bi_2S_3 in a teflon autoclave reactor (100-mL capacity), equipped with a stainless steel shell. Commercial Bi_2S_3 (Sigma-Aldrich, Missouri, USA), MoS_2 (Climax Molybdenum, , Phoenix, USA) and graphite (Aceitex, Moreno, Buenos Aires, Argentina) were used for comparison. To avoid misunderstandings, synthesized Bi_2S_3 will be clearly distinguished by using the "solvothermal" term. The other commercial particles will be named as Bi_2S_3, MoS_2 and graphite.

Synthesis of bismuth(III) sulfide

Nanoparticles were synthesized by using an enviromentally friendly solvothermal technique (Li *et al.*, 2013). In brief, $Bi(NO_3)_3.5H_2O$ (485 mg) and CH_4N_2S (238 mg) were dissolved in 70 mL of distilled water, under continuous stirring, during 1 h. The mixture was transferred to a reactor and subsequentely heated at 150°C, during 6 h, to promote synthesis. The reaction product (black powder) was cooled down to ambient temperature, and carefully filtered and washed many times with distilled water. After that, it was dried in a vaccum oven, at 30°C, during 24 h, until constant weight.

Lubricant formulation

Solvothermal Bi_2S_3 nanoparticles (1, 2.5, 4, 5, 6 and 8 Wt.%) were added to PDMS-Vi to obtain different formulations. Mixtures were placed in an ultrasonic bath to favor homogeneous dispersion. The formulations so obtained were then used in tribological tests. A similar procedure was employed for commercial Bi_2S_3, MoS_2 (1, 2.5, 4, 6 and 8 Wt.%) and graphite (6 Wt.%).

Chemical characterization

PDMS-Vi

Cast films from tetrahydrofuran (THF) solutions were used to register Fourier-transform infrared (FTIR) spectra in a Nicolet® FTIR 520 apparatus. Size-exclusion chromatograpy data (SEC) obtained from a Waters® 515 HPLC pump and a Waters® 410 differential refractometer, equipped with three mixed-gel columns and a 5-μm porosity pre-column; 200 μL of sample solution in toluene was injectied at 25°C by using a flow rate of 1.0 mL/min (Ninago *et al.*, 2009). The system was calibrated by using poly(styrene) standars (PS, Pressure Chemical®). The Mark–Houwink constants used were the following: K_{PS} = 0.012 mLg^{-1}, α_{PS} = 0.71 for PS; and K_{PDMS} = 0.0136 mLg^{-1}, α_{PDMS} = 0.69 for PDMS-Vi (Brandrup *et al.*, 1999).

Additives

Solvothermal and commercial Bi_2S_3, MoS_2 and graphite were characterized by X-rays diffraction (XRD), X-rays fluorescence spectroscopy (XRF) and scanning electron microscopy (SEM). A Philips® PW 1710 difractometer, with copper anode and a curved-graphite monochromator, was used for XRD. A Magi'X® apparatus, with rhodium anode, helium atmosphere, crystals (FLi 200, LiF220, Ge, PX1, PX4 and PE) and suitable flow detectors, was used. Finally, an EDAX-SEM-JEOL® Model JSM-35CF apparatus, was used to perform the SEM analysis.

Tribological tests

High contact pressure test

A fixed roll is pressed against a revolving wheel (similar to the Reichert test). Both parts were made of SAE 52100 (62 HRC) steel (Figure 1). The wheel was immersed with its lower third in the formulations under evaluation. Rotating speed was chosen at a rate that ensured that a sufficient quantity of lubricant was supplied to the contact region. Tests conditions: sliding speed 1.7 m/s under 200 N of applied load (contact pressure, 1.1 GPa), during 4 min (sliding distance, 408 m). The temperature of the roll, was measured throughout the test, and 3 valid tests were performed per formulation by using fresh lubricant. Wear scars were measured in each test by a binocular stereoscopic magnifying glass "Motic" DM 39B.

Low contact pressure test

A block on ring geometry was used, according to ASTM G77-06 test. A high-density poly(ethylene) sample (HDPE, 6997, 0.9437 g/cm^3; MFI = 0.38 g/10 min at 190°C/5 Kg; DOW® Chemicals) was pressed against a revolving high alloy steel wheel SAE 52100 (Figure 2). Tests conditions: temperature, 20°C; sliding speed,

Figure 1 Reichert's test system

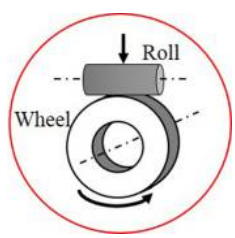
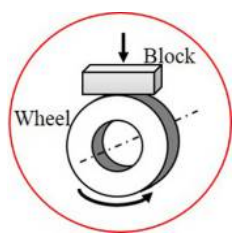


Figure 2 Polymer/steel system



0.033 m/s; applied load, 10, 15, 20, 30 and 57 N (Hertzian pressure 4.2 MPa with a maximum applied load); sliding time, 2 min (sliding distance, 4 m). Coefficient of friction (COF) was measured throughout the test and reported according to ASTM G135. At least three tests were performed per formulation by using fresh lubricant and a new test piece.

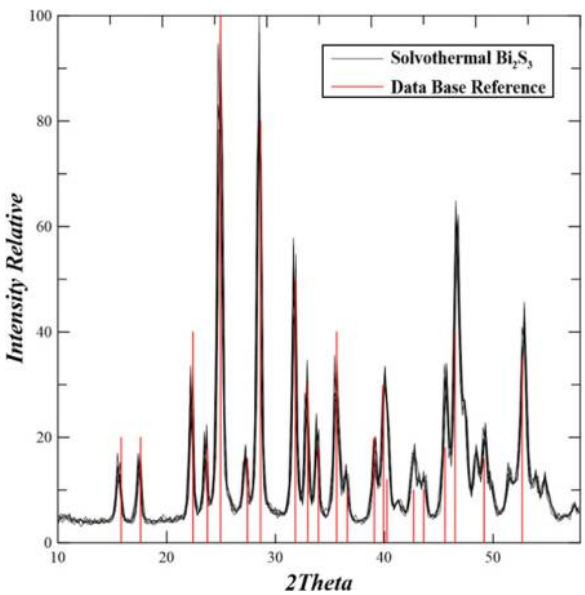
Results and discussion

Materials characterization

Typical absorption bands from PDMS-Vi were observed at 1,261, 1,092, 1,024 and 800 cm^{-1} according to FTIR. A medium-intensity band around 1,660 cm^{-1} (assigned to carbon–carbon bond streching in terminal vinyl groups) was also observed. From SEC analysis, it was verified that PDMS-Vi has M_n = 11,200 g/mol and PD = 2.01.

Figure 3 shows results from XRD analysis of the solvothermal Bi_2S_3 by scanning 2Θ from 10° to 80°. The sample difractogram matches nicely with that corresponding to orthorhombic crystal lattice of Bi_2S_3 according to JCDS N° 17-0320 database. Only Bi and S were detected according to XRF which is indicative of a high-purity compound.

Figure 3 XRD of solvothermal Bi_2S_3 (2θ axis displayed from 10° to 58° range)



The SEM image (Figure 4, left) shows elongated, plate-shaped particles, forming rosette-like structures homogenously distributed. Typical dimensions: 2.5 μm in length, 100 nm in width and 220 nm in thickness. Rosette-like structures have an average diameter of 5 μm, in accordance with a previous paper (Li *et al.*, 2013).

For commercial Bi_2S_3, XRD and XRF analyses show the corresponding crystalline structure, with only Bi and S present. The SEM microphotograph (Figure 4, right) shows un-homogeneous particles of different size, as shaped laminar agglomerates. Laminates have a length of 6 μm and a thickness of 5 μm on average. Each laminate has an average thickness of 100 nm.

For MoS_2, XRD and XRF analyses confirm the chemical formula (only Mo and S are present). A typical SEM microphotograph (Figure 5) shows laminar agglomerates, resembling a puff pastry cake, with a length of 3 to 5 μm and a thickness of 500 to 700 nm, on average. Each laminate has an average thickness ranging from 40 to 60 nm (10-15 laminates per agglomerate).

XRD and XRF from graphite show the corresponding crystalline structure, with only C present. A typical SEM microphotograph (Figure 6) shows un-homogeneous particles of different shapes (laminates, agglomerates and grain-like). Laminates are 2 μm in length, 1.7 μm in width and 0.06 in

Figure 5 SEM from MoS_2 particles (30000× magnification)

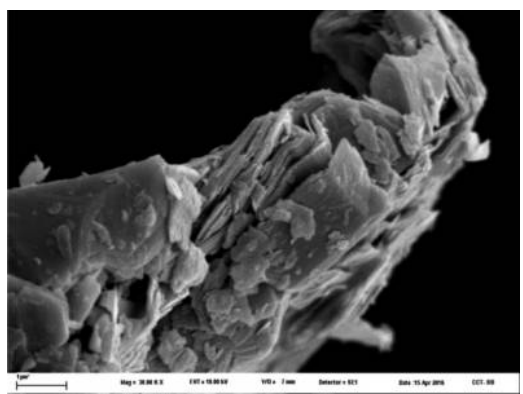
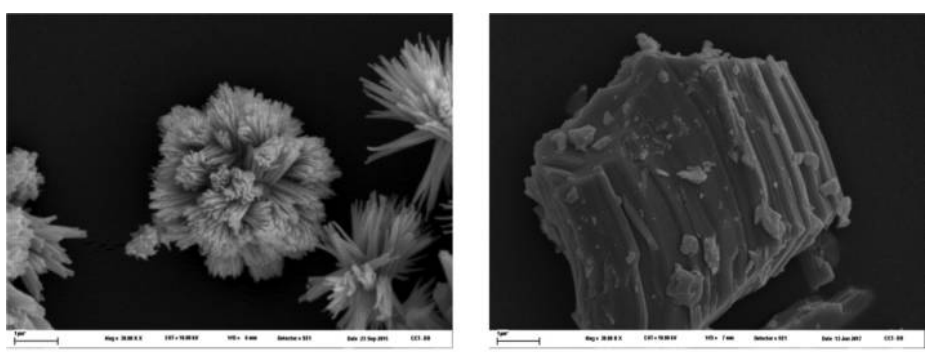
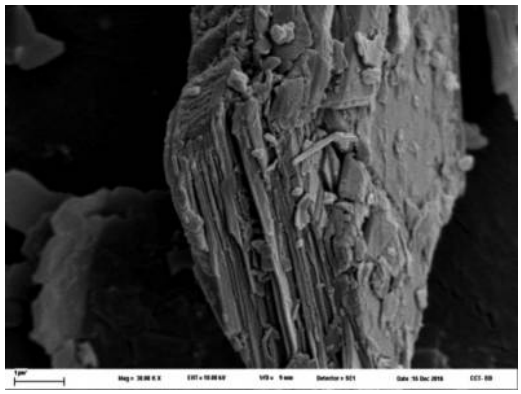


Figure 4 SEM from Bi_2S_3 particles (30000× magnification)



Notes: Solvothermal Bi_2S_3 (left); commercial Bi_2S_3 (right)

Figure 6 SEM from graphite flakes (30000× magnification)

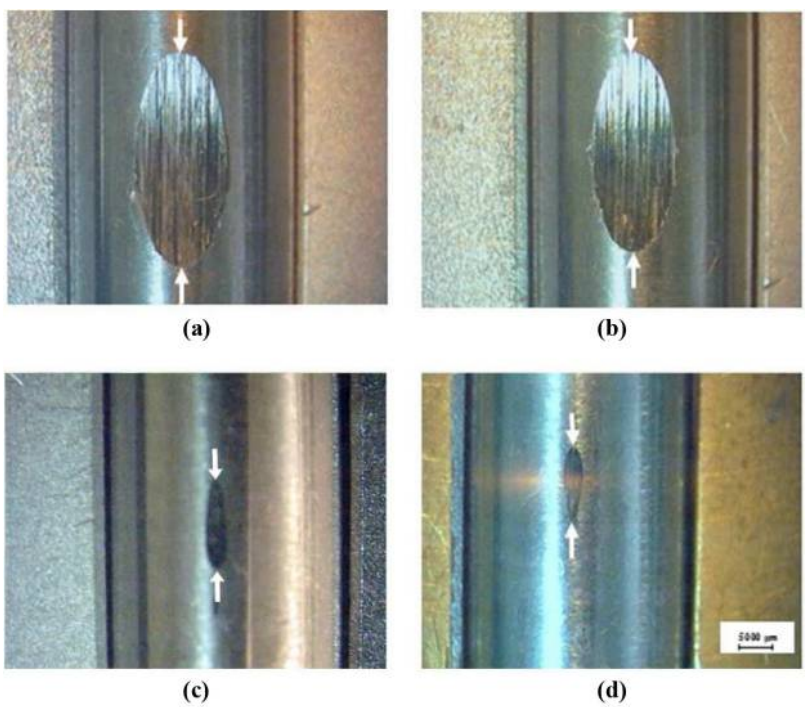


thickness; agglomerates are 12.3 μm in length, 5 μm in width and 1.25 in thickness; other agglomerates have a diameter of 10.45 μm (average values).

Wear behavior under high contact pressure test

Formulations of PDMS-Vi and different weight-per cent of solvothermal Bi_2S_3 were tested. The same procedure was used for commercial Bi_2S_3 and MoS_2. Wear effects were studied by analyzing the wear scar over 5,21,00 steel test rolls. As soon as the charge of the lubricant increases, the wear mark decreases during specific conditions (Figure 7).

Figure 7 Wear marks over stainless steel test rolls (3× magnification)

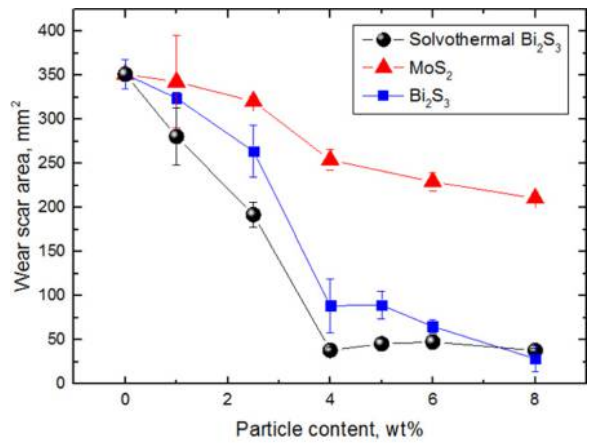


Notes: (a) Without additive; (b) 1 Wt.%; (c) 4 Wt.%; (d) 6 Wt.% solvothermal Bi_2S_3

The wear area decreases as soon as the weight-per cent of the solvothermal Bi_2S_3 increases. A similar trend is observed for commercial Bi_2S_3 and MoS_2, but the reduction of the wear area is more marked for solvothermal Bi_2S_3 (Figure 8).

For solvothermal Bi_2S_3, addition of 1 Wt.% decreases up to 20 per cent of the wear area value, whereas for commercial Bi_2S_3 and MoS_2, this reduction reaches only 8 and 6 per cent, respectively. As soon as solvothermal Bi_2S_3 weight-per cent increases (8 Wt.%), wear area decreases up to 87 per cent and

Figure 8 Wear area vs weight-per cent of additive



Note: Error bars refer to standard error

as a consequence of friction, the highest temperature reached in tests decreased from 130°C (0 Wt.%) to 70°C (8 Wt.%). This extremely high reduction in wear area must be attributed to the lubricant properties of the Bi_2S_3 particles which, in turn, depend on their morphological and chemical characteristics. The electrical polarization of the cristal layers should be also taken into acount to explain lubricity effects (Haycock *et al.*, 1979; Jamison and Cosgrove, 1971).

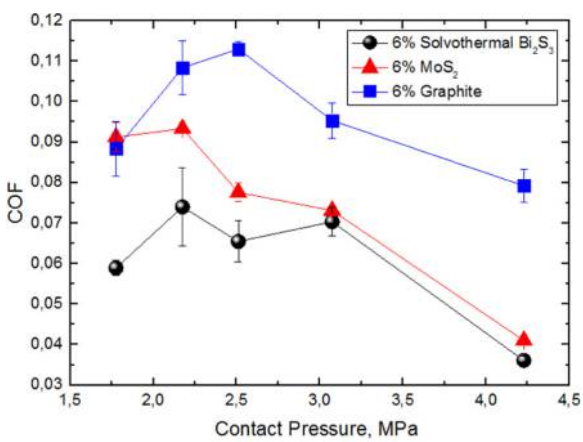
The Bi_2S_3 crystal structure consists of two-dimensional sheets. Interplane spacing to the bond length ratio is correlated with better lubricity. For MoS_2, this value is 1.5; in Bi_2S_3, the ratio is 3.7 Å/2.6 Å, which also gives 1.5 (Hart *et al.*, 2009). The fact that Bi_2S_3 is a layered solid strongly suggests that the interlayer shear provides lubricity in EP tests (Jamison, 1972; Melcher and Faullant, 2000). Tribochemical protective films from Bi compounds were already studied (Xu *et al.*, 2016), concluding that Bi-containing additives possess good EP and anti-wear performance, and exhibit good synergism with sulfur-containing additives. In this work, nanosized structures give an extra reason to explain friction and wear decrements, as well as better sliding between surfaces. It has been reported that particle size, shape and concentration influence lubricating properties (Bartz, 1972; Heshmat, 1995; Lovell *et al.*, 2010; Wu *et al.*, 2007). Nanoparticles of smaller size have more likely to interact with the surfaces of the friction pairs to form a surface protective film, which increases anti-wear ability.

Friction behavior under low contact pressure test

Formulations (PDMS-Vi and 6 Wt.% of additive) were tested by changing contact pressure from 1.8 to 4.2 MPa (Figure 9). A slightly increase in COF values is observed when the contact pressure increases from 1.8 to 2.5 MPa, depending on the tested additive. From this value, increasing the load decreases the COF values in all cases. However, solvothermal Bi_2S_3 and MoS_2 display better performance as in the case of sputtered MoS_2 films (Singer *et al.*, 1990).

Solvothermal Bi_2S_3 displays a slightly better performance than MoS_2, and COF values decreases up to 50 per cent when comparing with the formulation without additives. This behavior can be explained because Mo and Bi derivatives are both EPAs and help to decrease friction and wear at higher loads. Compared with graphite (30 per cent reduction), both additives display better performances: for the lowest COF values reached, the COF for graphite formulation is 125 per cent higher when compared to that for solvothermal Bi_2S_3 or MoS_2. At 3MPa, it is observed that the COF is similar in both solvothermal Bi_2S_3 and commercial MoS_2; it is assumed that this behavior is due to the fact that at lower loads, solvothermal Bi_2S_3 particles are more ordered than commercial MoS_2 owing to their more uniform microstructure, and for this reason, they have a better protective behavior. At high pressures, the particles are crushed and once exfoliation occurs, it is believed that they provide low-shear-strength sheets that reduce the sliding friction (Spikes, 2015). Because this phenomenon occurs for both materials, additives behave similarly.

Figure 9 COF vs contact pressure (6 Wt.% additive)



Note: Error bars refer to standard error

Conclusions

Solvothermal Bi_2S_3 ("green chemistry" synthesis) was added to a commercial PDMS-Vi fluid to obtain different weight-per cent mixtures. Tribological response was studied by Reichert's test for the steel/steel system and the block on ring test for polymer/steel systems. The results obtained were compared with those of other formulations prepared from commercial Bi_2S_3, MoS_2 and graphite, by using the same conditions. For both tests, solvothermal Bi_2S_3 displayed better performance, and its use can be considered in enviroment-friendly EP formulations.

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