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Tribological behavior of vegetable oil-based lubricants with nanoparticles of oxides in boundary lubrication conditions

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ABSTRACT

This work studied the development of vegetable based lubricants and the addition of oxides nanoparticles (ZnO and CuO) as additive for extreme pressure (EP), exploring the EP and oil base influence in tribological behavior. The results showed that with the addition of nanoparticles to conventional lubricant, the tribological properties can be significantly improved. A smoother and more compact tribofilm has formed on the worn surface, which is responsible for the further reduced friction and wear. Also, lubricants developed from modified vegetable oil can replace mineral oil, improving the tribological and environmental characteristics. However, the addition of nanoparticles in vegetable base lubricants is not beneficial to wear reduction.

1. Introduction

Conservation of materials and energy is becoming a very important issue. The main cause of energy loss in a mechanical system is the friction but this can be reduced by lubrication. Thus, it is very important to improve the lubrication properties. A good combination between oil base and additives is the key to improve this process.

For most lubricated applications, the conventional choice is a mineral oil-based lubricant, because of its well-known properties. However, due to their inherent toxicity and non-biodegradable nature, they pose a constant threat to ecology and vast ground water reserves. In this context, environmentally adapted lubricants have become more and more important in industrial applications. The properties of different base fluids vary widely and it is important to understand their effects on the performance of a lubricant in different lubrication regimes [1–3].

Vegetable oil lubricants are potential substitutes for mineral oil not only because they are renewable raw materials but also because they are biodegradable and non-toxic. Furthermore, they show most properties required for lubricants, such as high index viscosity, low volatility, good lubricity, as well as excellent solvents for fluid additives [1]. However, vegetable oils show poor oxidative and thermal stability, due to the presence of unsaturation. An improvement in these thermal properties can be achieved by a chemical modification, such as epoxidation, transesterification or selective hydrogenation [4].

As cited before, the lubricant properties can be changed by using oil additives. There are many kinds of additives, such as antioxidants, detergents, dispersants, extreme pressure (EP) and anti-wear (AW). The latter two are important at severe frictional conditions, such as high temperature, load and sliding speed. Sulfur, chlorine and phosphorus are traditional EP and AW additives; they cover chemical metal surfaces by forming easily sheared layers of sulfides, chlorines or phosphides, preventing severe wear and seizure [5–7]. Chlorine and phosphorus compounds used as lubricant additives have been restricted for environmental protection measure, and so developing new additives that pollute less is the goal of many researches. Due to the outstanding tribological and environmental properties, nanoparticles have been regarded as excellent candidates to traditional EP and AW additives.

In recent years, many studies have been carried out on applications of nanoparticles in the field of lubrication. The reduction of friction and wear are dependent on the characteristics of nanoparticles such as size, shape and concentration. Hu et al. [8] prepared nanoparticles of amorphous lanthanum borate with a particle size of 20–40 nm, which were added to mineral base oil. The results showed that B_2O_3 and FeB were formed on the wear scar surface given a good wear resistance. Many researchers have been evaluating Cu nanoparticles due to their outstanding tribological performance, self-repairing and environmental-friendly properties [9–11]. Nanoparticles with size from 20 to 60 nm were prepared, and its surface was modified in order to avoid aggregation. The excellent anti-wear and friction-reducing properties of Cu nanoparticles were explained by the formation of a protective deposit film of metallic copper on the steel surface.

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Different metallic oxides have been used as lubricant additives. The tribological properties of ZnO [12–14], ZrO_2 [13–15], TiO_2 [16,17], SiO_2 [7] and CuO [13,14,17] were investigated. Results show that these nanoparticles can deposit on the rubbing surface and improve properties of the base oil. Moreover, a low concentration of nanoparticles is sufficient to improve the friction and wear behavior, such as below 2 wt%; although, for various nanoxides, 0.5 wt% is the optimum concentration.

Some mechanisms of action of nanoparticles have been proposed to understand how nanoparticles work as additives in oil to reduce friction and wear. Chiñas-Castilho and Spikes [21] investigated the mechanism of action of colloidal solid nanoparticles in lubricating oils. They noticed that nanoparticles do indeed penetrate the rolling contacts to form patchy films at low speeds, colloids formed a boundary film of at least one or two times the particle size. Furthermore, the boundary film formed by the nanoparticles inside the contact is solid-like and it is unable to re-form on the surface at high speeds when the film thickness is thicker than the particle diameter.

Based on literature research, Peng et al. [7] cited four mechanisms whereby nanoparticles added to the base oil could act: (1) smaller nanoparticles are more likely to interact with the surfaces of the friction pairs to form a surface protective film; (2) small spherical nanoparticles are more likely to roll between the surfaces and change the sliding friction for a mixing of sliding and rolling friction; (3) compressive stress concentrations associated with high contact pressure can be reduced by many nanoparticles, which bear the compressive force, 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." A combination of four effects explains the good friction and wear properties of nanoparticles in base oil.

However, a large number of papers have reported the addition of nanoparticles to lubricant, all of them are focused on mineral and synthetic base oil. Thus, this paper investigates the effect of the addition of nanoparticles in vegetable based lubricant. The anti-wear behavior of CuO and ZnO was studied using a HFRR equipment and SEM/EDS analysis of worn surfaces.

2. Experimental

2.1. Preparation and characterization of vegetable base lubricant

Vegetable base lubricants were prepared by epoxidation reaction, which is one of the most important double bond addition reactions and because the double bond is conversed to oxirane ring, this conversion improves the thermal and oxidative stability as well as its lubricity of vegetable oil.

The epoxidized Soybean and Sunflower oil was prepared by reacting each vegetable oil with peracetic acid generated *in situ*. This reaction was catalyzed with 4% sulfuric acid. The chosen molar ratio of hydrogen peroxide/acetic acid/double bonds of the oils was 20/2/1.

The reagents were jointly placed into a well-stirred, round-bottom glass reactor kept at 50 °C. The reaction time was 5 h. The mixtures were then washed with distilled water until the complete removal of acids from the organic phase was achieved, and then with $NaHCO_3$ (10 wt%).

The epoxidized oils were analyzed in terms of viscosity, density and Iodine value. Iodine value was obtained using the Wijs method according to AOCS Cd 1-25. Density was measured by pycnometer and viscosity was determined by Brookfield RS 2000 rheometer at 40. Table 1 presents the characteristics of the oils studied. Also, for effect of comparison, mineral oil and synthetic oil (polyalphaoleifin) were used as oil base.

Table 1
Physical and chemical properties of soybean oil and sunflower epoxidized.

	Density (g/cm^3)	Iodine number ($g\ I_2/100\ g$)	Viscosity (cSt) at 40 °C
Soybean oil	0.97988	4.8340	144.72
Sunflower oil	0.98052	4.8478	149.04
Mineral oil	0.8474	–	45.70
Synthetic oil	0.8303	–	79.92

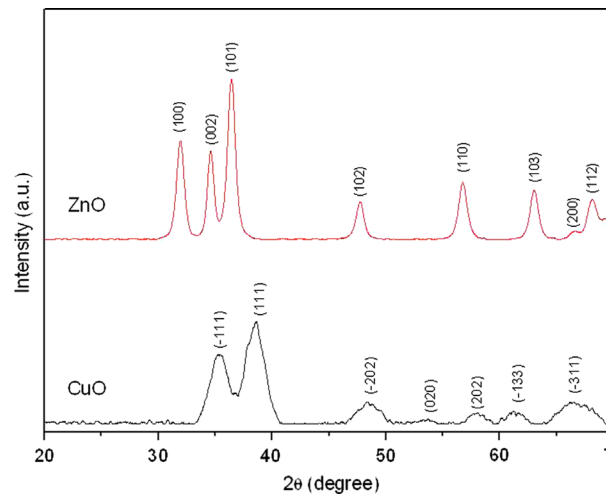

Fig. 1. X-ray powder diffraction patterns of the prepared samples.

The oxide nanoparticles (CuO and ZnO) were separately dispersed in the lubricant in concentration of 0.5 wt%, using an ultrasonic probe for 30 min.

2.2. Preparation and characterization of nanoparticles

CuO and ZnO nanoparticles were prepared by an alcothermal method using copper nitrate, zinc nitrate, sodium hydroxide, acetic acid and ethanol as starting materials. First, 5 and 10 mmol of metal nitrate (Cu or Zn) and acetic acid, respectively, were dissolved in 0.5 L of ethanol and then heated at 78 °C under vigorous stirring. Next, 20 mmol of NaOH powder, previously pulverized from pellets, were added. The reactions were carried out for 1 h producing a colloidal suspension. The nanoparticles were collected from these suspensions by centrifuging at 3600 rpm for 2 h. The collected material was washed several times with hot water and then dried overnight at 60 °C. Afterwards, the produced samples were characterized by X-ray diffraction (XRD) and scanning electronic microscopy (SEM).

The X-ray diffraction analyses were carried out using a XRD-6000 powder diffractometer with Cu Kα radiation, operating at 30 kV and 30 m, in the range from 20° to 70° with 0.02°/ min. Fig. 1 shows the diffraction patterns of the samples. In both the cases pure phases were obtained and all diffraction peaks indexed to the hexagonal structure with space group P63mc (ZnO) and monoclinic structure with space group Cc (CuO). These data are in agreement with the JCPDS files # 75-0576, zinc oxide, and # 80-1916, copper oxide. Subsequently, the crystallite size was calculated using the Scherrer's equation [18] $D_{hkl}=k\lambda/\beta\cos\theta$, where D_{hkl} is the crystallite size, k is the sphere shape factor (0.89), θ is the angle of the diffraction, β is the full width at half-maximum (FWHM) of the peak and λ is the wavelength of X-ray (1.54056 Å).

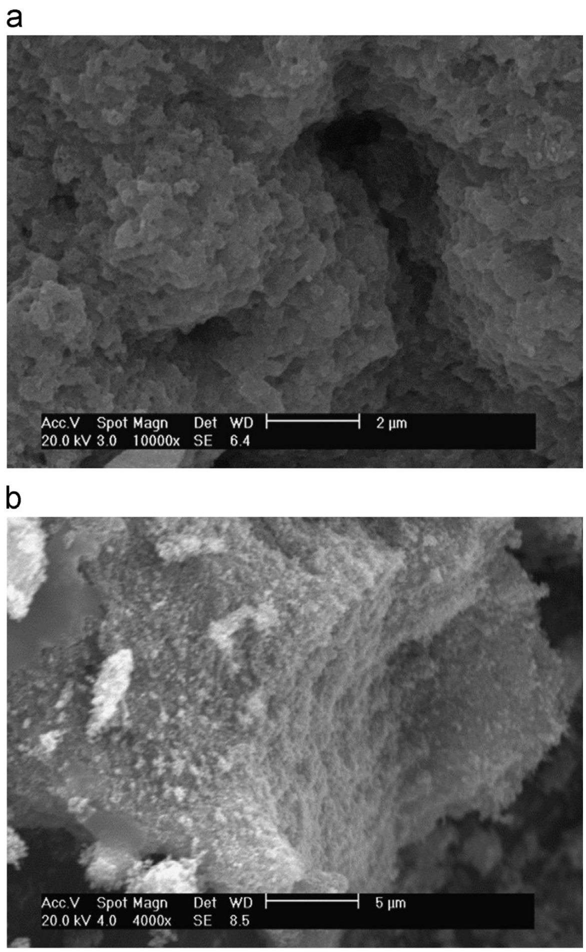

Fig. 2. SEM micrographs of the prepared samples (a) CuO and (b) ZnO.

The obtained average crystallite size of ZnO and CuO powder samples are about 11.71 and 4.35 nm, respectively.

The powders were analyzed by scanning electron microscopy on a Philips ESEM-XL30 microscope. The results are depicted in Fig. 2. It can be seen that soft agglomerates formed during the collection process by centrifugation of the nanoparticles, the SEM image reveals a nearly-spherical shape. These nanoparticles were previously dispersed by ultrasonic treatment in order to assure the formation of a stable suspension in the base oil.

2.3. Friction and wear test

The high frequency reciprocating test rig (HFRR) was applied to investigate the friction and wear performances of lubricants. The HFRR system is shown in Fig. 3 and consists of a ball-on-disk test to measure the friction and wear under boundary lubrication conditions using a highly stressed ball-on-disk contact.

A hard steel ball (570–750 HV) of 6.0 mm diameter reciprocates on a softer steel disk (190–210 HV) of 10 mm diameter under the fully submerged oil condition at normal load of 10 N and a 1 mm stroke length at a frequency of 20 Hz for 60 min. Both ball and disk were made of AISI 52100 steel. The lubricant temperature was kept at 50 °C. The friction coefficient was measured by a piezo-electric force transducer and the formation of electrically insulating films at the sliding contact was measured by the ECR (Electrical Contact Resistance) technique. According to Tonck et al. [19] this technique has been found to be a convenient tool for use in tribological studies, including lubricant additives studies. 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.

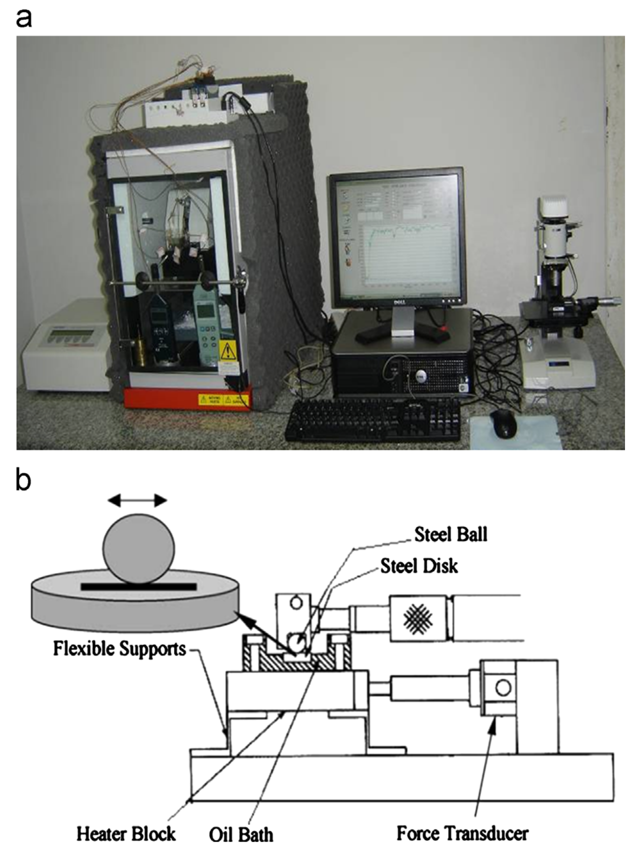

Fig. 3. HFRR test: (a) image of equipment used in tests and (b) schematic diagram of HFRR.

Both ball and disk were cleaned by ultrasonically agitated bath of acetone and toluene before and after the HFRR test. Each test was run carried out for three times in order to provide mean values of friction coefficient and film formation reported in this study.

2.4. Worn surface analysis

Morphology and element distribution of the worn surface on the disk were examined using scanning electron microscopy (SEM) Hitachi TM3000 equipped with energy dispersive X-ray spectroscopy (EDS).

3. Results and discussions

Different base oils and additives were evaluated using the HFRR test. Tests with mineral oil and PAO without/with additive were used as reference in order to analyze the influence of vegetable oil lubricant and nanoparticles on the wear of metallic surface.

3.1. Friction and wear behavior

The friction coefficients for all lubricants are displayed in Fig. 4a–d, also for comparison effect the Table 2 presents the mean friction coefficient and the standard deviation. The performance of lubricant without and with additives was evaluated. The friction coefficient shows high value, mainly for mineral and synthetic oils without additives. While with the addition of CuO and ZnO nanoparticles, the friction coefficient significantly decreases compared with mineral (Fig. 4a) and synthetic pure oils (Fig. 4b).

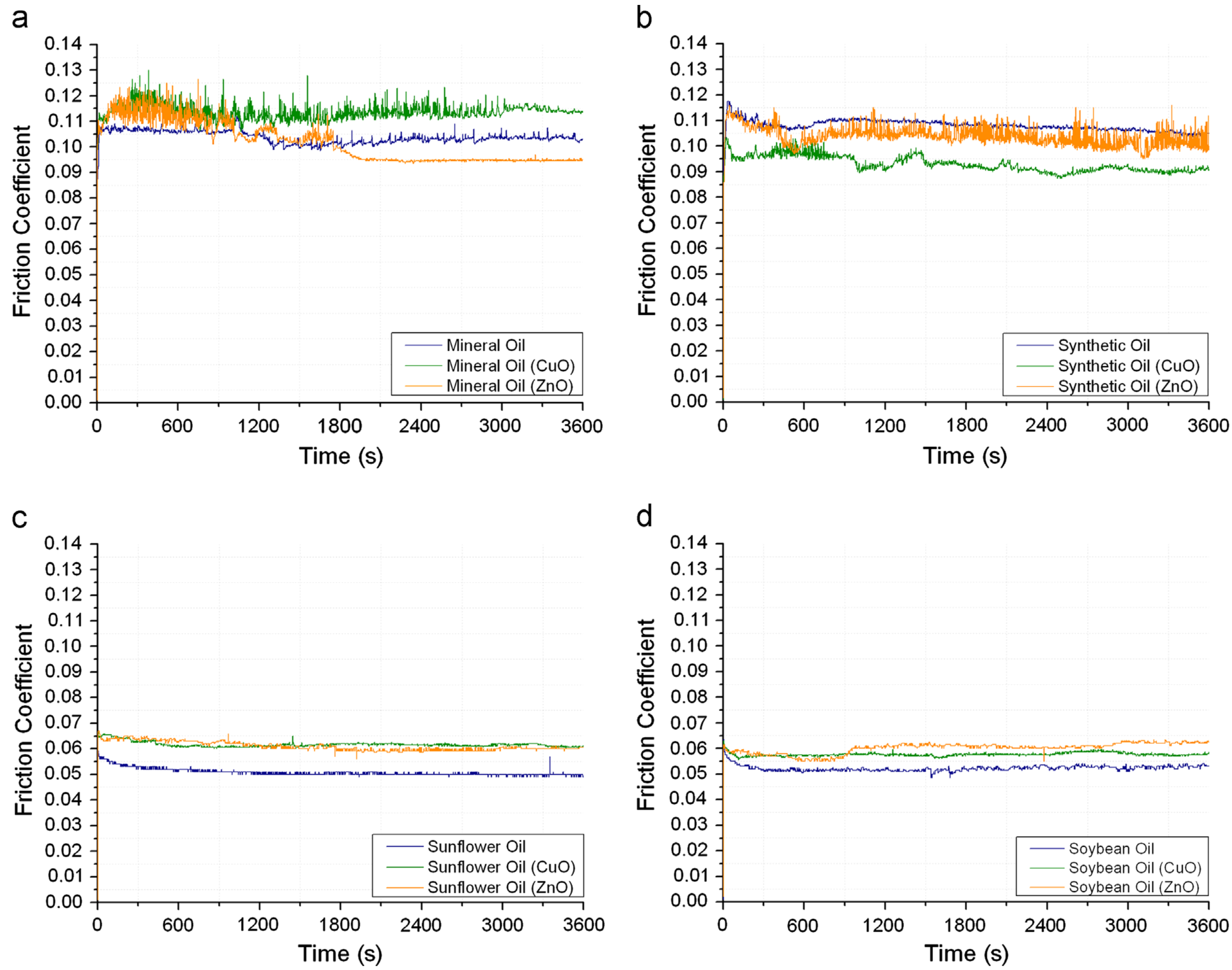

Fig. 4. Friction coefficients as functions of time lubricated with different oil base without and with nanoparticles additive: (a) mineral oil, (b) synthetic oil, (c) sunflower oil and (d) soybean oil.

Table 2
Mean friction coefficient of HFRR test and standard deviation.

Lubricants	Friction coefficient	Standard deviation
Mineral	0.104	0.00707
Mineral+CuO	0.113	0.00078
Mineral+ZnO	0.099	0.00354
Synthetic (PAO)	0.108	0.00283
PAO+CuO	0.084	0.00283
PAO+ZnO	0.096	0.00778
Sunflower	0.051	0.00071
Sunflower+CuO	0.061	0.00071
Sunflower+ZnO	0.060	0.00071
Soybean	0.053	0.00141
Soybean+CuO	0.057	0.00212
Soybean+ZnO	0.062	0.00354

However, this behavior was not observed in vegetable base oils (Fig. 4c and d), which the addition of nanoparticles showed a little increase of the coefficient friction. In these cases, the nanoparticles did not act as anti-wear additive. Thus, the performance of nanoparticles of CuO and ZnO are related with base oil. For example, considering mineral oil, the best result was observed with a combination of ZnO, while Synthetic oil shows better synergism with CuO. Also, vegetable base oils are not indicated for use with nanooxides (CuO and ZnO). Probably this observation is due to nature of boundary lubrication, in which regime chemical interactions between the lubricant and the surface take place; the reaction products a significant role in the effectiveness of the lubrication process; the lubricant viscosity has little or no effect on friction and wear [20]. For mineral and synthetic fluids the more important aspect to improve lubrication was nanoparticles interaction with metal surface. However, vegetable lubricant, due to chemistry nature and its polarity, promotes the adsorption on metal surface resulting in reduced wear and friction, forming a thin layer for better metal-to-metal separation. When nanoparticles were added, they present behavior of third body increasing the friction coefficient.

Also, according to Chiñas and Spikes [21], nanoparticles penetrate in the contact area and then deposit on it because they are smaller or similar in size to lubricant film thicknesses. On the other hand, nanoparticles have a harmful effect in some cases, increasing either friction or wear, as observed for mixture of vegetable oils and nanoparticles.

The formation of electrically insulating films was measured during the HFRR test by means of the ECR. The surface coverage, caused by generation and removal of surface films, was measured under boundary lubrication conditions with a steel ball sliding against a steel disk. According to Viesca et al. [22], the electrical resistance between the two contacting surfaces gives an idea of the amount of direct metal–metal contact. Although deducting the real area of contact by the resistance value is not obvious, the measured values are often used for qualitative analysis. The films covering the rubbing surfaces affect the surface roughness and structure. Thus, the friction behavior shows a corresponding response to the film

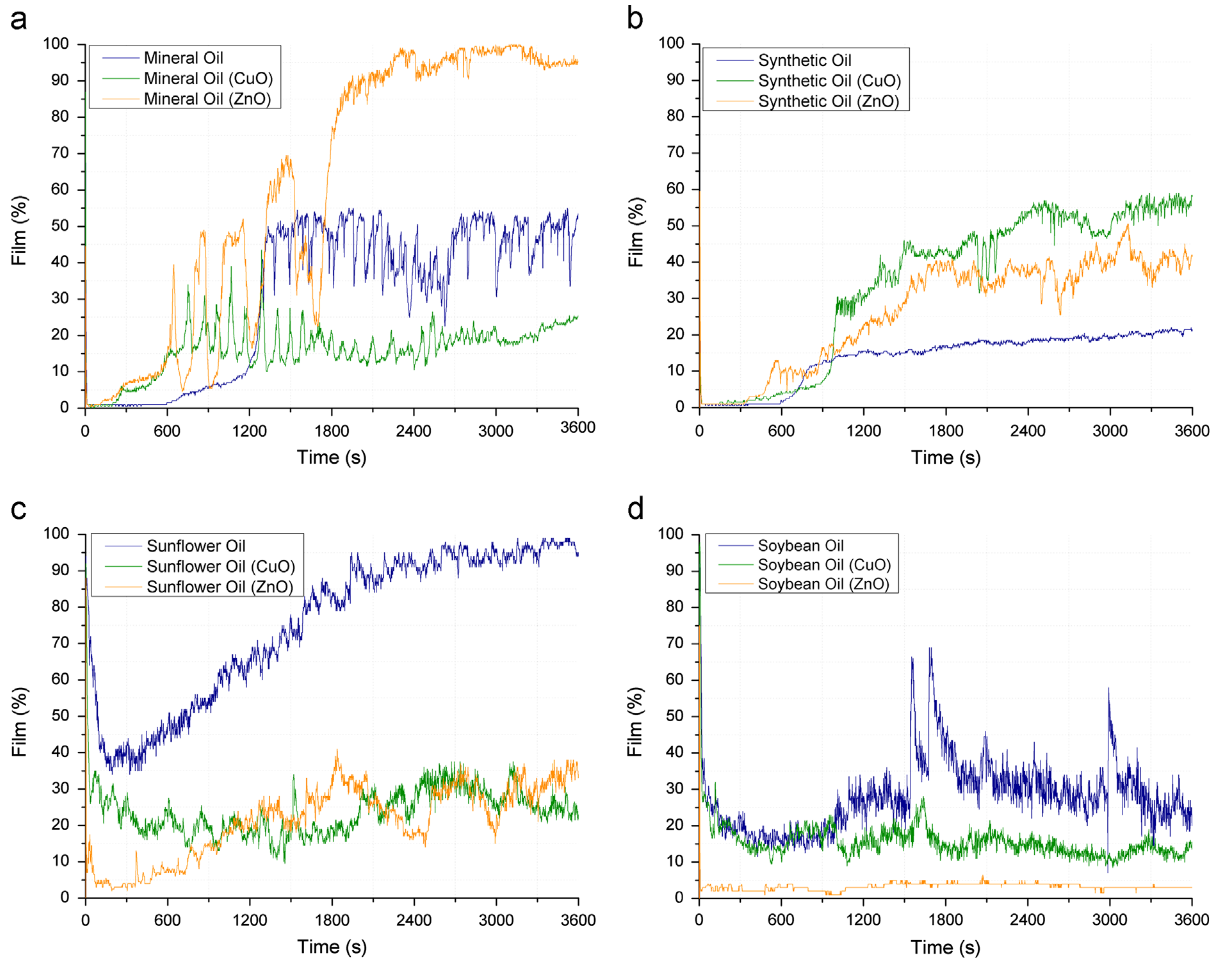

Fig. 5. Film formation as measured by ECR for all lubricant and additives tested: (a) mineral oil, (b) synthetic oil, (c) sunflower oil and (d) soybean oil.

formation between the contacts under boundary lubrication conditions. Fig. 5 shows the film formation behavior of the studied lubricants. The film formation is strongly influenced by oil base and EP additive. From test with mineral (Fig. 5), it was observed that the film formation takes some time to be developed (about 300 s) and, in this time friction coefficient is similar for all mineral base lubricants. After this time, different behaviors were observed for each lubricant. Mineral oil without additives after 1200 s shows the maximum of film formation about 50%, but some fluctuations during the test were verified. Probably this fact has occurred because of adhesion of layer lubricant is not strong and it was removed because of the motion of the ball. At 1800 s of test, the mineral oil with ZnO shows a good percentage of film. Since the percentage film for the mineral oil was kept at 50%, this increase can be attributed to the beginning of boundary film formation due to the presence of ZnO nanoparticles. At the same time a decrease in friction coefficient was observed. When CuO nanoparticles were added to mineral oil the percentage film was lower than pure oil even the COF is close to mineral oil without additive. This might be attributed to the nanoparticle acting as a rolling medium between the contact surfaces.

The percentage film formation for synthetic lubricants was lower than mineral oil (Fig. 5), but with less fluctuation. The addition of nanoparticles increased the percentage of film, and better performance was observed to synthetic oil with CuO, confirming its ability to reduce friction (see Fig. 4). These results agree with boundary lubrication theory that says the efficiency of lubrication depends on EP additives and their interaction with surface.

On the other hand, vegetable base lubricants showed that addition of nanoparticles worsens film formation. However, sunflower lubricant without additive presents good film formation ability. Vegetable oil, naturally, contains molecular species with boundary lubrication properties (like, acid oleic) [23]. It has already been established in literature that polar functional groups in the triacylglycerol molecule maintain excellent boundary lubricating properties by strong physical and chemical adsorption on the metal surface in contact. The point of attachment to the metal is through the polar group in the molecule, with the non-polar end forming a molecular layer separating the rubbing surfaces [24]. The behavior of film formation for soybean lubricant is not good as for sunflower; even both present similar viscosities, the film formation was not as efficient. According to Waara et al. [25] the presence of more polar functional groups in the chemical derivatives establishes stronger interaction with the metal surface and therefore a stable lubricant film. Probably, soybean lubricant has less polar groups than lubricant sunflower and the formed film was weak and not stable, so with sliding of ball under high contact pressure the film was removed and formed constantly. This fact justifies high fluctuations in percentage film.

The different results for vegetable base lubricant with oxide nanoparticles could be associated to third body behavior of these oxides that increase the friction and reduce the electrical conductivity between specimen surfaces (less ECR).

3.2. Worn surface analysis

The morphologies and chemical elements distribution of the worn disc surfaces were analyzed by SEM equipped with EDS. The SEM micrographs in Figs. 6 and 7 correspond to center of worn

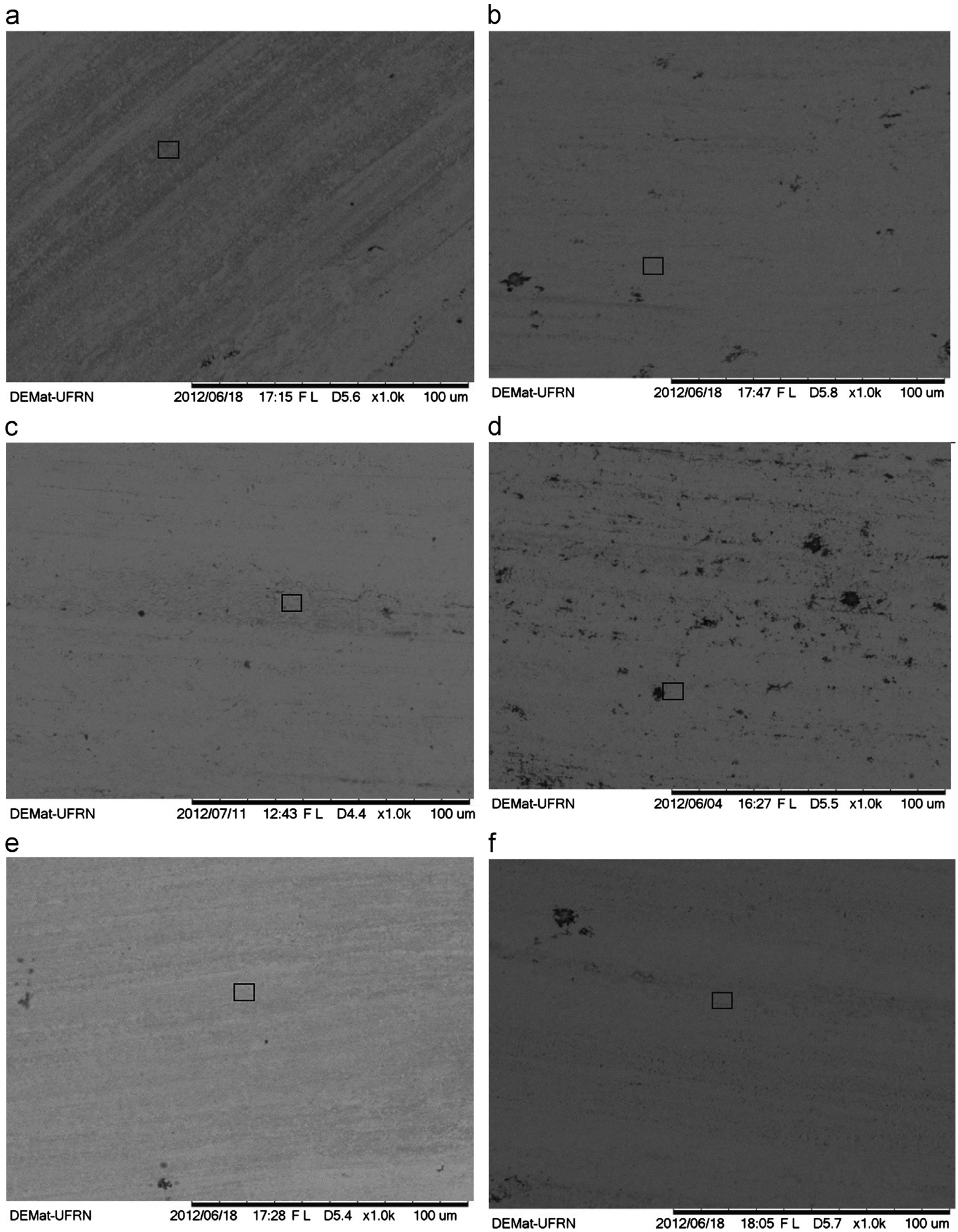

Fig. 6. SEM micrographs of the worn surfaces lubricated with: (a) sunflower oil (WSD = 187.5 ± 0.7 μm) (b) soybean oil (WSD = 203.5 ± 0.4μm) (c) sunflower oil+CuO (WSD = 198.5 ± 4.9 μm) (d) soybean oil+CuO (WSD = 230.2 ± 1.1 μm) (e) sunflower oil+ZnO (WSD = 202 ± 1.4 μm) and (f) soybean oil+ZnO (WSD = 240.5 ± 2.1 μm).

scar on the disks (1000x magnification) under various lubricating conditions and the value of WSD (wear scar diameter) of ball. With these images, it is possible to evaluate the anti-wear ability of nanoparticle and oil base. Worn surface for vegetable pure oils (Fig. 7(a–b)) shows almost no sign of severe scuffing and it is smoother and flatter than worn surface for mineral and synthetic oils (Fig. 6(a–b)). However, when CuO and ZnO nanoparticles were added to vegetable oils (Fig. 7(c–f)), it is possible to observe small signs of abrasive wear in the sliding direction. This result shows that nanoparticle of CuO and ZnO do not present a good anti-wear ability when combined with vegetable lubricants, on the contrary these particles increase the wear. Comparing CuO and ZnO effects, it is possible to conclude that for both oils, sunflower and soybean epoxidized oils, ZnO showed less compatibility given surface with little scratches and consequently more wear. This fact is clearly confirmed by WSD observation. Higher WSD were verified to vegetable oil added to ZnO nanoparticles. The epoxidized vegetable oil presented smaller WDS.

Different tribological behavior is verified to mineral and synthetic oil base (Fig. 7). The worn surfaces after tests with mineral

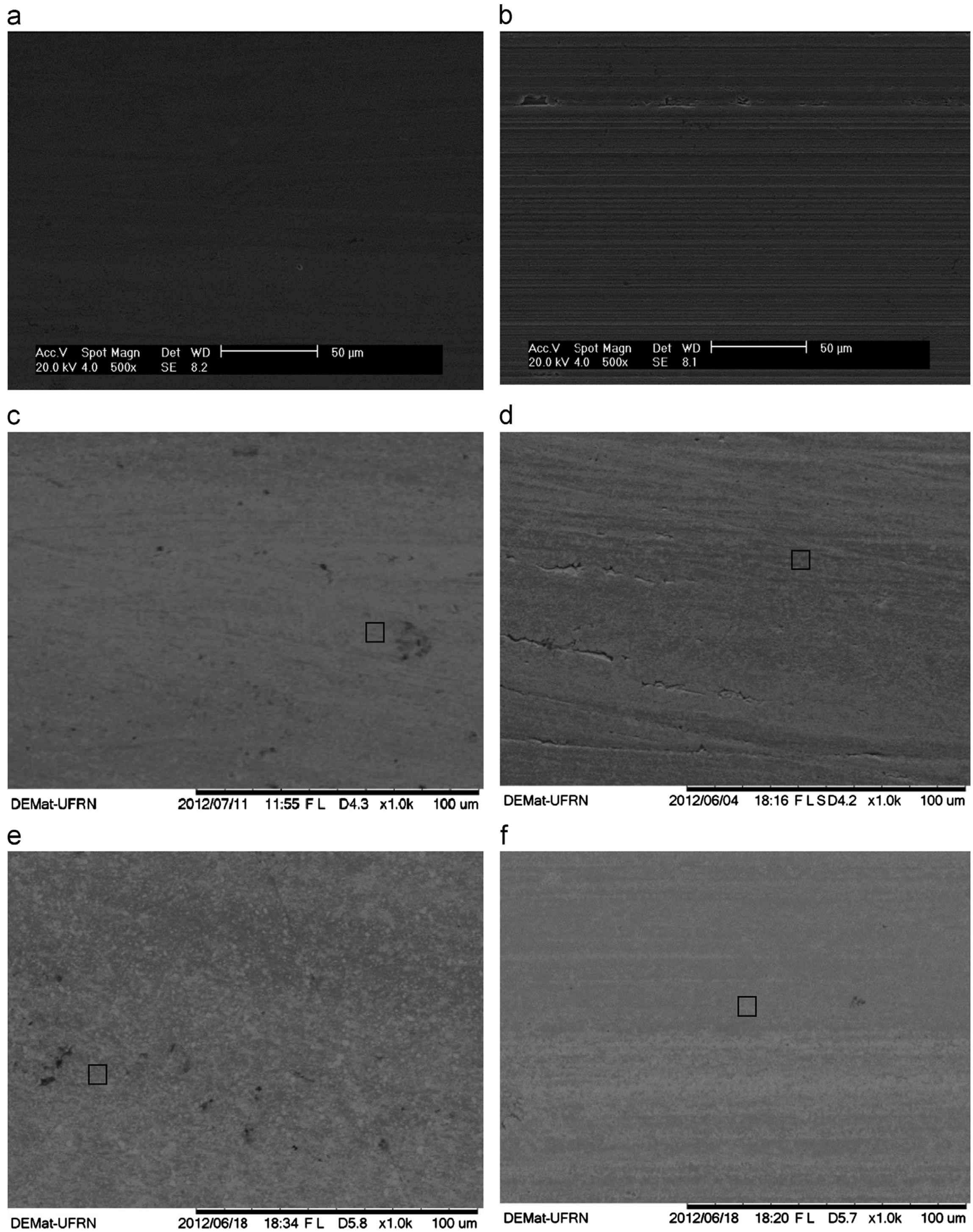

Fig. 7. SEM micrographs of the worn surfaces lubricated with: (a) synthetic oil (WSD = 303,5 ± 2.2 μm) (b) mineral oil (WSD = 269.5 ± 4.9 μm) (c) synthetic oil+CuO (WSD = 280.2 ± 2.5 μm) (d) mineral oil+CuO (WSD = 276,5 ± 3.2 μm) (e) synthetic oil+ZnO (WSD = 293.0 ± 4.5 μm) and (f) mineral oil+ZnO (WSD = 256.0 ± 4.2 μm).

and synthetic pure oil are a little rough with grooves in comparison to vegetable oils. Therefore, when CuO and ZnO were added, the worn surface are relatively smooth and with only slight signs of wear. However, it is clear that the nanoparticles have different performance depending on the oil base. For synthetic based oil, the more adequate nanoparticle is CuO resulting in less wear and WSD. Hernández Battez et al. [13] concluded that synthetic oil (PAO) added with CuO exhibited the best EP behavior with lower WSD. On the other hand, mineral oil shows better performance when ZnO was added, in this case smaller WSD were verified. Also, the WSD for oil and nanoparticle combination confirm the results of friction coefficient.

In order to evaluate the film formation on the worn surface, EDS analysis was conducted, as shown in Fig. 8. This figure shows the elementary analysis of the contact regions lubricated with different lubricants containing CuO or ZnO nanoparticles. Also, these EDS show the chemical elements present in areas indicated in Figs. 6 and 7.

Based on Fig. 8(a–d), it was possible to evaluate the CuO effect on wear reduction. The higher content of Cu was found for

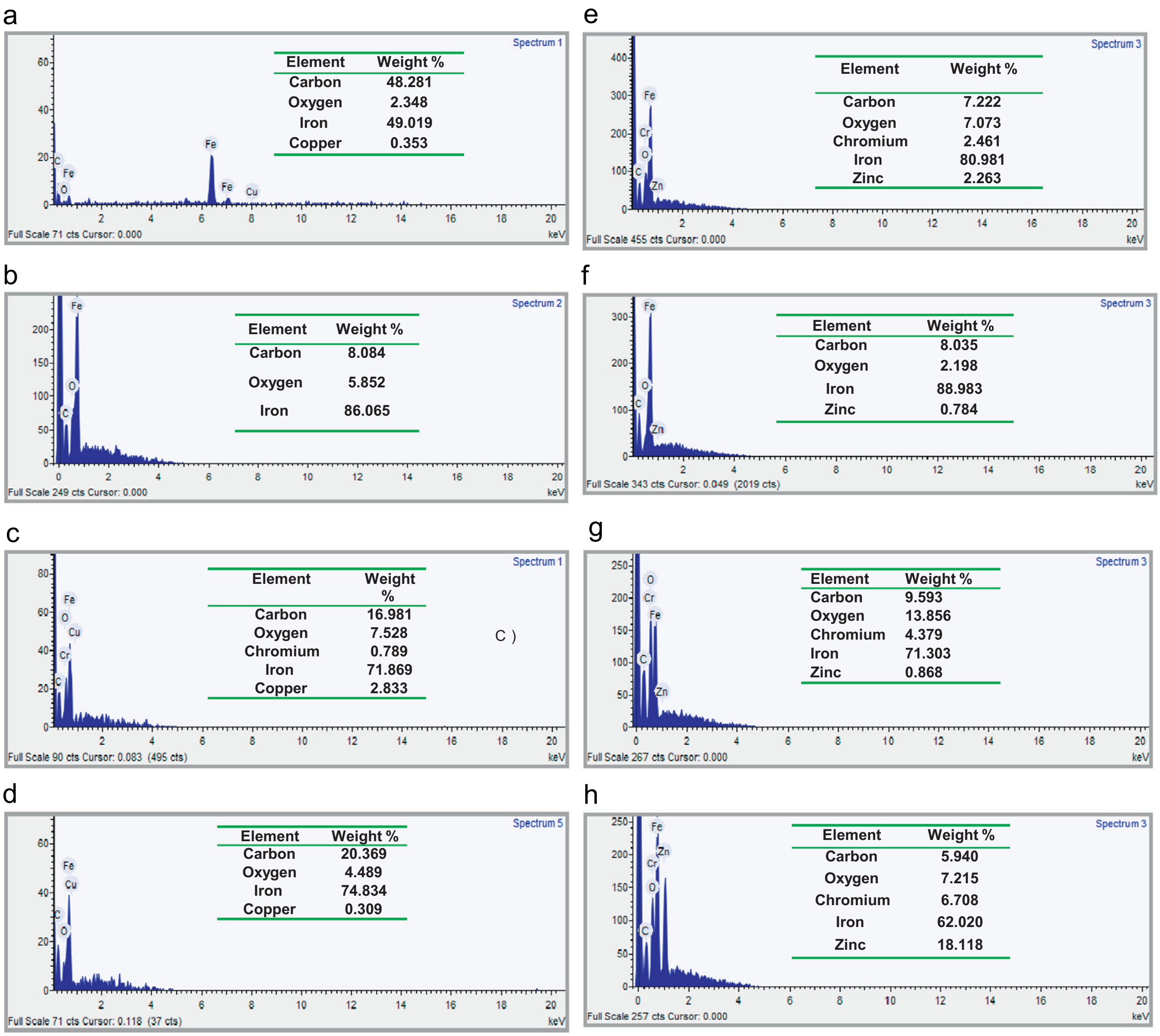

Fig. 8. EDS analysis of worn surface of steel disc for: (a) sunflower oil+CuO, (b) soybean oil+CuO, (c) synthetic oil+CuO, (d) mineral oil+CuO, (e) sunflower oil+ZnO, (f) soybean oil+ZnO, (g) synthetic oil+ZnO and (h) mineral oil+ZnO.

synthetic oil. As it was mentioned above, the best performance for synthetic oil is obtained with CuO nanoparticle, this fact was proved by EDS spectrum. For sunflower and mineral oil the Cu content was lower, indicating less CuO deposition on worn surface. Curious is the soybean oil spectrum, Cu is not identified in worn surface and consequently no CuO film was formed. Other important observation is the higher content of Carbon (C) in worn surface lubricated with sunflower oil+CuO in comparison with other surface EDS spectrums, C possibly derives from oil composition, due to its higher polarity that helps its surface adhesion.

Analyzing Zinc (Zn) content in EDS spectrums (Fig. 8(e–h)) verified that Zn is present in all worn surface in lower concentration for synthetic oil and epoxizided soybean oil, indicating a smaller deposition in worn surface. On the other hand, higher Zn content was found in worn surface for mineral oil, showing the more effective ZnO film formation. This observation may be confirmed by SEM image and percentage of formed film, the worn surface (Fig. 7f) is smoother than worn surface for mineral pure oil (Fig. 7b), and through Fig. 5a, ZnO improves the film formation for mineral oil.

The mechanism by which CuO and ZnO nanoparticles reduces friction and wear can be explained by the formation of a nanoparticles film. However, three different processes can take place: the nanoparticles may be melted and welded on the shearing surface (this is not possible for this research, due to melting points of nanoparticles studied, between 1326 and 2700 °C); reacted with the metal surface to form a protective layer (this is unlikely due to the nature of metal oxide nanoparticle), or nanoparticles are deposited on the surface, and form a physical tribofilm that compensates for the loss of mass. This last option was also verified by Choi et al. [5]. Nanoparticles in the lubricant oil can fill scars and grooves of the friction surface. At the same time, a physical film is formed above the nanoparticles. However, the physical film is formed when the temperature and real contact pressure are high enough to cause a reaction among the materials of oil, surface, and nanoparticles or physical adsorption. When there is good deposition of nanoparticles, the results are a decrease in the frictional force and the surface flat and smooth, as observed in mineral oil added with ZnO (Fig. 8d).

4. Conclusions

The effect of CuO and ZnO on the tribological properties of different base oils was investigated. On the basis of results presented above, it can be concluded that:

- The anti-wear behavior of the oxide nanoparticles depends on the lubricant base oil. They do not show good anti-wear ability when combined with epoxizided vegetable oil like sunflower and soybean oils, because of the influence of chemical nature of vegetable oil on film formation due to polar groups that adhere to surface. In this case, the nanoparticles have a third body behavior increasing the friction.
- ZnO shows excellent performance in friction and wear reduction when combined with mineral oil. A good film formation was found as observed in Figs. 5a, 7f and 8h.
- Synthetic oil has its tribological properties improved with addition of CuO.
- The anti-wear mechanism is attributed to the deposition of nanoparticles in surface and physical film formation, which may reduce the friction and wear.

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