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# Alumina Nanoclusters Additives for Upgraded Regenerated Oils

Claudia Cirillo[a,*], Mariagrazia Iuliano[b], Eleonora Ponticorvo[a], Giuseppe Pica[b], Renata Adami[a], Adolfo Senatore[b,c], Maria Sarno[a,c]

[a]Department of Physics "E.R. Caianiello", University of Salerno, Via Giovanni Paolo II, 132, 84084, Fisciano (SA), Italy.
[b]Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II, 132, 84084, Fisciano (SA), Italy.
[c]NANO_MATES, Research Centre for Nanomaterials and Nanotechnology at the University of Salerno, University of Salerno, Via Giovanni Paolo II, 132, 84084, Fisciano (SA), Italy.
clcirillo@unisa.it

In this work, alumina nanoclusters have been synthesized by a "wet chemistry" approach directly in a regenerated oil. The produced alumina nanoclusters have a quasi-spherical shape with diameter size < 20 nm. A systematic study of their stability in regenerated Group I lubricant oil, with and without low amounts of viscosity modifiers, was performed. Tribological tests, at an optimum concentration of 0.1 wt. %, showed a significant reduction of friction coefficient and wear scar diameter up to 21 % and 11 % with the addition of polyisobutylene as viscosity modifier.

## 1. Introduction

Conventional lubricants in the field of vehicles and industrial systems have reached limit performance. Nanotechnologies represent a real opportunity for innovation towards the generation of new green lubricants based on nanosized additives (Zhao et al., 2021) with tailored anti-wear, anti-wear friction, antioxidant properties, etc ... Recently, advanced nanomaterials, such as metals (Chou et al., 2010; Sánchez-López et al., 2011; Padgurskas et al., 2013), metal oxides based on boron (Hasan and Karabacak, 2014), zinc (Hernández Battez et al., 2008), nanocarbons (Sarno et al., 2020; Sarno et al., 2021), nano chalcogenides (Fernández-Coppel et al., 2018), nano polymers (Dey et al., 2020), and others (Hernandez Battez, et al., 2006; Viesca et al., 2011; Gulzar et al., 2015; Srinivas et al., 2017) have been developed, showing very promising results.
Lubricating oils are used in almost all fields of human technological activity since they are able to satisfy multiple needs: they reduce friction, protect against wear between the surfaces in contact, remove wear debris, reduce heating and contribute to cooling, improve fuel economy reducing emissions and, consequently, the impacts on humans and on the environment. Typically, additives are added to specifically perform all these functions.
Waste lubricating oils disposed in landfills or used as fuel cause significant and severe environmental impacts. On the other hand, the regeneration of oils to reuse them as base oils for new formulations leads to a significant reduction in the impacts on the environment and humans, as well as to tangible economic and social benefits.
To develop a new "green" product by regenerated oils, innovative additives based on high-performance nanotechnologies were prepared. New aluminium oxide-based nano-additives (diameter size < 20 nm) were synthesized directly in the regenerated oil, through a "wet chemistry" approach to confer suitable properties to the oil. The nanoadditives were functionalized with polymeric molecules capable of functioning as a viscosity modifier and as stabilizing agent, making them completely dispersible in lubricating oils.
Tribological properties of lubricating oil with different concentrations of $Al_2O_3$ additives were studied. The performed tests showed a significant reduction of the coefficient of friction and wear scar diameter up to 21 % and 11 %. Furthermore, a noteworthy reduction of the surface roughness was also recorded both at room temperature and at 80 °C due to the addition of 0.1 wt. % of alumina nanoclusters.

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## 2. Experimental

### 2.1 Materials

Aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), 1,2-hexadecanediol, acetone and n-hexane were purchased from Sigma-Aldrich and used as received. All the chemicals were of analytical grade and used as received. Cylinder gas (99.999 pure nitrogen) was purchased from SOL Spa (Italy).

### 2.2 Alumina nanoclusters preparation

The synthesis of nanoclusters was carried out using standard airless procedures and under magnetic stirring. The temperature of the reaction batch is monitored continuously via a thermocouple and a TLK-38 controller. Before synthesis, the reagents were mixed in a batch reactor and stirred magnetically with 20 ml of oil supplied by RILUB SPA. First of all, aluminium oxide ($Al_2O_3$) nanoclusters were synthesized directly in the regenerated base oil LBR 3/R RAMOIL. Then, nanoclusters of $Al_2O_3$ in oil were also synthesized with the addition of viscosity modifiers, Hydrogenated Styrene-Dyene (HSD) and Polyisobutylene. For the synthesis of the nanoclusters in oil, the alumina precursor was loaded into the reagent mixture, consisting of 20 ml of regenerated base oil LBR 3/R and 1,2-hexadecandiol, used as reducing agent, and magnetically stirred under nitrogen flow (Sarno et al., 2016). Different temperatures synthesis and times were examined, in order to ensure a high yield in nanoclusters for the considered process and to obtain reduced dimensions. Set of temperatures and synthesis conditions are shown in Table 2. After synthesis, the obtaining mixture was washed through centrifugations cycles (7,500 rpm; 30 minutes) in acetone and hexane for 3-4 times. Subsequently, the produced material was left to dry for 24 hours at 25°C.

### 2.3 Lubricant base oil and viscosity modifiers

A regenerated base oil named LBR 3/R by RAMOIL (Group I) supplied by the RILUB SPA Company (Ottaviano – Italy) was chosen for this study, see Table 1. For the surface functionalization, two kinds of viscosity modifiers (VM), which have not only the role of aluminium oxide nanoclusters coating but also act as a reducing agent during the synthesis, were tested, in order to optimize the dispersibility of the produced additive. Two commercial VMs were adopted. They were the following ones: Hydrogenated Styrene-Dyene (HSD), named in the following VM1, and Polyisobutylene, named in the following VM2. Both the VMs were purchased from Sigma-Aldrich and used as received.

*Table 1: Performance index of regenerated base oil LBR 3/R*

| Index | Density (15°C) (Kg/m$^3$) | Viscosity 40°C (cSt) | Viscosity 100°C (cSt) | Viscosity Index | Flash point (°C) | Pour point (°C) |
|---|---|---|---|---|---|---|
| Value | 873 | 27-34 (min-max) | 5.2 | 95 | 205 | -6 |

Subsequently, mixtures of the regenerated base oil and the obtained nanoclusters were prepared at three weight percentages (0.05 wt. %, 0.1 wt. %, and 1 wt. %). For dispersion, the desired amount of nanoclusters was sonicated (Hielscher UP 400S ultrasound system) for 60 min in 25 mL of regenerated oil. Then, the suspension thus obtained was mixed with the remaining part of the oil by the use of a homogenizer (Silverson L5M) for 60 minutes. To test the stability of the dispersion, UV-Vis spectrophotometry coupled with periodic centrifugation was used. After dispersion into the regenerated base oil, the dispersions were precipitated by centrifugation at 1,000 rpm. The supernatant was then evaluated for the absorbance using a UV-VIS spectrophotometer. According to the Lambert-Beer law, the absorbance is proportional to the concentration and therefore the absorbance ratio between the absorbance before and after the centrifugation (named as A ratio in the present study) was calculated.

### 2.4 Characterization techniques

The obtained alumina nanoclusters were characterized using several techniques. Scanning electron microscopy (SEM) pictures were obtained with a TESCAN-VEGA LMH electron microscopy (230 V) coupled with an EDS probe. The samples, without any pre-treatment, were covered with a 30 Å thick chromium film using a sputter coater (QUORUM 150 T). Nanoparticle Tracking Analysis (NTA) measurements were performed with a Malvern NanoSight LM10 (Malvern Instruments) equipped with a sample chamber, which is approximately 250µL in volume. Before measurement, 10 mg of the sample was sonicated in 20 ml of hexane and then was injected in the sample chamber with sterile syringes until the liquid reached the tip of the nozzle. All measurements were performed at room temperature of (22±1) ºC.
Transmission electron microscopy (TEM) images were acquired using a FEI Tecnai electron microscope, operating at 200 kV with a $LaB_6$ filament as the source of electrons, equipped with an energy-dispersive X-ray

spectroscopy (EDX) probe. For the preparation of the TEM samples, drops of nanoclusters suspension in ethanol were deposited on carbon-coated electron microscope grids. In order to test dispersion stability, tests with a UV-vis spectrophotometer (Thermo Fisher Scientific, Evolution 60S) in quartz cuvettes (Hellma Analytics-Light path 10 mm) were performed.

*Table 2: Operating conditions of synthesis of alumina nanoclusters in 20 ml of LBR 3/R RAMOIL*

| ID | Sample | Feed | | Operating Conditions | | | |
|---|---|---|---|---|---|---|---|
| | | | | *I step* | | *II step* | |
| | | | | Temperature | Time | Temperature | Time |
| 1 | $Al_2O_3$_1 | $Al(NO_3)_3 \cdot 9H_2O$<br>1,2-hexadecandiol | 2 mmol<br>10 mmol | 200 °C | 120 min | 285 °C | 60 min |
| 2 | $Al_2O_3$_2 | $Al(NO_3)_3 \cdot 9H_2O$<br>1,2-hexadecandiol | 2 mmol<br>10 mmol | 200 °C | 60 min | 285 °C | 10 min |
| 3 | $Al_2O_3$_VM1 | $Al(NO_3)_3 \cdot 9H_2O$<br>1,2-hexadecandiol<br>HSD | 2 mmol<br>10 mmol<br>6 mmol | 200 °C | 60 min | 285 °C | 10 min |
| 4 | $Al_2O_3$_VM2 | $Al(NO_3)_3 \cdot 9H_2O$<br>1,2-hexadecandiol<br>Polyisobutilene | 2 mmol<br>10 mmol<br>6 mmol | 200 °C | 60 min | 285 °C | 10 min |

### 2.5 Tribological tests description

In this study, the adopted tribometer was a Ducom TR-BIO-282 equipped by a setup for performing reciprocating sliding tests in both dry and lubricated contacts. It is also equipped with specimens of several shapes/sizes to allow application of a wide range of contact pressures.

The upper element of the investigated tribopair is made up of X45Cr13 steel ball (diameter of 6 mm, 52–54 HRC), with a reciprocating motion, while the lower element is X210Cr12 steel disc (thickness of 6 mm, a diameter of 25 mm, roughness Ra of 0.30 µm, 60 HRC), immersed in a lubricant bath with electrical resistances as a heating source. The sliding motion, characterized by a triangular speed profile, was set with 10 Hz as frequency, and with 5 mm stroke, as well as a maximum and a mean sliding speed for each stroke of 240 mm/s and 120 mm/s respectively. As for the evaluation of the coefficient of friction and the wear scar diameter, the error of each value was determined as the average of the errors over 3 tests. The average Hertzian pressure achieved at the ball/disc interface with normal load equal to 19 N is 1.17 GPa.

Experiments were carried out at both room temperature and at 80 °C, and the mean lubricant temperature was kept constant by means of a temperature-based feedback control system. The data reported in the following refers to the ones obtained at room temperature unless otherwise indicated.

## 3. Results and discussion

### 3.1 Alumina nanoclusters characterization

The characterization of the obtained nanoclusters following the experimental conditions reported in Table 2-ID 1 and named $Al_2O_3$_1, not shown here, revealed a diameter size bigger than 35 nm. With the aim to obtain smaller nanoparticles, the reaction time was decreased and the sample named $Al_2O_3$_2 (Table 2-ID 2) was obtained. In this case, the characterization, not shown here, revealed a diameter size of about 24 nm.

In Figure 1, scanning electron microscopy pictures of $Al_2O_3$_VM1 (Table 2-ID 3) and $Al_2O_3$_VM2 (Table 2-ID 4) were reported. The images exhibited the presence of irregularly shaped structures with average dimensions less than 200 µm. The characteristics of the powder and the resolution of the instrument did not allow distinguishing well the single nanoparticles, which was, however, possible with the TEM and NTA characterizations shown below. EDS maps evidencing the homogeneous distribution of Al and O overlapped by C, were also shown in the Figure 1. The nanometric size of the produced nanoclusters was then made evident by the higher resolution TEM images. In particular, two TEM images of $Al_2O_3$_VM1 and $Al_2O_3$_VM2, shown in Figure 2a and 2b respectively, revealed the presence of almost spherical particles with average dimensions below 20 nm. The analysis of the size distribution obtained with the NTA technique shows good control of the dimension for the samples. For both samples, $Al_2O_3$_VM1 and $Al_2O_3$_VM2, dimensions < 20 nm were observed, as can be seen from the mean values (or mean particle size) shown in Figure 3.

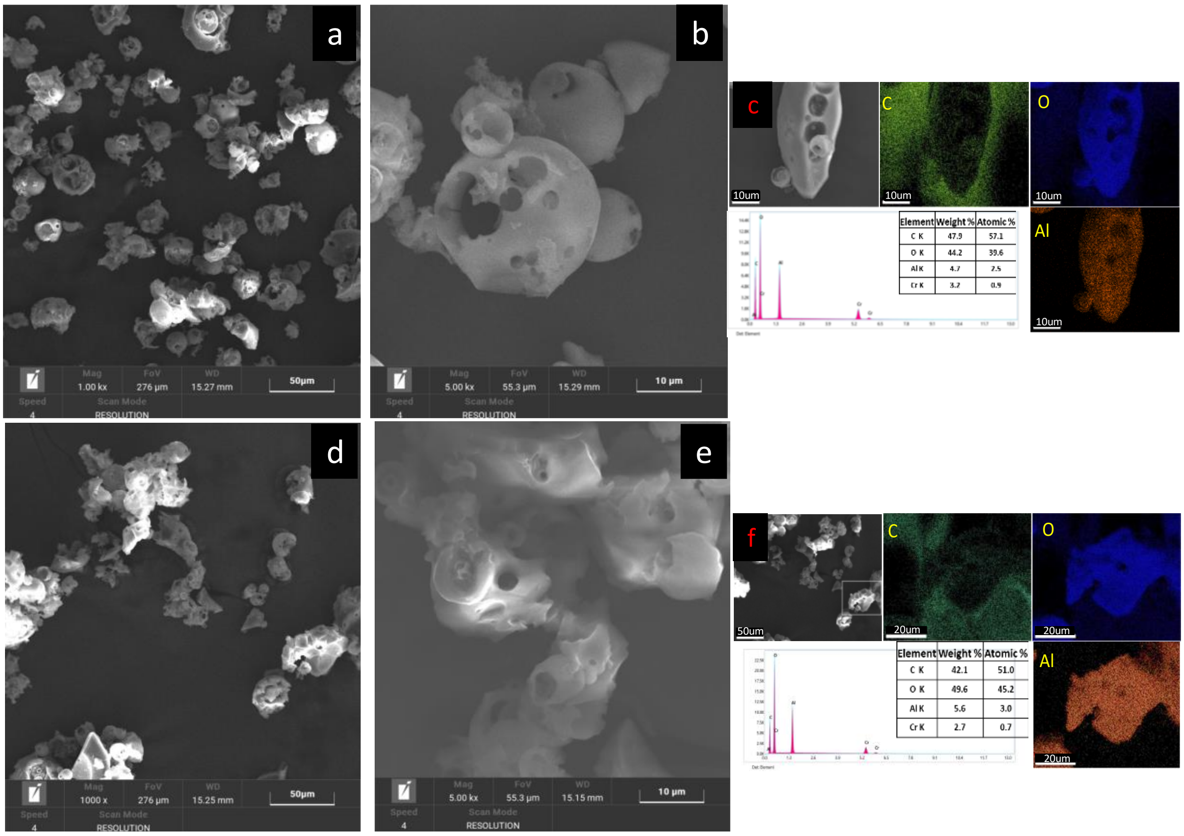


*Figure 1: SEM images and EDS analysis of $Al_2O_3$_VM1 (a,b,c) and $Al_2O_3$_VM2 (d,e,f). Scale bar 10 µm in the elements map of Figure c. Scale bar 20 µm in the elements map of Figure f*

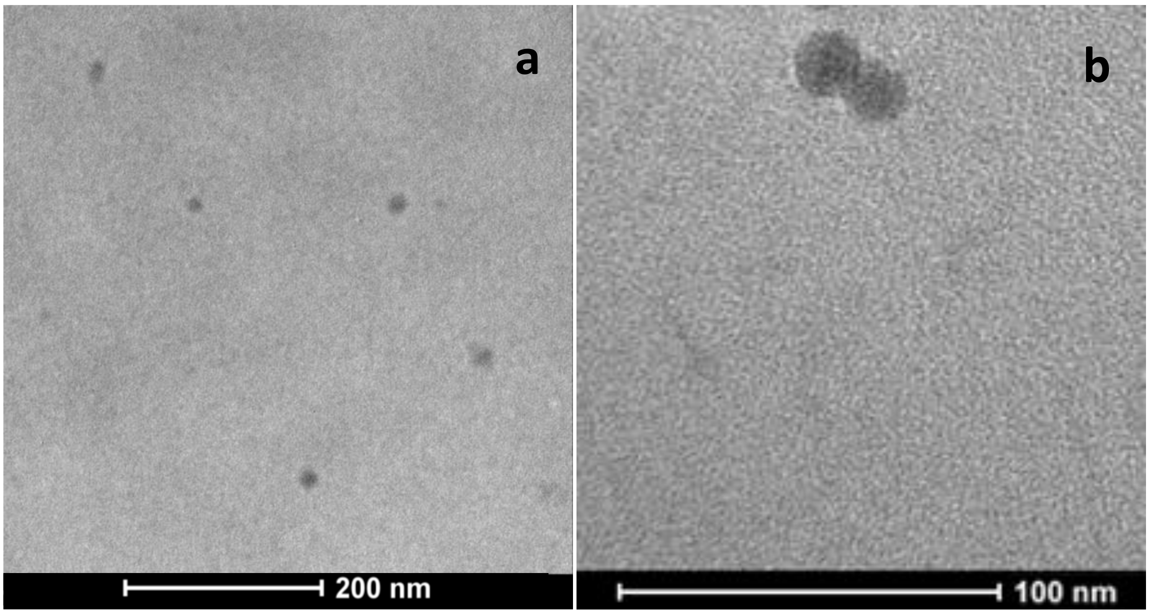


*Figure 2: TEM images of $Al_2O_3$_VM1 (a) and $Al_2O_3$_VM2 (b)*

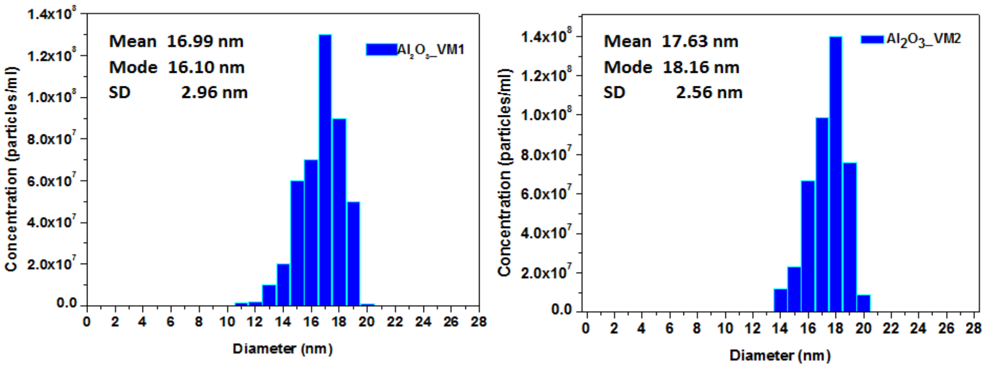


*Figure 3: NTA analysis of $Al_2O_3$_VM1 and $Al_2O_3$_VM2*

## 4. Stability dispersion tests

All the prepared dispersions were precipitated by centrifugation at 1,000 rpm for 30 minutes. The resulted supernatant was successively evaluated for the absorbance using a UV-VIS spectrophotometer and the absorbance before and after the centrifugation (A ratio) was calculated. The stability in LBR 3/R RAMOIL was analyzed in the presence of the two viscosity modifiers, HSD and polyisobutylene. In particular, the A ratio, obtained under UV-Vis, with different concentrations of alumina nanoclusters, was reported in Table 4.

*Table 4: Stability of viscosity modifier and free formulations in LBR 3/R RAMOIL*

| ID | Sample | Nanoadditives concentration (wt. %) | Viscosity Modifier (VM) | A ratio (Absorbance before and after centrifugation) |
|---|---|---|---|---|
| 1 | $Al_2O_3$_2 | 0.05% | / | 0.38 |
| 2 | $Al_2O_3$-VM1 | 0.05% | HSD | 0.84 |
| 3 | $Al_2O_3$-VM1 | 0.1% | HSD | 0.83 |
| 4 | $Al_2O_3$-VM1 | 1% | HSD | 0.80 |
| 5 | $Al_2O_3$-VM2 | 0.05% | Polyisobutylene | 0.95 |
| 6 | $Al_2O_3$-VM2 | 0.1% | Polyisobutylene | 0.94 |
| 7 | $Al_2O_3$-VM2 | 1% | Polyisobutylene | 0.92 |

The presence of the VM significantly influences the stability of produced aluminium oxide nanoclusters in the used lubricating oil. The best results were obtained at the lowest concentration, but they remain significant even at the highest concentration. Furthermore, stability is better in the presence of polyisobutylene.

## 5. Tribological characterization

The results of the tribological tests performed on LBR 3/R RAMOIL are summarized in Table 5.

*Table 5: Mean COF (%) and WSD reduction (%) for different formulations in LBR 3/R RAMOIL at room temperature after 60 min of operation. Measurements were performed in triplicate.*

| ID | Sample | Nanoadditives concentration (wt. %) | VM | Mean COF reduction (%) | Mean WSD reduction (%) |
|---|---|---|---|---|---|
| 1 | $Al_2O_3$_2 | 0.05% | / | 6±0.3 | 6±0.2 |
| 2 | $Al_2O_3$-VM1 | 0.05% | HSD | 12±0.4 | 9±0.3 |
| 3 | $Al_2O_3$-VM1 | 0.1% | HSD | 18±0.7 | 9±0.9 |
| 4 | $Al_2O_3$-VM1 | 1% | HSD | 11±0.3 | 6±0.4 |
| 5 | $Al_2O_3$-VM2 | 0.05% | Polyisobutylene | 13±0.5 | 8±0.2 |
| 6 | $Al_2O_3$-VM2§ | 0.1% | Polyisobutylene | 21±1.3 | 11±0.4 |
| 7 | $Al_2O_3$-VM2 | 1% | Polyisobutylene | 12±0.2 | 7±0.2 |

§T=80°C. Mean COF (%) and WSD reduction (%): 23 and 14, respectively

Mean reductions of Coefficient of Friction (CoF) and Wear Scar Diameter (WSD) were recorded for the synthesized alumina nanoclusters in LBR 3/R RAMOIL at three different concentrations (0.05 wt. %, 0.1 wt. %, and 1 wt. %). As shown in Table 5, alumina nanoclusters, with a concentration at 0.1 wt.% and in presence of polyisobutylene, exhibit the best tribological performance, showing a mean reduction during 60 min operation of CoF and WSD, at room temperature, of 21 % and 10 %, respectively. At 80 °C, at an optimum concentration of 0.1 wt. %, the reductions are 23 % and 14 %, respectively. This highlights the role of the nano-additive, which, indeed, at higher temperatures where the base viscosity decreases, locally precipitates on the metal surfaces in contact by protecting them.

## 6. Conclusions

New aluminium oxide-based nano-additives, with a diameter size < 20 nm, were directly prepared in a regenerated oil (LBR 3/R RAMOIL) through a “wet chemistry” approach. The obtained nanoclusters were functionalized with polymeric molecules with a double function of viscosity modifier and as stabilizing agent, making them completely dispersible.

The performance of lubricating oil using $Al_2O_3$ nanoclusters additives were investigated by the four-ball test and results indicated that the optimal additive concentration of $Al_2O_3$ nanocluster was 0.1 wt%.

Tribological tests showed also a significant reduction of CoF and WSD, especially for the 0.1 wt. % and with the addition of polyisobutylene as viscosity modifier.

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