Experimental evaluation of the tribological behaviour of CeO$_2$ nanolubricants under extreme pressures

L Pena-Paras, D Maldonado-Cortes, J Taha-Tijerina, M Irigoyen and J Guerra
University of Monterrey, Engineering Department, Av. Morones Prieto 4500 Pte. San Pedro Garza García, N. L. 66238, México
E-mail: laura.pena@udem.edu

Abstract. Lubrication of moving components is critical for lowering friction and reducing energy consumption. Nanoparticles have been recently studied as additives for improving the load-carrying capacity and overall tribological performance of lubricants employed for metal-mechanic applications. Cerium oxide is a lanthanide metal oxide (rare earth) with environmentally friendly characteristics that is widely used for consumer products, and most recently for enhancing the tribological performance of composite materials and lubricants. In this work, formulated polymeric lubricants employed for metal forming processes with dispersed cerium oxide (CeO$_2$) nanoparticles were characterized under extreme pressure (EP) conditions. Nanoparticle concentrations of 0.01, 0.05, and 0.10 wt.% were dispersed by homogenization and ultrasonication in the selected lubricant. Tribological characterization under EP was performed with a T-02 four-ball tribometer according to the ITcE-PIB Polish method for testing lubricants under conditions of scuffing. This method applies and increasing load of 0-7200 N to the tribopair in a very short amount of time (18s) and is employed to find the maximum pressure a lubricant film can withstand. The scuffing load ($P_t$), and pressure loss limit or load carrying capacity ($p_{oz}$) were determined after each test. Wear scar diameters (WSDs) of worn ball materials were measured with an Alicona optical 3D measurement system. The anti-wear (AW) and friction-reducing characteristics of CeO$_2$ nanolubricants were determined with a T-05 block-on-ring test. No seizure was found for all lubricants likely due to the presence of additives in the polymeric lubricant. Nanoparticles were found to delay scuffing initiation at concentrations up to 0.05 wt.%, and the load required for scuffing increased by 35 %. The load-carrying capacity was enhanced by up to 84% with only 0.01 wt.% CeO$_2$. Higher concentrations (0.10 wt.%) had a detrimental effect, most likely due to nanoparticle agglomeration. The coefficient of friction (COF) was lowered from 0.035 for the polymeric lubricant to 0.006 with a concentration of 0.01 wt.% CeO$_2$. The tribological results obtained by both tests demonstrate that CeO$_2$ nanoparticles have friction-reducing and EP characteristics, making them suitable as lubricant additives in the metal-mechanic industry.

1. Introduction
In the metal-mechanic industry lubricants are employed to reduce the contact between tooling and workpiece [1]. Nanoparticle additives have been studied for the purpose of improving, the tribological characteristics of load-carrying capacity, wear, and coefficient of friction of these lubricants [2–4]. Due to their small size nanoparticles may be able to provide a mending effect [5], a polishing effect [5], function as a nano-bearing or third-body [6], among others, according to their shape, size, and physical properties [7].
Few tribological studies have been performed using rare-earth nanoparticle additives which possess environmentally friendly characteristics [8–11]. For example, Zhao et al. [10] prepared water-based nanofluids with rare-earth cerium oxide (CeO$_2$) nanoparticle additives. Results showed that nano CeO$_2$ provided anti-wear (AW) properties due to a third-body effect. Gu et al. [9] added combinations of CeO$_2$ and calcium carbonate (CaCO$_3$) nanoparticles to a lubricating oil and obtained better AW and friction reducing behaviour than lubricants with only one type of nanoparticle. Here, extreme pressure (EP) characteristics were also improved by 40.25% compared to the base oil. Lithium greases prepared by He et al. [8] with 0.6 wt.% nano CeO$_2$ decreased coefficient of friction (COF) and wear scar diameter (WSD) by 28% and 13%, respectively, compared to the base grease. These improvements were attributed to a mending effect or a filling of a surface roughness valleys provided by CeO$_2$ nanoparticles. Furthermore, a titanium complex grease with CeO$_2$ was characterized under EP conditions by Shen et al. [11]. These nanoparticles demonstrated to behave both as an AW agent and EP agent.

For this study, we characterized the tribological performance of formulated polymeric lubricants employed for metal-forming processes with varying concentrations of CeO$_2$ nanoparticles. Tribological tests were performed under EP and AW conditions with a four-ball and block-on-ring tribotester, respectively. Load-carrying capacity, wear volume loss, and COF were obtained for the prepared nanolubricants.

2. Experimental details
Nanoparticles of CeO$_2$, obtained from Sigma-Aldrich, of dimensions of <25nm were dispersed into a polymeric lubricant with a viscosity of ~80 Cst in concentrations of 0.01, 0.05, and 0.10 wt.% through homogenisation for 5 min. followed by ultrasonication for 5 min. These concentrations were chosen based on previous studies by our group [3,12].

Prepared nanolubricants were tested under EP conditions with a T-02 four-ball tribotester according to the ITeE-PIB Polish method for testing lubricants under conditions of scuffing [13,14]. Here, the three lower balls are covered with the lubricant and the upper ball rotates at 500 rpms under a linearly increasing load applied from 0 to 7200 N, at 25°C, and for a duration of 18 s. Ball materials were of an AISI 52100 steel with a hardness of 60 HRC. The tribological characteristics of scuffing load ($P_c$), seizure load ($P_s$), and load-carrying capacity or pressure loss-limit of the lubricant film ($p_{lim}$) were obtained with this test. The AW properties and friction-reducing properties of nanolubricants were characterized with T-05 block-on-ring tribotester under the following conditions: a load of 3000 N, 200 rpms, and time of 1080 s. Tests were performed at room temperature (25°C). Ring materials were of AISI D2 steel with a hardness of 62 HRC; blocks were of an AISI 1018 steel with a hardness of 78 HRB. Five tests were performed for each nanolubricant and tribological test in order to obtain statistically significant results [15]. Wear scars of worn ball and disk materials were measured through an Alicona optical 3D measurement system.

3. Results and discussions
The results obtained by the EP test are shown in figures 1-3. Figure 1 shows the frictional torque under increasing loads (0-7200 N) for nanolubricants. The sudden increase in frictional torque indicates material scuffing; thus, the scuffing loads ($P_c$) for the base lubricant was ~2000 N. For the nanolubricants with CeO$_2$ in concentrations of 0.01 wt.%, 0.05 wt.%, and 0.10 wt.% these values were ~2300 N, ~2700 N, and ~1950 N, respectively. At 0.01 wt% concentration a detrimental effect is observed, likely due to nanoparticle agglomeration.
Figure 1. Frictional torque at linearly increasing load from 0-7200 N for CeO₂ nanolubricants.

The WSDs of worn materials were measured after each test through optical microscopy. Figure 2 shows the WSDs of the polymeric lubricant (Figure 2a) and the 0.05 wt.% CeO₂ nanolubricant (Figure 2b), with a significant reduction observed when nanoparticles were added.

Figure 2. Wear scar diameters (WSD) of worn balls after the EP test performed with: (a) polymeric lubricant, and (b) 0.05 wt.% CeO₂ nanolubricant. A significant reduction in WSD is observed.

Figure 3 shows the plot of the load-carrying capacity ($p_{oc}$) for the prepared nanolubricants at varying nanoparticle concentrations. These values were calculated by the following relationship: $p_{oc} = 0.52(P_{oc}/\text{WSD}^2)$, where WSD are the wear scar diameters of the three lower balls, and $P_{oc}$ is the seizure load that occurs at a frictional torque of 10 N.m. Due to the presence of additives in the polymeric lubricant this frictional torque value was not reached, therefore the maximum load of the test of 7200 N was taken as the seizure load. Load-carrying capacity increased from 2200 N/mm² for the polymeric lubricant to 4050 N/mm² with a concentration of 0.01 wt.% representing an improvement of 84%. As proposed by Zhao et al. [10] CeO₂ are able to provide a third-body effect, limiting metal-metal contact, therefore improving the load-carrying capacity of the polymeric lubricant.

The AW and friction-reducing tribological characteristics of nanolubricants are shown in figures 4-6. Curves of COF versus time are shown in Figure 4. It can be observed that all nanoparticle additions were able to reduce COF values, particularly for the CeO₂ concentration of 0.01 wt.%.
Figure 3. Load-carrying capacity of CeO$_2$ nanolubricants obtained by the four-ball test at extreme pressures (EP).

Figure 4. Coefficient of friction (COF) versus time for CeO$_2$ nanolubricants obtained by the block-on-ring test.

Average COF values of nanolubricants obtained in the steady-state from Figure 4 are plotted in Figure 5. COF was reduced from 0.035 for the polymeric lubricant to 0.006 with 0.01 wt.% CeO$_2$. A lower coefficient of friction represents lower energy loss caused by friction [16].

Figure 5. Average COF for CeO$_2$ nanolubricants obtained by the block-on-ring test.

The wear volume loss of blocks recorded after the AW test is plotted in Figure 6. Contrary to the positive results shown in figure 1-5 the addition of CeO$_2$ nanoparticles at all concentrations was found to increase the wear volume loss of blocks. This is attributed to the abrasive nature of CeO$_2$, previously observed by Balamurugan et al. [17] that resulted in material removal. This polishing effect (that is able to reduce surface roughness) and the third-body mechanism explain the reduction in COF observed in Figure 4-5.
Figure 6. Wear volume loss of blocks lubricated with varying concentrations of CeO₂ nanoparticles dispersed in a polymeric lubricant.

These results demonstrate that CeO₂ nanoparticle additives possess good EP and friction-reduction properties that can be taken advantage for obtaining lower energy consumption in metal-forming processes.

4. Conclusions
In this study, the tribological properties of CeO₂ nanolubricants under EP and AW conditions were studied. It was found that CeO₂ nanoparticles have good EP and friction reducing characteristics, but poor AW properties. Load-carrying capacity and COF values were enhanced for all nanoparticle concentrations, with the highest improvements found at 0.01 wt.%. This was attributed to a third-body mechanism, which provided load bearing, and a polishing effect that reduced surface roughness, thus reducing friction. Wear volume loss however was higher with the addition of nanoparticles due to abrasive properties of CeO₂.

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5. References
[1] Schmid SR and Wilson WRD 2001. Tribology in Manufacturing. Modern Tribology Handbook ed. Bhushan B (CRC Press Taylor & Francis Group) pp 1–27
[2] Shahnazar S, Bagheri S and Abd Hamid S B 2016 Enhancing lubricant properties by nanoparticle additives Int J Hydrogen Energy. 41 3153–70
[3] Peña-Parás L, Maldonado-Cortés D, García P, Irigoyen M, Taha-Tijerina J and Guerra J 2017 Tribological performance of halloysite clay nanotubes as green lubricant additives Wear 376 885–92
[4] Peña-Parás L, Gao H, Maldonado-Cortés D, Vellore A, García-Pineda P, Montemayor OE, Nava K L and Martini A 2018 Effects of substrate surface roughness and nano/micro particle additive size on friction and wear in lubricated sliding. Tribol Int. 119 88–98
[5] Sharma A K, Tiwari A K, Dixit A R, Sharma K A, Tiwari A K and Dixit A R 2015 Mechanism of Nanoparticles functioning and Effects in Machining Processes: A review. Mater Today Proc. 2 3539–44
[6] Song X, Zheng S, Zhang J, Li W, Chen Q and Cao B 2012 Synthesis of monodispersed
ZnAl$_2$O$_4$ nanoparticles and their tribology properties as lubricant additives. Mater. Res. Bull. 47 4305–10

[7] Peña-Parás L, Maldonado-Cortés D and Taha-Tijerina J 2018. Eco-friendly nanoparticle additives for lubricants and their tribological characterization Handbook of Ecomaterials eds. Martínez L, Kharissova O, Kharisov B (Springer) pp 1–21

[8] He Q, Li A, Guo Y, Liu S, Zhang Y and Kong L 2017 Tribological properties of nanometer cerium oxide as additives in lithium grease. J Rare Earths 36 209-14

[9] Gu C, Li Q, Gu Z and Zhu G 2008 Study on application of CeO$_2$ and CaCO$_3$ nanoparticles in lubricating oil. Wear 26 163–7

[10] Zhao C, Chen Y K and Ren G 2013 A study of tribological properties of water-based ceria nanofluids Tribol Trans. 56 275–83

[11] Shen T, Wang D, Yun J, Liu Q, Liu X and Peng Z 2016 Tribological properties and tribochemical analysis of nano-cerium oxide and sulfurized isobutene in titanium complex grease Tribol Int. 93 332–46

[12] Peña-Parás L, Maldonado-Cortés D, Taha-Tijerina J, García-Pineda P, Garza G T, Irigoyen M, Gutiérrez J and Sánchez D 2016 Extreme pressure properties of nanolubricants for metal-forming applications Ind Lubr. Tribol. 68 30–4

[13] Szczerek M and Tuszyński W 2002 A method for testing lubricants under conditions of scuffing. Part I. Presentation of the method Tribotest 8 273-84

[14] Piekoszewski W, Szczerek M and Tuszyński W 2002 A method for testing lubricants under conditions of scuffing. Part II. The anti-seizure action of lubricating oils Tribotest 9 35–48

[15] Dean R B and Dixon W J 1951 Simplified Statistics for Small Numbers of Observations. Anal Chem. 23 636–8

[16] Hu Z, Dong J and Chen G 1998 Study on antiwear and reducing friction additive of nanometer ferric oxide. Tribol Int. 31 355–60

[17] Balamurugan S and Sajith V 2017 Experimental investigation on the stability and abrasive action of cerium oxide nanoparticles dispersed diesel. Energy 131 113–24