

Tribological performance of green nanolubricants using functionalized CaCO_3 nanoparticles

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ABSTRACT

In response to the mounting concern over environmental pollution and the depletion of petroleum reserves, biolubricants have emerged as a promising alternative to mineral oil-based lubricants. Thus, the aim of this research is the tribological characterization of green castor and soybean nanolubricants containing functionalized CaCO_3 nanoparticles. Friction improvements were reached with maximum friction decreases of 14 % and 18 % compared to castor and soybean oils. Concerning wear, optimal concentration for castor and soybean nanolubricants was intermediate concentration of 0.15 wt% with width wear reductions of 27 % and 24 % compared to castor and soybean oils, respectively. Tribological mechanisms of tribofilm formation, repairing and rolling-bearing were identified. In rolling-sliding tests, the use of nanoparticles was crucial at low speeds with outstanding friction reductions.

1. Introduction

Nowadays, the conservation of materials and energy is a crucial issue, being the major reason of energy loss in mechanical systems the friction and produced wear that could be decreased by means of lubrication. Thus, around 90 % of the internal elements of earthmoving machinery are lubricated [1], being more than 95 % of the used lubricants from a mineral nature [2], but these type of petroleum-based lubricants have numerous issues and dangerous impacts on the environment. Hence, mineral lubricants are made from crude oil through typical oil refining processes and comprise several chemical components, therefore having an elevated ecotoxicity and a poor biodegradability [3]. It is calculated that 20 % of around 5 million tons of lubricant used every year in Europe is released to environment. One kilogram of a mineral oil is able to pollute a million liters of water [4]. Consequently, contamination produced by lubricants is far from irrelevant. Additionally, mineral lubricants can also contaminate the soil and the air owing to their volatility [5]. Some investigations have documented the adverse effects of mineral lubricants on human health, since

chronic inhalation or dermal exposure to these lubricants can consequence in inflammatory effects on the respiratory system and the site of contact, while also being carcinogenic [6]. In this perspective, environmentally improved lubricants have become more important in industrial applications, therefore biolubricants are promising as a substitute to the aforementioned mineral lubricants to evade their damaging effects [7], because biolubricants are degradable, environment-friendly, clean, and therefore pose little or no risk to the environment or operators [8]. Furthermore, Miller et al. [9] perform a comparative life cycle analysis between petroleum and soybean lubricants considering carbon sequestration and end-of-life impacts. This analysis determined that soybean oil lubricants had a significantly reduced impact on climate change and fossil fuel use. With biodegradable and nontoxic nature, vegetable oils obtain their appropriate place as a base oil for biolubricants. The enhancement of biodegradable lubricants is very valuable for the environment as they decompose 100 % and does not damage the environment. Applying biolubricants in industrial applications would help decrease friction and wear. Apart from the major advantages, there are many issues that must be resolved

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Table 1

Main tribological findings found with biolubricants using NPs as additives.

Lubricant	NPs	Friction reduction %	Wear reduction %	Reference
Castor Oil	MoS ₂	NA	NA	[21]
Sunflower Oil	CuO, ZrO ₂	35, 28	11, 24	[22]
Soybean Oil	CuO, ZrO ₂	40, NI	5, 7	[22]
Jojoba oil	CaCO ₃	34	40	[23]
Castor Oil	f-CuO	34	28	[24]
Rapeseed Oil	CuO, CeO ₂	40, 54	NI, 10	[25]
Neem Oil	SiO ₂	15	10	[26]
Palm Oil	TiO ₂ , CuO	8, 13	62, 40	[27]
Olive Oil	Cu, h-BN	NA	8, 17	[28]
Bio-PAO	Cu/Ti/Mn-GO	40	46	[29]

*NI= not improved, NA= not available

before effective use. These lubricants have a very restricted working temperature range, poor oxidation stability or lack of viscosity range. Therefore, to solve these issues, nanoparticles (NPs) are being included in biolubricants to reach enhancement of specific properties. A number of recent articles have demonstrated that the incorporation of NPs into lubricants can significantly reduce both friction and wear [10–13]. The principal advantages of using NPs as additives in comparison to other materials are due to their superior capabilities to reduce friction and wear, and even to repair the worn surface. This is due to the small size of NPs, which allows them to enter the contact area, resulting in a positive lubrication effect [8]. Moreover, due to these unique properties NPs can also be used in other systems, for example as reinforcement in different alloy matrix finding interesting results [14,15]. Furthermore, several researchers have verified that adding some NPs to biodegradable lubricant oils, better improvement of tribological performance was reached [16–20]. Thus, Table 1 summarizes the main tribological findings using biodegradable nanolubricants.

For example, Yu et al. [21] examined the tribological performance of MoS₂ NPs in castor oil. They observed that MoS₂ NPs reduced the friction and adhesive wear. Furthermore, Kumar and Gautam [22] investigated the tribological properties of vegetable oil-based nanolubricants composed by soybean and sunflower oils with CuO and ZrO₂ NPs. These authors found that using CuO NPs as additives of both vegetable oils improved antifriction behavior with reductions in friction around 40 %. Regarding the ZrO₂ NPs, the addition to sunflower oil led to a 28 % reduction in friction and 24 % in wear. Additionally, Mousavi et al. [29] studied the tribological performance of a novel synthetic biodegradable PAO using Cu/TiO₂/MnO₂-doped GO nanocomposites as additives, achieving significant friction and wear enhancements.

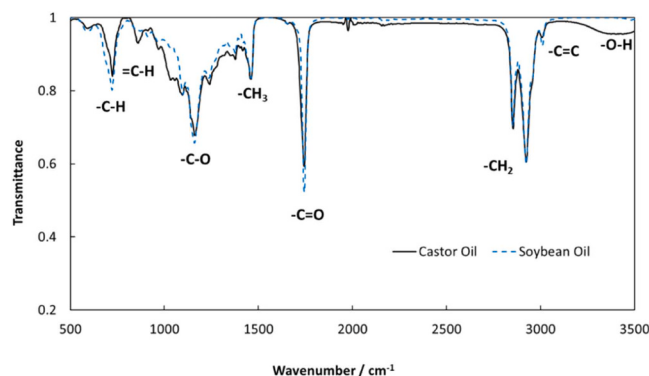
Despite these encouraging results, one of the greatest challenges in the formulation of nanolubricants is their poor stability due to the sedimentation of NPs [30,31]. The stability of nanofluids can be achieved through two distinct stabilization mechanisms: electrostatic stabilization and steric stabilization. The first mechanism is that the aggregation of nanoparticles is inhibited due to the presence of a double layer of electric charges that envelopes the nanoparticles. In order to prevent the aggregation of nanoparticles, the repulsive forces between particles must be stronger than the attractive forces (van der Waals) [32]. On the other hand, steric stabilization entails the coating of nanoparticles with distinct molecules through surfactants or chemical modifications, thereby establishing a distance between nanoparticles that prevents their aggregation with other nanoparticles [33]. In a comprehensive review of the temporal stability of various nanolubricants, Chen et al. [31] addressed this topic. The study examined several characteristics of nanoparticles, including their size and surface modification agent. The findings indicated that surface modification is a crucial factor in the efficient dispersion of nanopowders in lubricant oils. Therefore, it is important to use surface modified nanoparticles in order to achieve good stability and a future potential use in industry for the

Table 2

Main physical properties of castor and soybean base oils.

	Viscosity (313.15 K)	Density (313.15 K)	Viscosity Index (VI) (313.15 to 373.15 K)
	η / mPa·s	ρ / g cm ⁻³	-
Castor oil	236.6	0.9462	92
Soybean oil	28.5	0.9075	232

*Viscosity and density determined by ASTM D7042 and VI by ASTM D2270.

**Fig. 1.** FTIR spectrum of Castor oil and Soybean oil.

nanolubricant. Furthermore, the full tribological characterization (pure sliding and rolling-sliding contacts) of biolubricants is very scarce in literature. Thus, in this work, the full tribological characterization of biodegradable nanolubricants composed by two different vegetable oils: castor and soybean oils and functionalized CaCO₃ nanoparticles were carried out. The greatest novelty of this work is that both NPs and oils are ecofriendly, and it is difficult to find tribological works in literature with this type of lubricant system, especially, that use functionalized type NPs. CaCO₃ NPs are environmentally friendly and verify the European Ecolabel standards for using as lubricant additives [34]. These NPs are also eco-friendly since the surface modification agent is a fatty acid and CaCO₃ is one of most rich biominerals in the Earth crust, formed in geological sources like limestone. Furthermore, the experimental works of CaCO₃ NPs as lubricant oil additives is limited [23,35,36]. Thus, Zhang et al. [36] analyzed the antiwear properties of CaCO₃ NPs as additive to PAO10 oil, viewing that CaCO₃ NPs can significantly improve the anti-wear properties of PAO10 base oil (around 90 % decrease in wear). Furthermore, Kulkarni et al. [23] examined the addition of CaCO₃ NPs in jojoba oil, reaching that non-functionalized CaCO₃ NPs addition to oil reveals notable antifriction and anti-wear performance, with maximum decreases around 34 % and 40 %, respectively. In comparison with our research, these authors have not studied the friction performance in rolling-sliding conditions. Additionally, in the present research two biodegradable base oils (castor and soybean) were used to obtain a greater knowledge about biodegradable lubricants.

2. Materials and procedures

2.1. Vegetable base oils

The vegetable base oils used in this research, castor oil and soybean oil, were provided by Merck (Darmstadt, Germany). The main physical properties of base oils are summarized in Table 2. Thus, Castor oil has a viscosity index of 92, a dynamic viscosity of 236.6 mPa s and a density of 0.9462 g·cm⁻³ at 313.15 K while soybean oil has a viscosity index of 232, a dynamic viscosity of 28.5 mPa s and a density of 0.9075 g·cm⁻³ at 313.15 K.

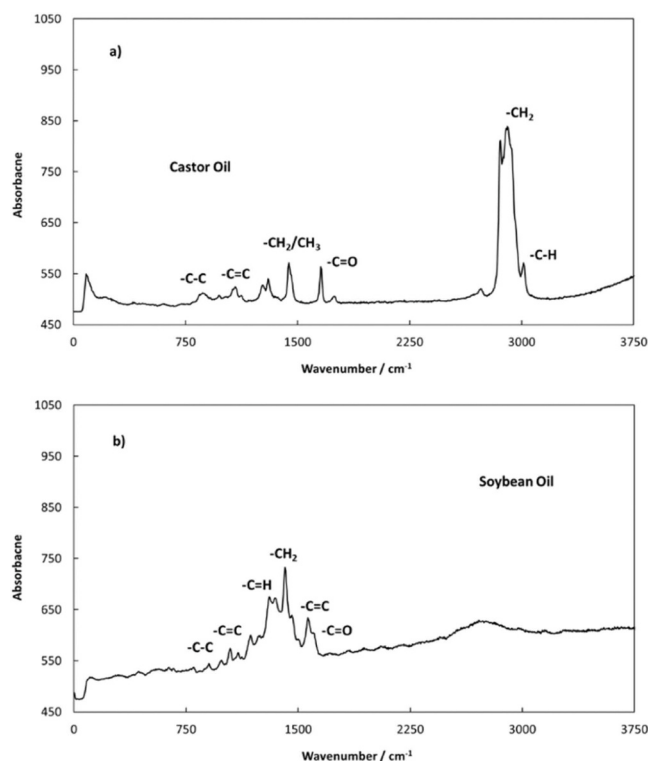


Fig. 2. Raman spectrum for Castor (a) and Soybean oils (b).

Both vegetable oils were characterized by infrared spectroscopy, FTIR, (VARIAN 670-IR spectrometer from Agilent, California, USA) and Raman spectroscopy (alpha300R+ from WITec GmbH, Kroppach, Germany) to find the main functional groups. Thus, Fig. 1 reveals the FTIR spectrum of castor oil and soybean oil. As it can be observed, for both oils the spectrum is very similar. Hence, adsorption bands around 3500 cm⁻¹ are assigned to O-H stretching vibration. A small stretching vibration band at 3010 cm⁻¹ is related to the C=C bond. Likewise, asymmetric and symmetric deformation vibrations of -CH₃ appear around 1460 cm⁻¹ and 1370 cm⁻¹. Besides, two strong bands at 2930 cm⁻¹ and 2840 cm⁻¹ are associated to the symmetric and asymmetric stretching vibration of CH₂, respectively. Furthermore, a very strong and narrow band at 1740 cm⁻¹ is linked to the C=O of ester compounds. Additionally, the bands at 1240 cm⁻¹ and 1160 cm⁻¹ are associated with the stretching vibration for C-O in ester group. Furthermore, a small band at 860 cm⁻¹ is ascribed to the out-of-plane bending vibration of =C-H and finally the intense band at 720 cm⁻¹ is characteristic of -CH for deformation vibration [37–39].

Regarding the Raman spectra of vegetable oils, as Fig. 2 shows, the spectra of castor oil and soybean oil are quite different. Fig. 2a displays the Raman spectrum of castor oil with the next characteristic peaks: The bands around 3010 cm⁻¹ and 2930 cm⁻¹ could be ascribed to the

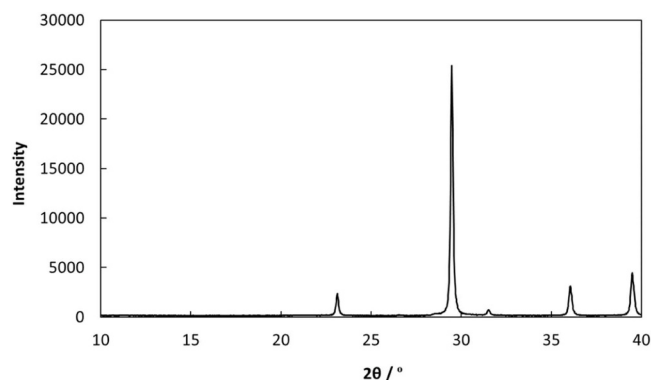


Fig. 4. XRD pattern of f-CaCO₃ nanoadditives.

stretching of CH and CH₂, respectively. Furthermore, the band around 1740 cm⁻¹ was ascribed to the C=O stretching of triacylglycerol structure that is present in the Castor oil. Finally, the band placed around 1440 cm⁻¹ is assigned to bending of CH₂/CH₃ groups. Regarding the soybean oil Raman spectrum, Fig. 2b, the presence of the following bands are observed: 870 and 1080 cm⁻¹ for C-C stretching, 970 cm⁻¹ ascribed to C=C trans deformation, 1270 cm⁻¹ regarding the CH= bond plane deformation; 1300 cm⁻¹ related to twisting motion of methylene, 1440 cm⁻¹ associated to CH₂ deformation, 1660 cm⁻¹ to C=C cis stretching and finally at 1750 cm⁻¹ owing to C=O stretching [40,41].

2.2. Nanoadditives

Regarding the nanoparticles used as additives of castor and soybean base oils, functionalized calcium carbonate nanoparticles, f-CaCO₃, were chosen (from US Research Nanomaterials, Houston, USA). f-CaCO₃ NPs coated with fatty acid have 98 % purity and a 40–80 m²/g specific surface area according to the supplier. These NPs were fully characterized using several characterization techniques. Therefore, f-CaCO₃ nanoparticles have been characterized through infrared spectroscopy (FTIR) and Raman spectroscopy to establish the bonds related with f-CaCO₃ NPs (Fig. 3). The FTIR spectrum of the f-CaCO₃ NPs (Fig. 3a) shows three pronounced peaks placed at 710 cm⁻¹, 870 cm⁻¹ and 1450 cm⁻¹ consistent to deformation in plane, deformation outside in-plane and doubly degenerate in-plane strain typical of CaCO₃, respectively. [42,43]. Furthermore, it can be also observed that around 2900 cm⁻¹ some peaks are present due to the fatty acid functionalization [44]. Besides, the Raman spectrum of f-CaCO₃ (Fig. 3b) displays a band around 710 cm⁻¹ that corresponds to E_g phonon, a strong Stokes band around 1100 cm⁻¹ that coincides with A_{1g} phonon, and another weak band at 1430 cm⁻¹ that corresponds to another E_g phonon [45,46].

Furthermore, f-CaCO₃ NPs were characterized using X-Ray diffraction to verify its crystalline pattern. Thus, a D8 Advance from Bruker (Massachusetts, USA) with Cu-Kα radiation (λ = 1.5418 nm) was employed. The XRD study was completed between 2θ = 10–40°. Additionally, the Debye-Scherrer's equation was used to estimate the size of

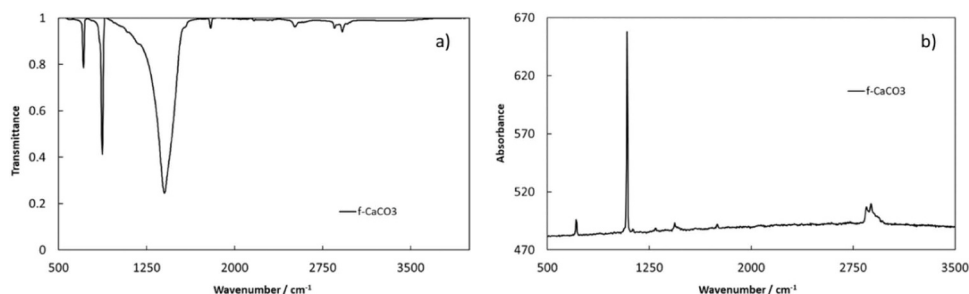


Fig. 3. FTIR (a) and Raman (b) spectrum of f-CaCO₃ nanopowders.

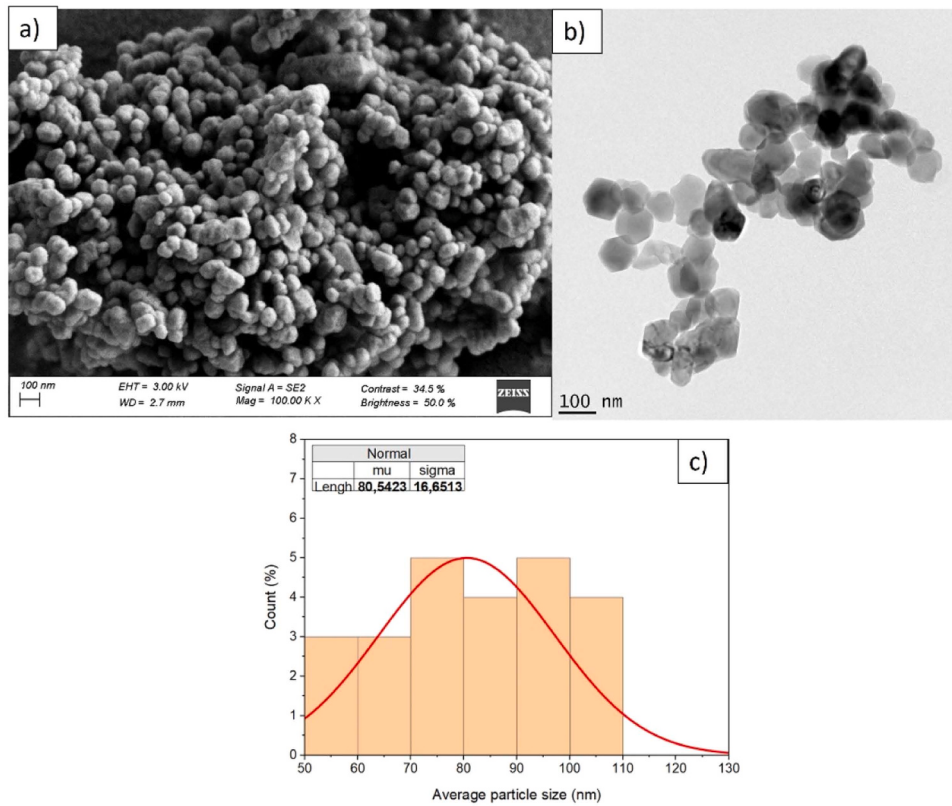


Fig. 5. SEM (a) and TEM (b) images and size nanoparticles distribution (c) of f-CaCO₃ nanopowders.

the NPs based on the subsequent formula [47]:

$$D_p = K \lambda / (\beta \cos \theta) \quad (1)$$

where D_p is the mean crystallite size (nm), K the Scherrer constant, λ the whole width at the half summit of the diffraction peak, β denotes the full width at half maximum (FWHM) and θ the Bragg angle of the peak. Fig. 4 displays the XRD pattern of f-CaCO₃ NPs. It can be observed that peaks are placed at $2\theta = 22.9^\circ$, 29.34° , 36.11° and 39.45° , corresponding to (012), (104), (110), (113) crystal planes [48]. Thus, this experimental XRD investigation matches with the ICSD Card of Calcite (No: 98-004-0107) [48]. The CaCO₃ NPs crystallite size calculated using the aforementioned Eq. 1 is 86.7 nm.

Finally, f-CaCO₃ NPs were also characterized by means of Scanning electron microscopy, SEM, (FESEM Ultra Plus from Zeiss, Jena, Germany) and transmission electron microscopy, TEM, (1011 from JEOL, Tokyo, Japan) methods in order to know their morphology and size. It must be noted that through TEM image (Fig. 5b) and using Image J

software the average particle size was calculated. SEM and TEM images (Figs. 5a and 5b) reveal that the studied f-CaCO₃ NPs exhibit an almost spherical shape. Furthermore, the obtained average size of NPs was around 80 nm (Fig. 5c). This average size is similar to that obtained with XRD characterization (86.7 nm).

2.3. Formulation and stability of potential green nanolubricants

To formulate the nanodispersions of castor oil and soybean oil with functionalized CaCO₃ NPs, the typical two-step process was performed [49]. Hence, the following eight potential nanolubricants were prepared by utilizing a MC 210 P Sartorius balance (0.01 mg readability):

Castor Oil + (0.05 wt% f-CaCO₃, 0.10 wt% f-CaCO₃, 0.15 wt% f-CaCO₃, 0.20 wt% f-CaCO₃).

Soybean Oil + (0.05 wt% f-CaCO₃, 0.10 wt% f-CaCO₃, 0.15 wt% f-CaCO₃, 0.20 wt% f-CaCO₃).

The main reason to choose these mass concentrations (0–0.20 wt%)

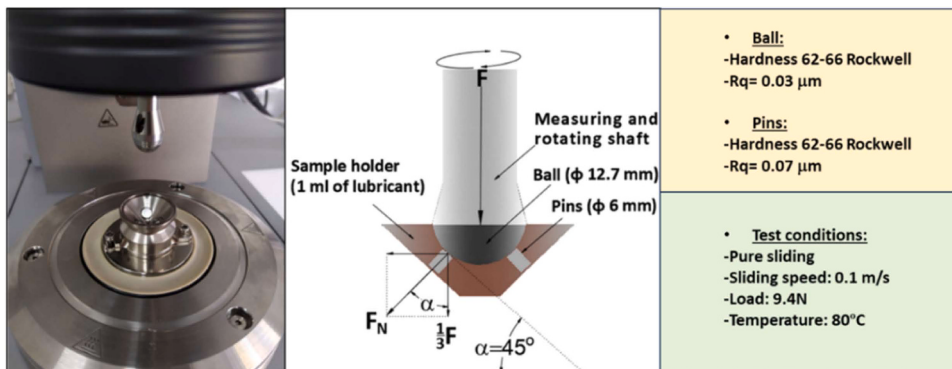


Fig. 6. Ball-on-three pins configuration and tribological details.

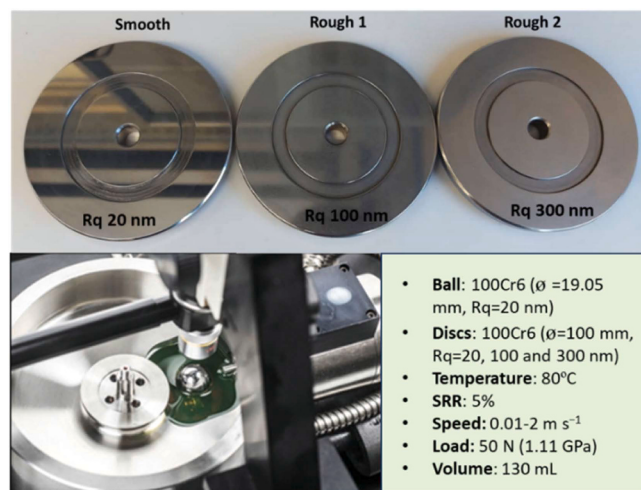


Fig. 7. Rolling-sliding tribometer configuration and tribological details of specimens.

was the good tribological performances obtained in previous studies of nanoparticles as lubricant additives [43,50]. After the preparation, the aforementioned nanolubricants were agitated during 3 h via ultrasonic bath working in continuous mode to obtain homogeneous nano-dispersions. The stability against sedimentation of the prepared nano-dispersions was examined through two different methods: visual control and refractometry. The former is a qualitative process, in which the nanodispersions are photographed each 24 h observing if the NPs are deposited or not. Regarding the latter, the refractive index evolution over time of nanolubricants is studied with the aim of quantifying the precipitation of NPs. For this task, a Metler Toledo refractometer was utilized [51].

2.4. Tribological characterization under pure sliding conditions

Tribological analyses were performed with the two base oils, Castor oil and Soybean oil, and their formulated f-CaCO₃ nanolubricants (0.05 wt%, 0.10 wt%, 0.15 wt% and 0.20 wt% f-CaCO₃) to examine if these nanoadditives present antifriction and/or antiwear properties. For this purpose, a rheometer of Anton Paar (Graz, Austria), MCR 302, set up

with a T-PTD200 tribology unit was utilized in ball-on-three pins disposition, being the ball situated on a tube and pins are set into a circular box (Fig. 6). Friction pure sliding tests were performed at 213 rpm rotational speed (0.1 m s^{-1} at the contact points) and 9.4 N load in each pin implying a maximum Hertzian pressure of 1.1 GPa, a duration of 3400 s and a temperature of 353.15 K. Pins are flooded after inserting around 1 mL of lubricant. Besides, three different trials were performed for each lubricant sample. More descriptions considering this device can be found in previous research [52].

After performing the friction analyses described previously, wear is generated in the pins. Therefore, to evaluate the produced wear and compare between base oils and nanolubricants, pins were analyzed through an optical profilometer Sensofar S-Neox to obtain information about the different wear indicators, wear scar diameter (WSD), wear track depth (WTD) and worn area, and about the roughness inside the worn surfaces employing the ISO4287 standard with a Gaussian filter (cut-off: 0.08 mm). Likewise, to examine the surfaces of worn pins and obtain knowledge concerning the nanolubricants elements in worn areas (base oil and NPs) and possible tribological mechanisms that could act, a Raman microscope WITec alpha300R+ was utilized to obtain raman mappings of worn surfaces. Finally, SEM characterization of worn surfaces was also carried out to improve the information concerning the tribological mechanisms.

2.5. Tribological characterization under rolling-sliding conditions

A tribometer EHD2 (PCS Instruments, UK) with a ball-on-disc disposition, was utilized to perform friction tests of a metal contacts formed by a ball and a rotational disc (Fig. 7). Both components are driven with two different electric motors to perform the rolling-sliding tests. The test conditions are also summarized in Fig. 7. More information concerning this apparatus can be seen in previous research [53]. These kind of tests were completed for the castor and soybean base oils and their respective optimal f-CaCO₃ nanolubricants with the greatest tribological performance reached in pure sliding tests. Thus, Stribeck curves were obtained for the base oils and f-CaCO₃ nanolubricants using three different discs (one smooth and two rough, Fig. 7) for a 5 % slide-to-roll ratio (SRR) [53]. Friction coefficient is established like the mean of those achieved from two individual tribological tests, the first ramp speed increasing speed and the second one reducing speed.

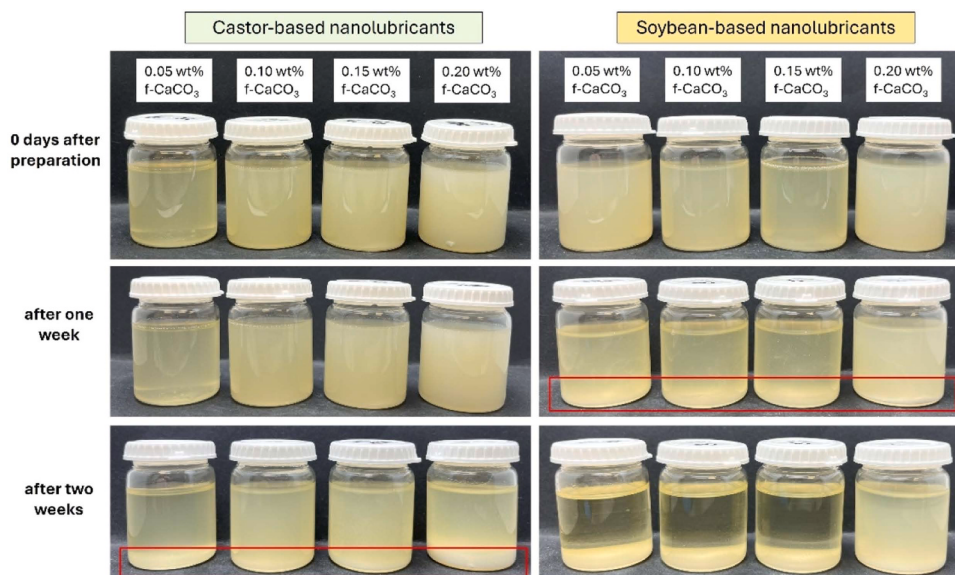


Fig. 8. Visual stability of castor and soybean based nanolubricants.

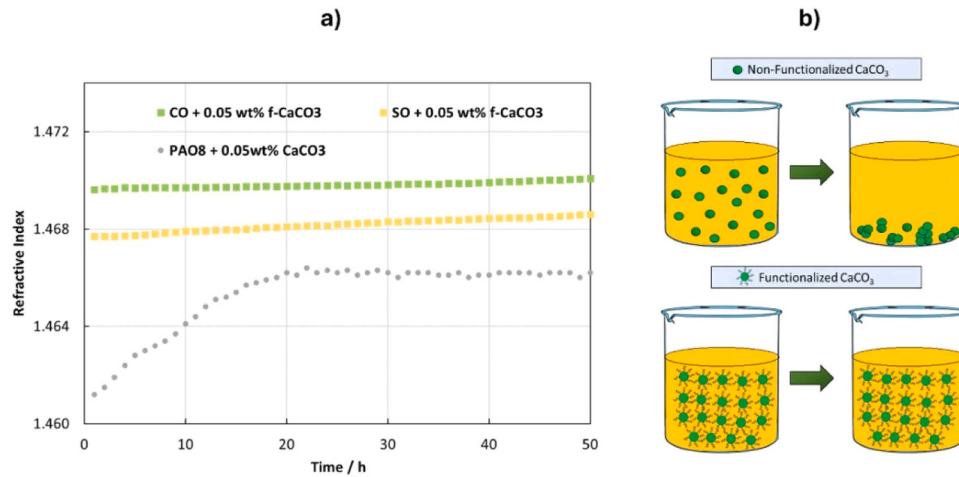


Fig. 9. Refractive index evolution (a) and schematic representation of coated and uncoated NPs in terms of stability (b).

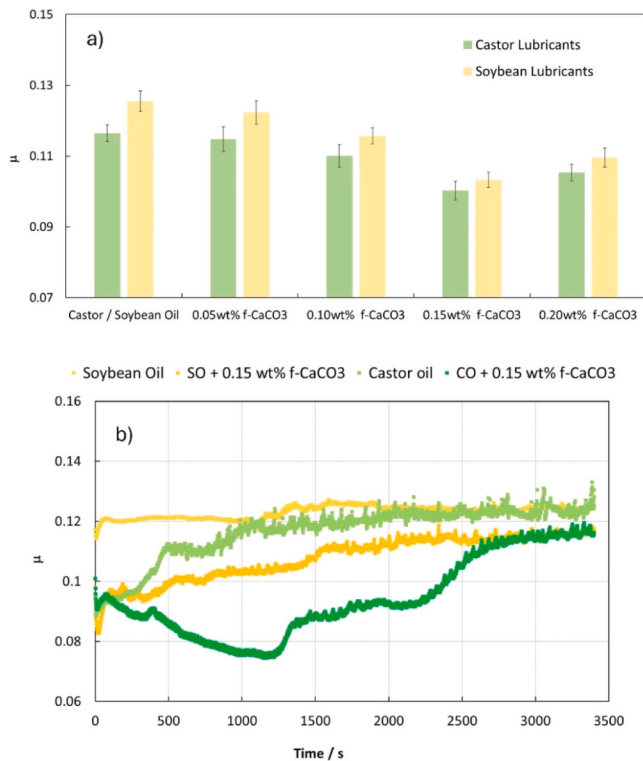


Fig. 10. Mean friction coefficients (μ) found with Castor and soybean base oils and their f-CaCO₃ nanolubricants (a) and their behavior during time (b).

3. Results

3.1. Nanolubricants stability

The stability against sedimentation of f-CaCO₃ nanolubricants based on castor oil and soybean oil was investigated qualitatively via visual observation and quantitative by means of refractometry technique. As Fig. 8 reveals, for the castor-based nanolubricants the sedimentation appears after two weeks of homogenization, while for the soybean-based nanolubricants, the sedimentation appears after the first week of sonication, therefore better visual stability was observed for the castor nanolubricants. This fact may be owing to the higher viscosity of castor oil in comparison to soybean oil.

Regarding the refractometry, Fig. 9a presents the refractive index progress during time for the f-CaCO₃ nanolubricants based on castor and soybean oils, in order to quantify the importance of presenting a fatty acid functionalization in the NPs. As it can be observed, the sedimentation rate for both type of nanolubricants is quite slow. Precisely, after 50 h the variation of refractive index was 0.03 % and 0.06 % for castor and soybean nanolubricants, respectively. These results indicate a very good stability against sedimentation for the used NPs in comparison to another previous research work [43] that uses uncoated CaCO₃ NPs. As it is presented in Fig. 9a, the stability for uncoated CaCO₃ nanolubricants is quite worse than that obtained for the f-CaCO₃ nanolubricants. Specifically, for the uncoated nanolubricants the variation of refractive index was 0.19 % after only 10 h. Thus, it can be observed that through the functionalization of NPs, the stability of nanolubricants is improved (Fig. 9b).

3.2. Friction and wear results in pure sliding

As it was mentioned previously, friction tests with castor and

Table 3

Attained mean friction coefficients, μ , and wear parameters (WSD, WTD and Area) with standard deviations, σ , for the Castor and Soybean lubricants at 353.15 K.

Lubricant	μ	σ	WSD/ μm	$\sigma/\mu\text{m}$	WTD/ μm	$\sigma/\mu\text{m}$	Area/ μm^2	$\sigma/\mu\text{m}^2$
Castor Oil	0.117	0.002	425	21	3.2	1.1	975	220
+ 0.05 wt% f-CaCO ₃	0.115	0.003	398	17	3.0	1.3	892	211
+ 0.10 wt% f-CaCO ₃	0.110	0.003	363	23	3.1	1.3	731	126
+ 0.15 wt% f-CaCO ₃	0.100	0.003	291	16	1.6	1.0	392	102
+ 0.20 wt% f-CaCO ₃	0.105	0.002	370	31	2.8	1.2	690	126
Soybean Oil	0.126	0.003	525	21	4.6	0.7	1387	380
+ 0.05 wt% f-CaCO ₃	0.122	0.003	508	17	3.8	0.8	1281	231
+ 0.10 wt% f-CaCO ₃	0.115	0.002	423	15	2.8	0.6	860	197
+ 0.15 wt% f-CaCO ₃	0.103	0.002	398	18	2.3	0.5	603	112
+ 0.20 wt% f-CaCO ₃	0.109	0.003	414	21	2.4	0.4	671	110

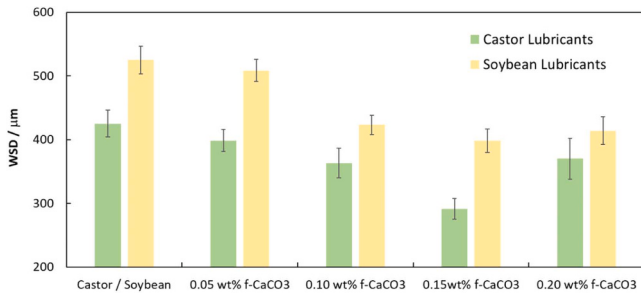


Fig. 11. Wear scar diameters (WSD) found with Castor and soybean base oils and their f-CaCO₃ nanolubricants.

soybean oils and with their corresponding f-CaCO₃ nanolubricants were performed, being the obtained values presented in Fig. 10a and Table 3. As it can be observed, for both kind of f-CaCO₃ nanolubricants (based on castor and soybean oils), the reached friction coefficients are quite smaller than those attained with the base oils. Thus, the greatest friction reductions were achieved for the 0.15 wt% f-CaCO₃ nanolubricants for both castor and soybean-based lubricants. In particular, maximum friction decreases of 14 % and 18 % were achieved compared to castor and soybean base oils, respectively. As it can be observed in Fig. 10a, friction coefficients decrease gradually from as the mass concentration of NPs increases, until reaching a bottom at the 0.15 wt% f-CaCO₃ (optimal performance) to then increase the friction behavior at the highest mass concentration of NPs (0.20 wt%). This singularity might be owing to very low mass concentrations the quantity of NPs is not enough to achieve a suitable friction performance and when the concentration is high (0.20 wt%), NPs are more expected to agglomerate in friction tests, being difficult for NPs to enter the tribological contact, producing inferior lubrication capacity. So, the produced aggregates as impurities can scratch the friction surface and consequently the friction rises. Furthermore, it is observed that soybean base oil and nanolubricants have a higher friction coefficient in comparison to castor oil lubricants. This fact may be due to the higher viscosity of castor oil in comparison to soybean oil. Finally, friction performance for castor and soybean base oils and nanolubricants with greatest performance during time can be observed in Fig. 10b.

After completing the aforementioned friction tests, the used pins presented wear. As displayed in Fig. 11 and Table 3, the wear generated in pins lubricated with f-CaCO₃ nanolubricants is much smaller than

those created with castor and soybean base oils, showing the NPs excellent antiwear properties. It is clear that the optimal mass concentration for castor and soybean nanolubricants was the intermediate concentration of 0.15 wt% with WSD reductions of 27 % and 24 % compared to base oils. Concerning of worn area, maximum reductions of 35 % and 56 % were achieved for the 0.15 wt% optimal nanolubricants, in comparison to castor and soybean base oils. Fig. 12 displays the important wear reductions of optimal nanolubricants in comparison with castor base oil (Fig. 12a) and soybean base oil (Fig. 12b). Therefore, outstanding reductions in wear were achieved through the addition of f-CaCO₃ NPs to the castor and soybean oils.

Additionally, roughness analyses on pins obtained after friction tribological tests reveal that the tested worn pins with f-CaCO₃ nanolubricants have less roughness than those achieved with the two base oils (Table 4). Hence, a Ra value of 33.6 and 35.8 nm were found for the worn pins lubricated with castor and soybean oils, respectively. On the other hand, pins with the optimal castor and soybean nanolubricants (0.15 wt% f-CaCO₃) reached the minimal Ra values (20.6 and 19.3 nm, respectively) indicating a remarkable roughness decreases around 40 % and 45 %, correspondingly. These results imply that owing to the f-CaCO₃ addition to base oils, a more regular worn surface is detected after pure sliding tests. For better visualization of roughness, the surface roughness images, and roughness profiles are presented in Fig. 13.

Raman mappings of the worn surfaces after friction studies were performed to investigate the distribution of the NPs in the worn tracks and how they can participate in the remarkable friction and wear improvements of nanolubricants. Previously, each Raman spectrum of

Table 4

Mean roughness values, Ra and Rq in worn pins examined with the f-CaCO₃ nanolubricants and base oils.

Lubricant	Ra/nm	σ	Rq/ nm	σ
Untested Pin	50.1	3.9	59.6	4.8
Castor oil	33.6	2.8	42.5	3.2
+ 0.05 wt% f-CaCO ₃	28.8	2.6	32.7	3.3
+ 0.10 wt% f-CaCO ₃	22.9	1.5	25.0	1.5
+ 0.15 wt% f-CaCO ₃	20.6	2.3	23.2	2.1
+ 0.20 wt% f-CaCO ₃	24.3	1.7	27.2	1.6
Soybean oil	35.8	3.1	39.4	4.5
+ 0.05 wt% f-CaCO ₃	27.2	2.4	30.4	3.0
+ 0.10 wt% f-CaCO ₃	24.5	2.2	27.9	2.4
+ 0.15 wt% f-CaCO ₃	19.3	1.6	22.9	2.1
+ 0.20 wt% f-CaCO ₃	24.1	2.3	27.2	2.3

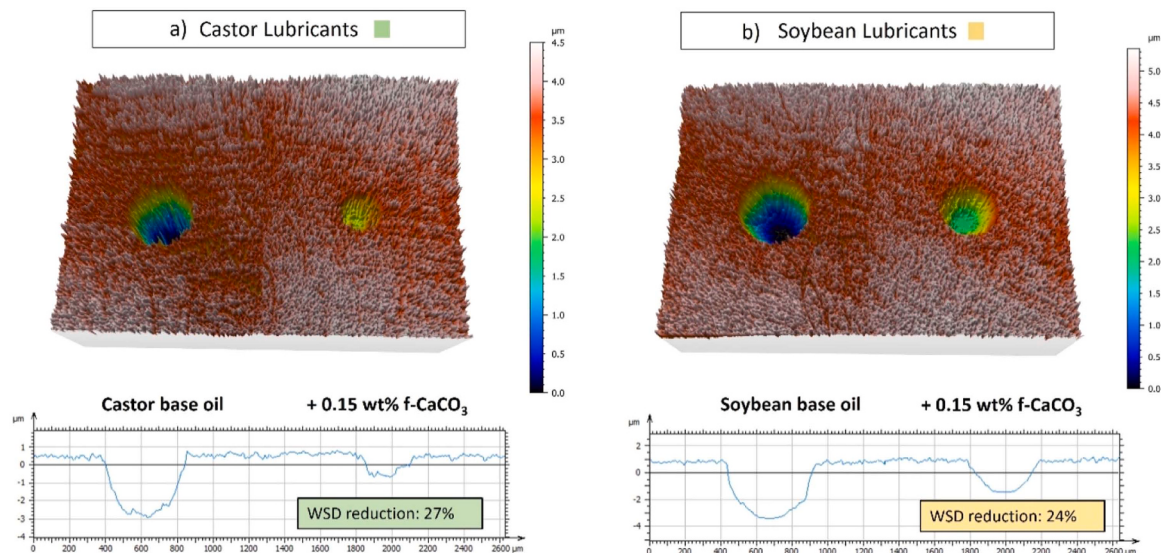


Fig. 12. Comparison between 3D profiles found with castor (a) and soybean (b) base oils and their optimal f-CaCO₃ nanolubricants.

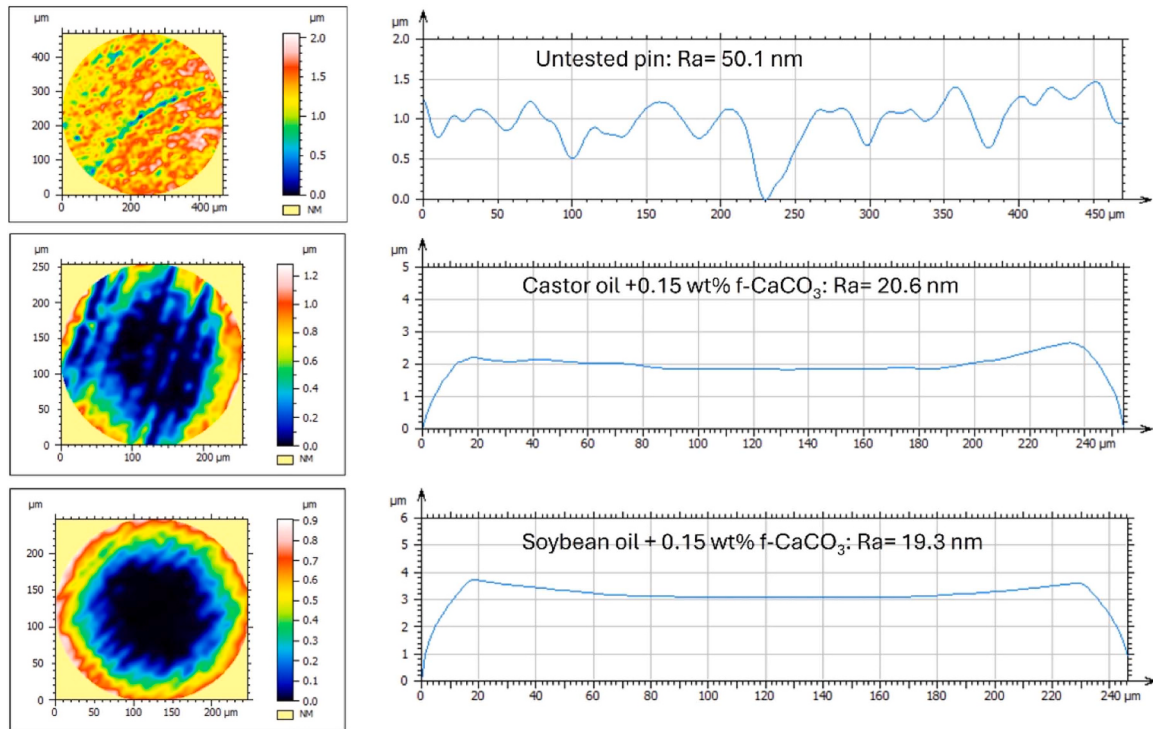


Fig. 13. Surface roughness and roughness profiles observed for untested and tested metallic samples.

nanolubricants components were presented: castor and soybean oils (Fig. 2) and f-CaCO₃ (Fig. 3b) to recognize the elements in Raman mappings. Two mappings were performed to observe the worn pins tested with the castor and soybean nanolubricants with the optimal antiwear behavior (0.15 wt% f-CaCO₃ for both base oils), Fig. 14. Regarding the castor nanolubricant, Fig. 14a, it presents the areas in blue and green, matching the peaks of the spectrum with those achieved for castor oil and f-CaCO₃ NPs, respectively. Similarly, for soybean nanolubricant, Fig. 14b, it also presents the areas in blue and green, coincide the peaks of the spectrum with those attained for soybean oil and f-CaCO₃ NPs, respectively. It is also observed that in the case of mapping with soybean nanolubricants, the spots of f-CaCO₃ have a lower size and are quite better distributed in the worn surface, in comparison with mapping of castor nanolubricants. This fact can be a possible reason for obtaining a greater roughness reduction in comparison to base oils. Thus, for both mappings (castor and soybean nanolubricants), considering the presence of f-CaCO₃ Raman spectrum in worn surfaces it is clearly observed that f-CaCO₃ are trapped in the metal contact and fill in the gap between the rubbing surfaces facilitating the decrease of friction and wear through prevent direct metal-metal contact. The deposits of f-CaCO₃ NPs are placed in the sliding direction and could form a protective layer of low shear strength on the worn surface that enhances the lubrication performance of castor and soybean base lubricants. The greater surface energy of NPs permits them to chemically react with the rubbing surfaces to produce a tribofilm, which can minimize direct contact with the steel surfaces. Considering these observations and the improved roughness values (Table 3) for the f-CaCO₃ nanolubricants it can be observed that formation of tribofilm and repairing mechanism (filling the NPs the valleys in the contact surfaces) played on the worn surface during tribological tests. Additionally, as the NPs present a spherical shape, the rolling-bearing mechanism could also be present in the reduction of friction and wear by changing the sliding friction between the rubbing surfaces to rolling friction. Similar results were observed by Sunqing et al. [35] who investigated the tribological characteristics of CaCO₃ NPs as 500SN base oil. They observed that CaCO₃ NPs have decomposed to CaO during tribological tests, and a film formed by

CaCO₃ and CaO was created on the contact surfaces. They concluded that the tribological mechanisms are the tribofilm formation and rolling-bearing. Furthermore, Zhang et al. [36] studied the antiwear properties of CaCO₃ NPs as additives of PAO10 base oil. These authors found that the tribological mechanism is ascribed completely to the deposition of CaCO₃ NPs, with the creation of CaO from CaCO₃ and other elements on the worn metal surface.

In order to improve the information regarding the tribological mechanism, SEM characterization of untested pin (Fig. 15a) and worn surfaces tested with castor and soybean base oils (Fig. 15b and Fig. 15c) and their optimal nanolubricants in friction and wear: castor oil + 0.15 wt% f-CaCO₃ (Fig. 15d) and soybean oil + 0.15 wt% f-CaCO₃ (Fig. 15e), were performed. As it can be observed in Fig. 15b and Fig. 15c, critical adhesive wear and plastic deformation just occurred on the steel surface when the base oils were used as lubricants, as proved by the formation of deep furrows. Nevertheless, in the lubrication with castor and soybean oils containing f-CaCO₃ NPs (Fig. 15d and Fig. 15e), the sliding surfaces were quite smooth and critical wear did not appear. These facts suggest that a tribofilm consisting of f-CaCO₃ NPs and the organic compounds from the NPs modifier (fatty acid) was created.

To sum up, considering the roughness analyses, Raman mapping and SEM observations of worn surfaces, it was resolved that the tribological mechanisms are the tribofilm formation, repairing mechanism and rolling-bearing mechanism due to the spherical shape of NPs. Thus, these tribological mechanisms are schematically described in Fig. 16.

3.3. Tribological results in rolling-sliding

Tribological rolling-sliding test for castor and soybean base oils and their respective optimal nanolubricants in pure sliding conditions (0.15 wt% f-CaCO₃) were carried out at operating temperature of 80 °C and SRR of 5 % reaching the friction characterization through Stribeck Curves (Fig. 17). The Stribeck curves is the result of plotting the coefficient of friction versus specific film thickness, Λ , which is calculated by: $\Lambda = \frac{h_t}{Rq}$ where h_t is the theoretic film thickness and Rq is the composite roughness of tribological pairs: $Rq = \sqrt{(Rq_{disc})^2 + (Rq_{ball})^2}$. The h_t

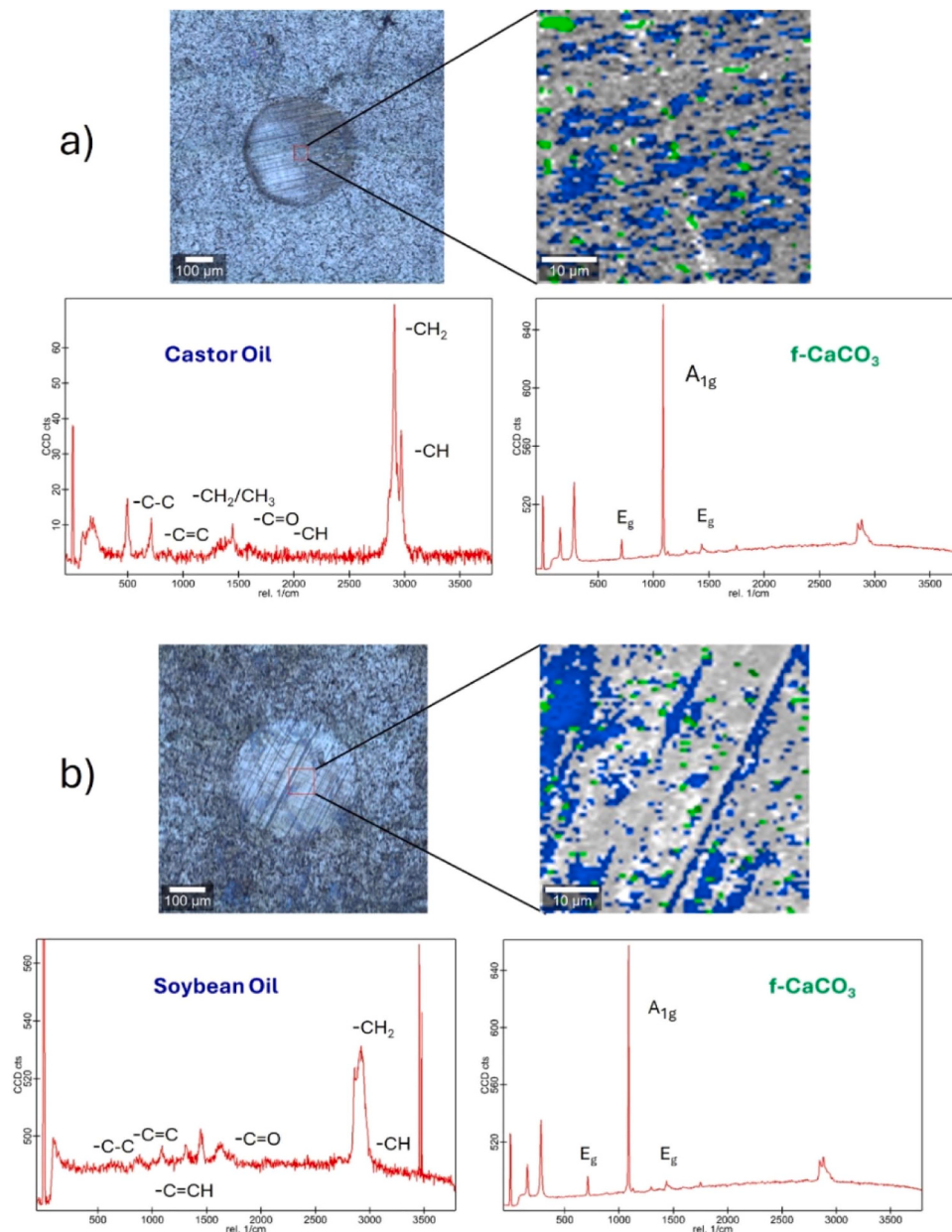


Fig. 14. Mapping Raman of surfaces tested with optimal castor (a) and soybean (b) nanolubricants.

at the 80 °C temperature was guessed with the Hamrock and Dowson's equation [54], contemplating diverse factors such as materials and lubricant properties or working conditions. For the approximation of h_b , the trimethylpropane trioleate base oil pressure–viscosity coefficient was employed [55]. Besides, a Stabinger SVM 3000 (Anton Paar, Austria) was employed to measure the dynamic viscosities up to 100 °C (Table S1).

The achieved Stribeck curves are plotted in Fig. 17a for castor and Fig. 17b for soybean base oils and their optimal f-CaCO₃ nanolubricants using three discs with different roughness (0.02, 0.10 and 0.30 Rq). As it can be seen in the graphs, for both kind of lubricants (castor and soybean) important friction reduction happens owing to the addition of f-CaCO₃, especially at low speeds with the roughest disc. Nonetheless, it is also observed that the added and non-added lubricants behave similarly with the two smoothest discs and with the roughest disc for speeds above 500–700 mm/s. In these conditions the specific film thickness is quite thick which decreases the synergetic effects of the nanoparticles that are thought to be effective under boundary

conditions. As the speed decreases, the direct contact between asperities start to occur and the inclusion of the nanoparticles decrease the coefficient of friction under rolling-sliding conditions. Thus, for small speeds the outcome of the f-CaCO₃ NPs addition is essential, with outstanding friction reductions when the hydrodynamic impact is minor (low speeds), therefore operating the NPs successfully at boundary conditions. The reached results are quite attractive for oil engine and gears applications, regularly operating at elevated temperatures [56].

Commonly, a Stribeck curve is divided in various lubrication regimes: boundary, mixed, elastohydrodynamic (EHL) and full film lubrication (FFL). Varying on the diverse criteria in literature, boundary regime appears when $\Lambda < 1$, mixed if $1 < \Lambda < 3$, EHL while $\Lambda > 3$ and with $\Lambda > 5$, FFL. Thus, in these rolling-sliding tests Λ values vary between a minimum over 0.04 (for the soybean lubricants with roughest disc) to about 13.9 (for the castor lubricants with smoothest disc). Accordingly, following the aforementioned classification, boundary lubrication occurs for all the examined discs (0.02, 0.10 and 0.30 Rq) except for the smoothest disc (0.02 Rq) with castor-based lubricants,

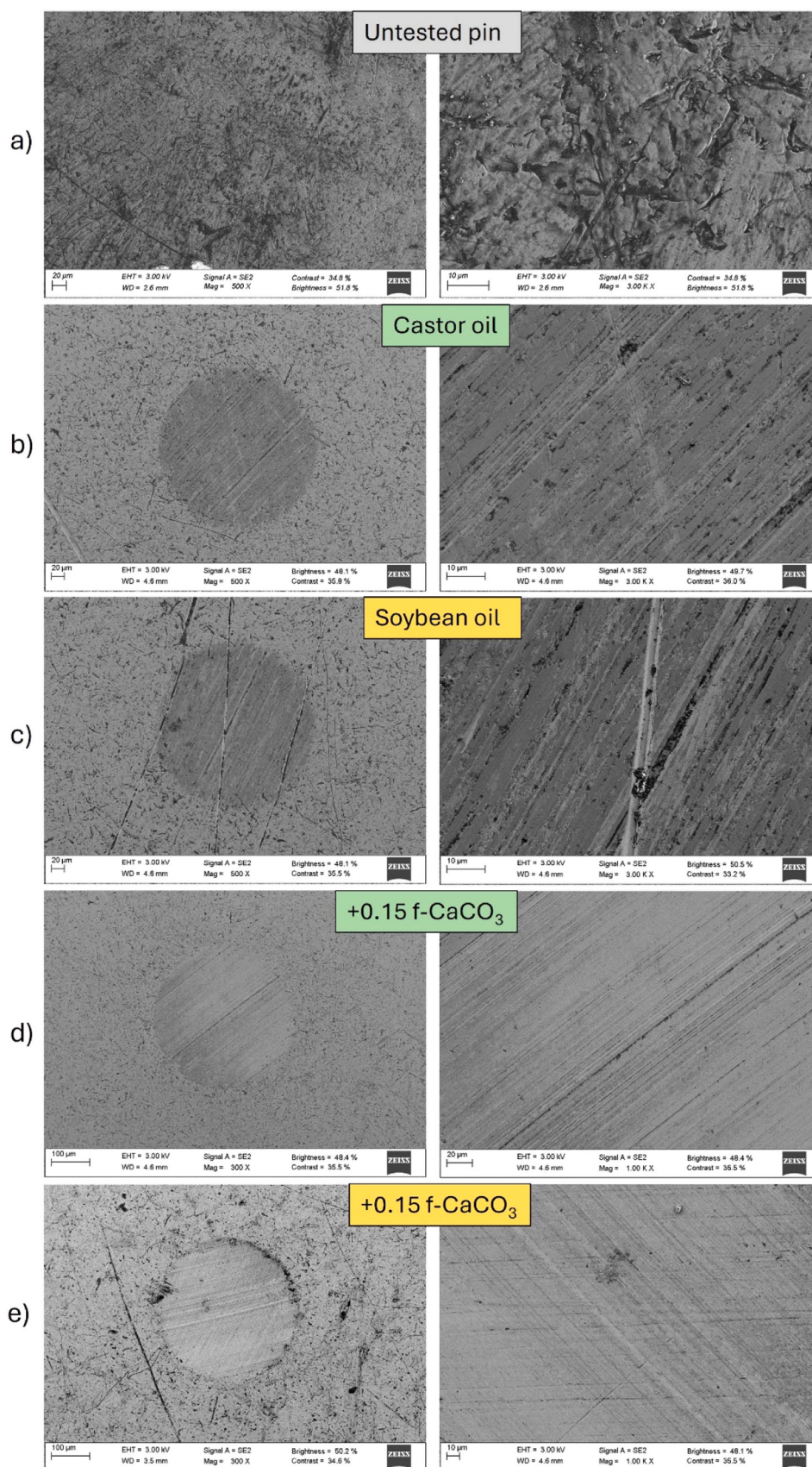


Fig. 15. SEM images of untested pin (a) and worn pins tested with castor (b) and soybean (c) base oils and optimal castor (d) and soybean (e) nanolubricants.

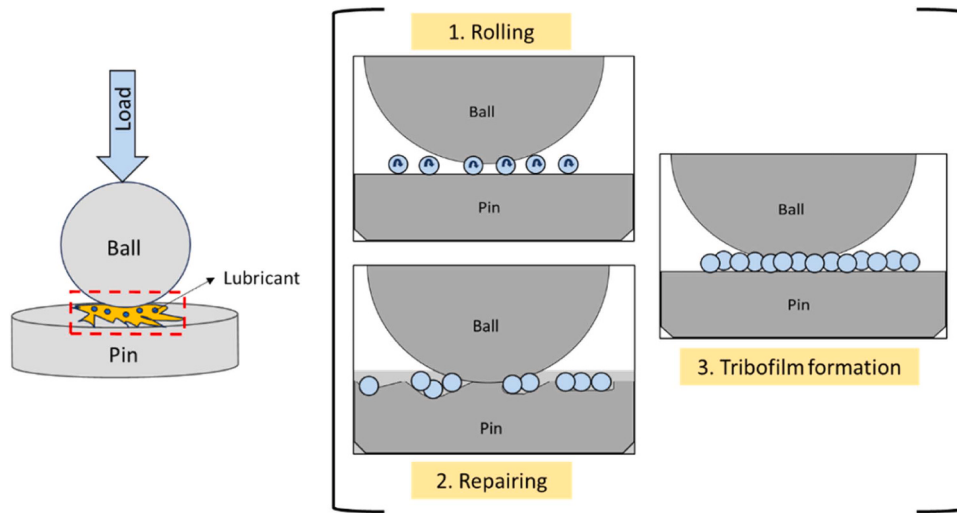


Fig. 16. Schematic representation of the possible tribological mechanisms.

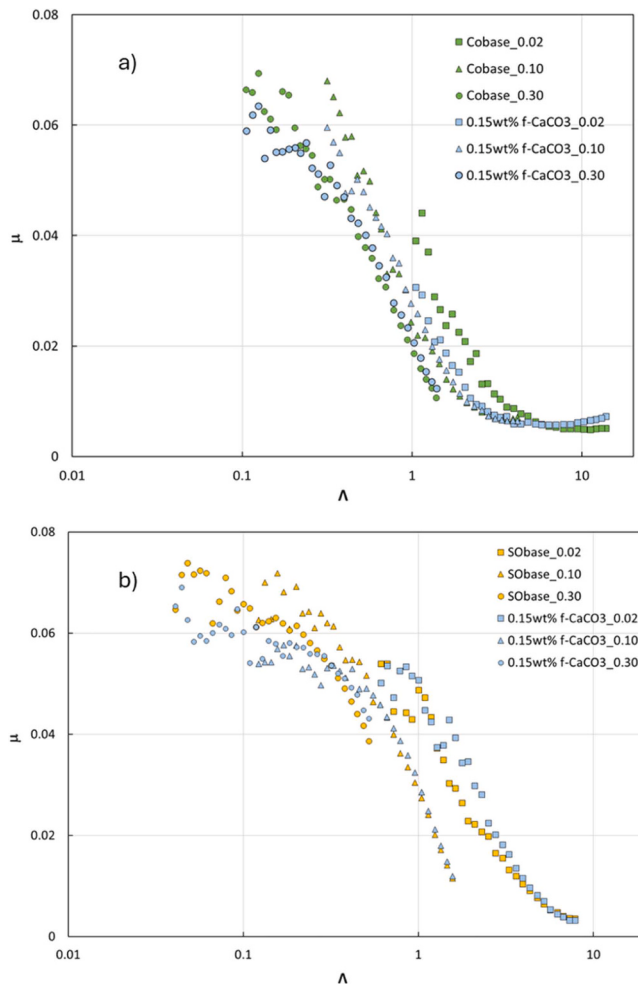


Fig. 17. Full Stribeck curves reached with castor oil (a), soybean oil (b) and their f-CaCO₃ nanolubricants (a and b).

mixed lubrication happens for all discs with castor lubricants and the two smoothest discs (0.02 and 0.10 Rq) with soybean lubricants whereas EHL and FFL occurs for the two smoothest discs (0.02 and 0.10 Rq) with castor-based lubricants and with the smoothest disc (0.02 Rq) for soybean-based lubricants. Therefore, a full friction characterization in

all the lubricant regimes were performed through rolling-sliding tests.

4. Current challenges and future considerations

The market penetration of biolubricants has been limited in many applications. This is likely due to their poor oxidative stability and their inferior properties at lower temperatures. The principal obstacle is the high degree of variability and seasonality of the feedstock, which gives rise to different chemical compositions of the starting vegetable oil [57]. Another challenge is the selection of the non-edible oil. Different research have been conducted with vegetable oils that could potentially disrupt the food chain, including sunflower, soybean, and palm oil, among others [57]. The use of these oils could potentially lead to price speculation and social differences. As a consequence, the promotion of non-edible oils, as jojoba oil and castor oil, has increased significantly over recent years as a green alternative [58]. Furthermore, microalgae have developed as a potential source of biodegradable oil owing to its high oil content, which has been observed to exceed 70 % [59]. The future of biolubricants should focus on the development of lubrication properties and ecotoxicity that are enhanced to those of conventional mineral oils. The development of more sustainable formulations is required in fields that include engine oils and hydraulic oils, among others. Regarding the economic issue, it is needed to identify reliable and cheap vegetable oils as starting materials making efforts in chemically modifying the preliminary vegetable oils to enhance the formulation of desired biolubricants. For this purpose, the lubricant-synthesizing companies should change their production chains in order to develop these lubricants efficiently, although it is evident that this process requires a huge investment and time. Regarding the use of nanolubricants, one of the main challenges for the tribology researchers, engineers and end users is recycle and reuse the nanolubricants components. As Kimura et al. [60] reported, near 30 % of lubricant oils in advanced countries is wasted, which relatively contaminate the global environment. Hence, applying a suitable recyclability process would reduce the overall cost of a nanolubricant, being economically feasible.

5 Conclusions

In this research, the following conclusions were found:

- Eco-friendly nanolubricants were formulated using castor and soybean oils additive with functionalized CaCO₃ nanoparticles (f-

- CaCO₃) observing time stabilities around two weeks castor nanolubricants and one week for soybean nanolubricants.
- Friction coefficients achieved in pure sliding conditions with f-CaCO₃ nanolubricants are lower than those attained for castor and soybean base oils with reductions of 14 % and 18 %, respectively, for an optimal concentration of 0.15 wt% f-CaCO₃.
 - Important wear improvements in pins tested with f-CaCO₃ nanolubricants were observed in comparison with those tested base oils, reaching maximum decreases of 27 % and 24 % compared to castor and soybean base oils for the 0.15 wt% f-CaCO₃ nanolubricants.
 - Based on the NPs shape, roughness analysis, Raman microscopy and SEM of worn surfaces, it is suggested that the lubrication mechanism is explained by rolling effect, the adsorbed tribofilm and repairing.
 - Relating the rolling-sliding tests, f-CaCO₃ NPs play a decisive role in the maximum boundary lubrication regime, substantially lowering the friction coefficient.
 - This research reveals the benefit of using CaCO₃ NPs and castor or soybean oils in the field of tribology, being the special importance the good tribological performance for castor nanolubricants for the nature of a non-edible oil.
 - High-performance CaCO₃-based nanolubricants seem to be a commercially feasible alternative to conventional and harmful petroleum-based lubricants.

Statement of Originality

The authors declare that the work described in this manuscript has not been published previously by any of the authors, that it is not under consideration for publication elsewhere, that its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright holder.

CRedit authorship contribution statement

Jorge H.O. Seabra: Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **David E.P. Gonçalves:** Writing – review & editing, Methodology. **Carlos M.C.G. Fernandes:** Writing – review & editing, Methodology, Investigation. **Jose Manuel Lineira del Río:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the

online version at doi:10.1016/j.triboint.2024.110007.

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