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Improving the tribological performance of a biodegradable lubricant adding graphene nanoplatelets as additives

José M. Liñeira del Río [a,*], María J.G. Guimarey [a,b], Jose I. Prado [c], Luis Lugo [c], Enriqueta R. López [a], María J.P. Comuñas [a]

[a] Laboratory of Thermophysical and Tribological Properties, Nafomat Group, Department of Applied Physics, Faculty of Physics, University of Santiago de Compostela, 15782 Santiago de Compostela, Spain
[b] Department of Design and Engineering, Faculty of Science & Technology, Bournemouth University, Talbot Campus, Poole BH12 5BB, United Kingdom
[c] CINBIO, Universidade de Vigo, Grupo GAME, Departamento de Física Aplicada, 36310 Vigo, Spain

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ABSTRACT

This research is based on the investigation of the tribological properties of a biodegradable polymeric ester lubricant (BIOE) additivated with two different pristine graphene nanoplatelets (GnPs), named as GnP7 and GnP40. These GnPs have lateral sizes of 7 and 40 μm, and thickness of 3 and 10 nm, respectively. Four different nanoadditive loadings: 0.015, 0.035, 0.055 and 0.075 wt% have been used. Stability of nanolubricants has been investigated using the visual control and the refractive index evolution during time, revealing a slightly better stability for the nanolubricants formulated with the largest lateral size graphene nanoplatelets (GnP40). The influence of the thickness and lateral size of these carbon-based nanoadditives on the antifriction and antiwear capabilities of BIOE is analysed. For this purpose, rotational friction tests were taken with the eight nanolubricants under a 20 N working load and 340 m sliding distance. All nanolubricants showed friction coefficients and worn area lower than those previously reported for the unadditivated BIOE. As regards friction, the ideal loading for both GnPs was 0.055 wt% GnP, being the best anti-friction behaviour obtained using GnP40 as additive (up to 26% reduction), whereas the 0.055 wt% GnP7/BIOE nanolubricant leads to the best anti-wear capability with wear reductions up to 56%. Finally, from Raman microscopy and roughness assessments on the worn surfaces, it can be determined that the good tribological performance of nanolubricants is owing to the protective film formation and surface repairing mechanism.

1. Introduction

Advanced lubrication is indispensable for improving durability, efficiency, mobility, as well as to reduce carbon emissions. From the energetic point of view, in 2017 almost a quarter (about 23%) of the worldwide total consumption of energy came from tribological contacts [1]. From the environmental point of view, most of base oils currently used in both automotive and industrial sectors are derived from crude oil, which have a negative impact not only on the soil, groundwater, vegetation, or animals, but also their mist affects health [2]. In this last work, Novak et al. [2] analyze the negative impact of lubricating oils on both the environment and health. These authors concluded that only biodegradable oils should be used if there is a risk that they may be released into the environment. Thus, it is crucial to develop enhanced and eco-friendly lubricants to diminish energy losses preventing the environmental pollution. In this vein, different researchers have also highlighted the necessity of biodegradable oils to substitute conventional lubricants [3,4]. Biodegradable oils provide important advantages over traditional oils, but still some disadvantages as low-temperature limitations [5]. Nevertheless, lubricants are not single-component systems, but different types of additives are blended, among them, tribological improvers, namely friction modifiers, and both anti-wear and extreme pressure additives [6]. In this regard, several researchers have proved significant tribological improvements through the dispersion of different nanomaterials (metals, carbon-based structures, oxides, among others) in conventional lubricants, as are reported in some current reviews [7–10]. Many mechanisms have been proposed to explain these improvements: rolling bearing effect, change of microstructure, surface repairing effect, tribofilm formation and synergistic effect, which were previously explained in detail [9,11–17].

* Corresponding author.
E-mail address: josemanuel.lineira@usc.es (J.M. Liñeira del Río).

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Graphene nanoplatelets (GnPs), that include short stacks of platelet-shaped graphene sheets, are carbon-based nanomaterials equal to those located in the carbon nanotubes walls, but with two-dimensional shape [18]. These nanopowders have been studied as lubricant additives by different authors [19–21], which have observed that using small quantities of GnP (0.02–0.5 wt%) as lubricant oil additives, both friction and wear performances can be improved. For example, Omrani et al. [19] achieved important friction and wear improvements (26% and 83%, respectively) adding 0.07 wt% of GnPs to canola oil. Furthermore, La et al. [20] observed that the addition of 0.05 wt% modified GnP additives to an engine oil, substantially improved the friction and anti-wear performance, with a decrease of 35% in the wear track. Moreover, Suresha et al. [21] proved that the addition of 1 wt% of GnPs to neem oil leads to the smallest friction coefficient and wear track, with reductions of 41% and 23%, respectively. In this work the influence of the lateral size of graphene nanoplatelets for different mass concentrations (0.015–0.075 wt%) on the friction and wear reduction of a biodegradable oil will be analysed.

2. Experimental section

2.1. Base oil and nanopowders

BIOE base oil is a biodegradable synthetic ester provided by Verkol Lubricantes, with a 0.9318 g cm^{-3} density and a 485.8 mPa s dynamic viscosity at 313.15 K and atmospheric pressure, besides has a viscosity index of 155.4 [22]. A BIOE sample was earlier characterized [22] through infrared spectroscopy (FTIR, VARIAN 670-IR) observing typical peaks of an ester: carbonyl stretching at 1743 cm^{-1} and the absorption of hydroxyl group at 1149 cm^{-1}, among others.

Pristine graphene nanoplatelets av-PLAT-7 (GnP7) and pristine graphene nanoplatelets av-PLAT-40 (GnP40) were supplied by Avanzare Innovacion Tecnologica S.L. Table 1 shows the main characteristics of these nanopowders, which were provided by the manufacturer.

In addition, a scanning electron microscope (SEM, Zeiss FESEM Ultra Plus) was utilized to characterize the morphology and size of nanopowders, using the following parameters: magnification of 100 kX, beam energy of 3 kV, working distance of 2.6 mm and an in-lens detector. Fig. 1 shows that both nanopowders present an almost square or rectangular laminar shape, with a little wrinkled appearance. It can also be seen that GnP40 nanopowders are larger than GnP7, which agrees with the supplier specifications (Table 1).

Infrared spectroscopy (FTIR, VARIAN 670-IR) technique was employed to find the characteristic functional groups of nanopowders. Fig. 2 shows the FTIR spectrum of both nanopowders (GnP7 and GnP40), revealing the same bands in both cases: a strong peak around 1000 cm^{-1} ascribed to C—O alcohol stretching, and very weak peaks attributable to other functional groups containing oxygen around 1450 cm^{-1}, 1730 cm^{-1}, and 3000 cm^{-1} assigned to O—H bending vibrations, C=O stretching, and O—H stretching, respectively [23].

Table 1
Main physical characteristics of pristine graphene nanoplatelets.

Properties	GnP7	GnP40
Lateral size (μm)	7.2	40
Average thickness (nm)	3	10
Oxygen content (%)	<1	<1
BET[a] (m^2/g)	70	22
Number of layers	5–10	<30

[a] Brunauer-Emmett-Teller (BET) surface area analysis

In order to complete the GnPs characterization, Raman spectra of GnP7 and GnP40 nanopowders were recorded with a confocal Raman microscope (WITec alpha300R+). Fig. 3 presents both Raman spectra, which exhibit the three characteristic bands of graphene derivatives around 1350 cm^{-1}, 1580 cm^{-1} and 2710 cm^{-1} that are assigned to the D, G and 2D bands [24]. The G band is owing to the bond stretch of pairs sp^2 atoms corresponding to chains and rings, D band corresponds to breathing of sp^2 rings atoms and the 2D one is due to the double resonant with two-phonon emissions. From the Raman spectra (Fig. 3) it can be concluded that both nanopowders are multi-layered due to the fact that the 2D band intensity is considerably lesser than that of the G band [20]. Furthermore, it can also be seen that the D band intensity is much smaller than that of the G band, especially in the case of GnP40 suggesting that these nanopowders have less defects and a lesser oxidation degree than GnP7 [25].

Finally, X-ray diffraction (XRD, Bruker D8 Advance) method was utilized to obtain the crystalline nature of both graphene nanoplatelets additives. In Fig. 4 it can be observed for both additives a characteristic peak around 2θ = 26.5° related to graphitic (002) plane [26]. In addition, a weak XRD peak at 2θ = 54.6° corresponding to the (004) plane is observed in the diffractogram of GnP7 [27]. In the case of GnP40 nanoplatelets, the intensity of this peak decreased to almost negligible, which is due to increased interlayer distances and a higher degree of exfoliation [28].

2.2. Nanolubricants formulation

BIOE based nanolubricants were prepared with different mass concentrations of GnP7 or GnP40 (0.015, 0.035, 0.055 and 0.075 wt%). These additive concentrations and the two-step method used to prepare them were selected based on previous work [29,30], respectively. The use of higher nanoadditive concentrations has been discarded, as our previous stability tests confirm that increasing concentration decreases the temporal stability of nanolubricants. Homogenization of nanodispersions is reached using an ultrasonic bath (Fisherbrand FB11203) for a 4 h continuous sonication time at an effective power of 180 W. Nanodispersions time stability was examined by two different methods: sediment photograph capturing technique and temporal evolution of the refractive index utilizing a Mettler Toledo RA-510 M refractometer [31].

2.3. Tribological tests

Friction coefficient tests for an AISI 52100/AISI 52100 tribological pair lubricated with the formulated GnP7 or GnP40 nanolubricants were conducted by means of a tribometer CSM Standard with a rotational ball-on-disk arrangement. The following conditions were used: 20 N load (maximum contact pressure, 1.8 GPa), 340 m sliding distance, 3 mm disk track radius, 0.10 m·s^{-1} sliding speed and room temperature. Set-up, experimental procedure, and characteristics of both specimens were previously detailed [32]. It should be noted that three replicates for each nanolubricant were performed to ensure the repeatability.

A 3D optical profilometer (Sensofar S Neox) in confocal mode (10×) was employed to analyse the wear generated during friction tests. Three different wear parameters were measured: wear track width (WTW), wear track depth (WTD) as well as worn area. To attain representative average values, these parameters were evaluated in three dissimilar areas for each worn track. Additionally, this device was employed to determine the roughness (R_a) of disk worn surfaces, according to the ISO4287 standard (Gaussian filter with cut-off wavelength of 0.08 mm). This analysis is helpful to describe the anti-wear capacity of each nanolubricant. To complete the anti-wear analysis of the nanolubricants, the confocal WITec alpha300R

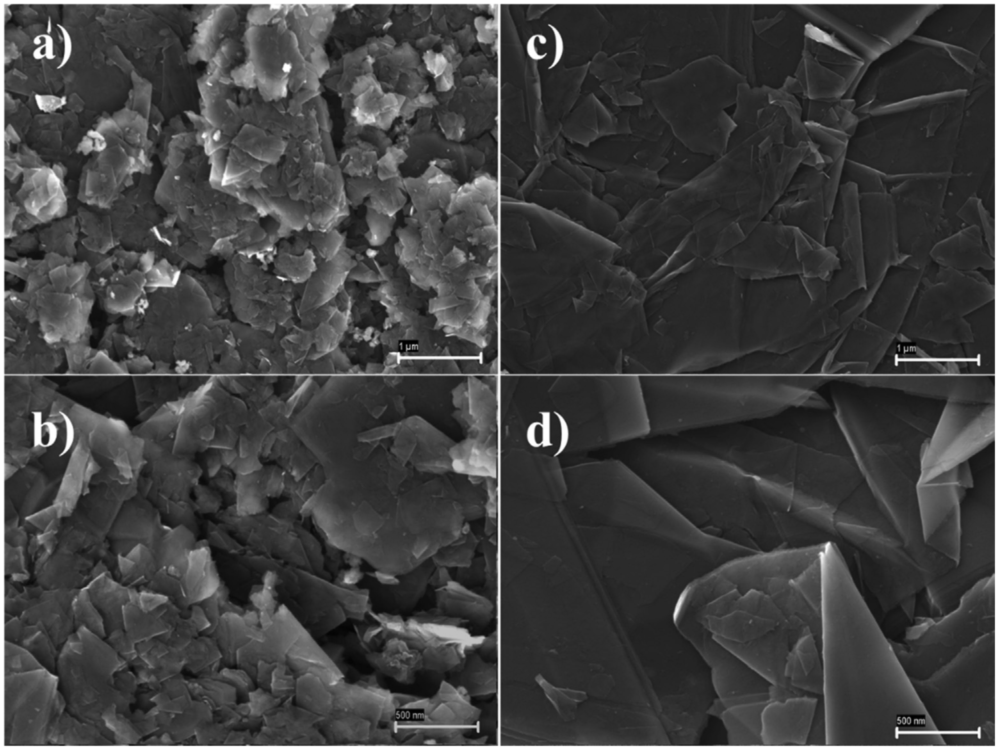

Fig. 1. SEM images of GnP7 (a, b) and GnP40 (c, d) nanopowders.

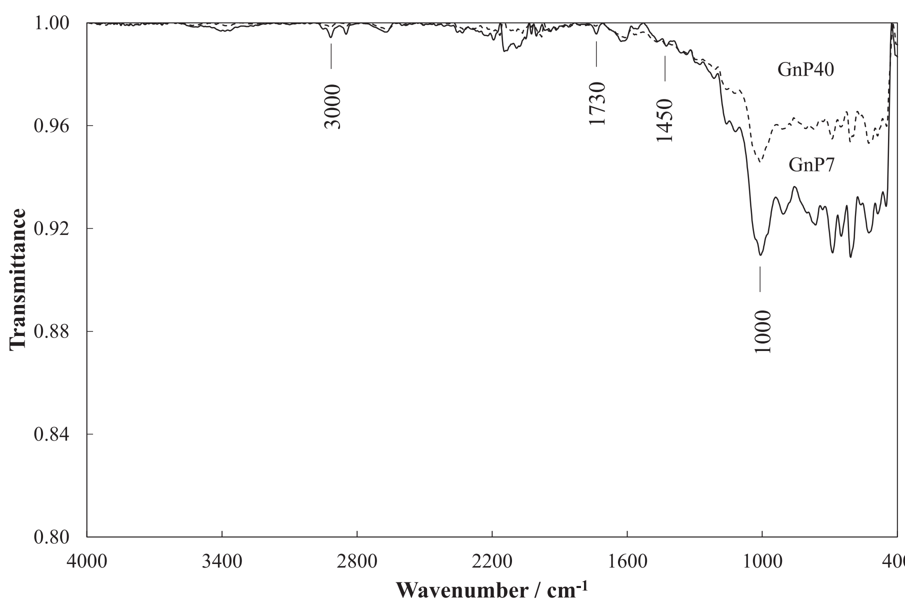

Fig. 2. FTIR spectrum of GnP7 (—) and GnP40 (—) nanopowders.

+ Raman microscope was utilized to map the worn scar surfaces, providing information of the nanolubricant components distribution (base oil and nanopowders) in the worn tracks, and about the produced tribological mechanisms.

3. Results and discussion

3.1. Stability of nanolubricants

Visual control was performed by keeping the nanolubricants at room temperature without any disruption. Fig. 5 shows photographs of the GnP7 and GnP40 based nanolubricants with 0.055 and 0.075 wt% nanopowder concentrations at different times. Visual sedimentation of the nanoadditives was not detected during the first four weeks after nanolubricants preparation as can be seen in Fig. 5.

On the other hand, for each nanolubricant, the refractive index (n) at 293.15 K was recorded as a function of the time (starting just after its sonication) using the aforementioned refractometer. Fig. 6 shows the temporal evolution of n for the nanolubricants with the highest loadings (0.055 and 0.075 wt%) of each nanopowder (GnP7 and GnP40). As can be observed, a good stability for all the pre-

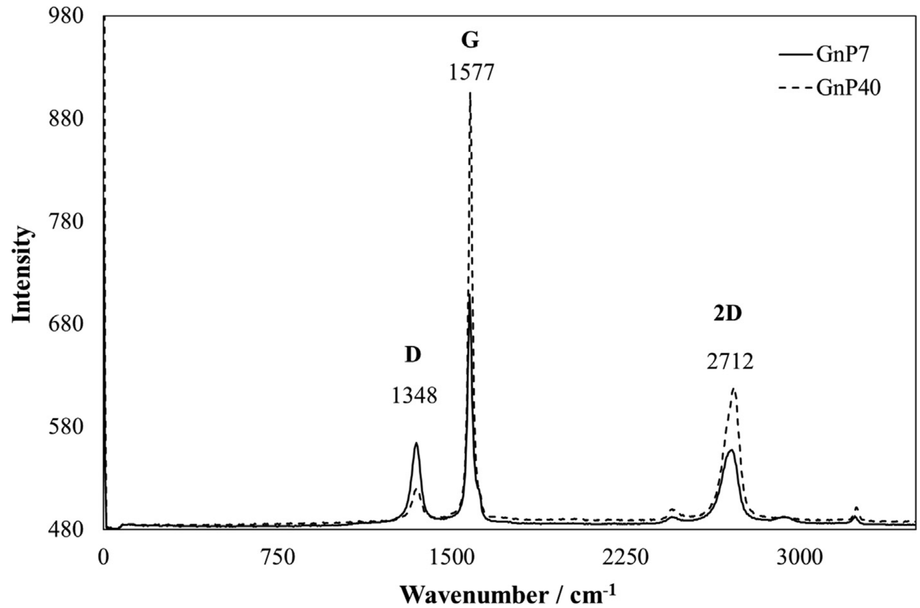

Fig. 3. Raman spectra of GnP7 (—) and GnP40 (—) nanopowders.

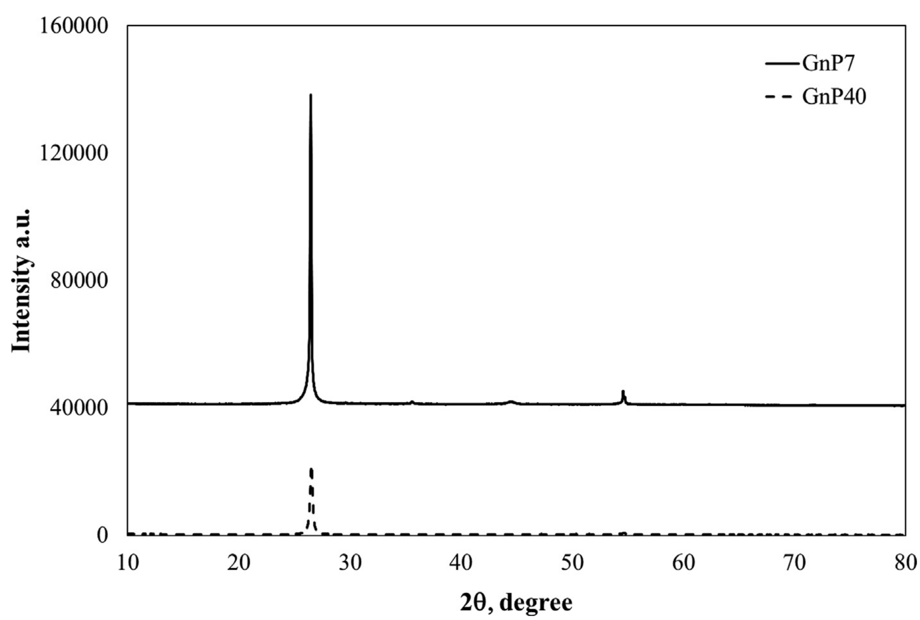

Fig. 4. XRD patterns of GnP7 (—) and GnP40 (—) nanopowders.

pared nanolubricants is obtained, the overall variation of n (over an interval time of 100 h) was 0.02% and 0.03% for GnP7 at 0.055 wt% and at 0.075 wt%, respectively, and 0.02% and 0.01% for GnP40 at 0.055 wt% and at 0.075 wt%, respectively. These results are lower than those found in previous works [31,33] for other base oils and nanoadditives, confirming the good temporal stability of the BIOE nanolubricants.

3.2. Tribological characterization

Table 2 reports the mean values of friction coefficients (μ) for the prepared nanolubricants based on BIOE. Friction coefficients achieved lubricating tribocontacts with nanolubricants based on GnP7 or in GnP40 are smaller than that previously obtained using the neat BIOE oil [22]. As Fig. 7 shows, the greatest friction decrease was reached with the nanolubricant BIOE + 0.055 wt% GnP40. Hence, a friction coefficient of 0.0757 was achieved for this nanolubricant against 0.1027 for BIOE [22], which implies a 26% reduction. Friction reductions for GnP7 nanolubricants range from 14% (for BIOE + 0.015 wt% GnP7) to 19% (for BIOE + 0.055 wt% GnP7) whereas for GnP40 nanolubricants range from 17% (for BIOE + 0.015 wt% GnP40) to 26% (for BIOE + 0.055 wt% GnP40). Therefore, a similar friction performance was observed for both type of nanolubricants, being slightly better for GnP40 nanolubricants. It is worth mentioning that an optimum concentration is reached (0.055 wt%) by using both nanoadditives, higher graphene loadings lead to a decreased efficiency [34]. To analyse qualitatively and quantitatively wear on disks after friction tests, 3D mappings and cross-sectional profiles of worn tracks were obtained (Fig. 8 and Fig. 9), measuring the following wear parameters for each lubricant (Table 2): WTW, WTD and worn area. For all the designed nanolubricants (based on GnP7 and GnP40), the three

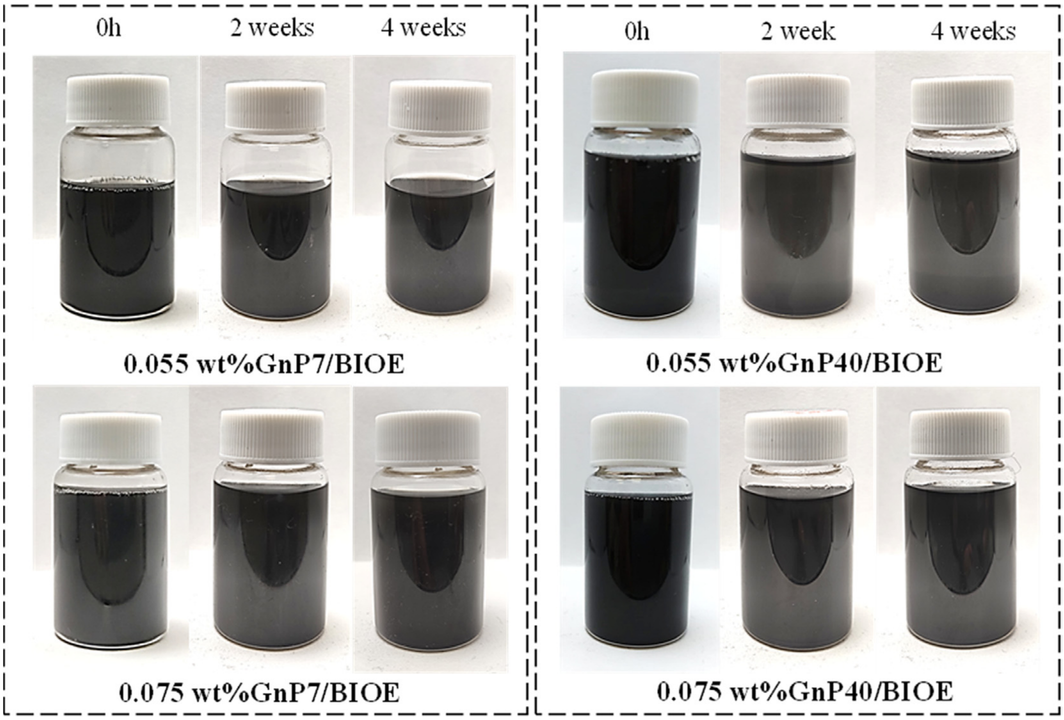

Fig. 5. Visual control images of GnP7 and GnP40 based BIOE nanolubricants.

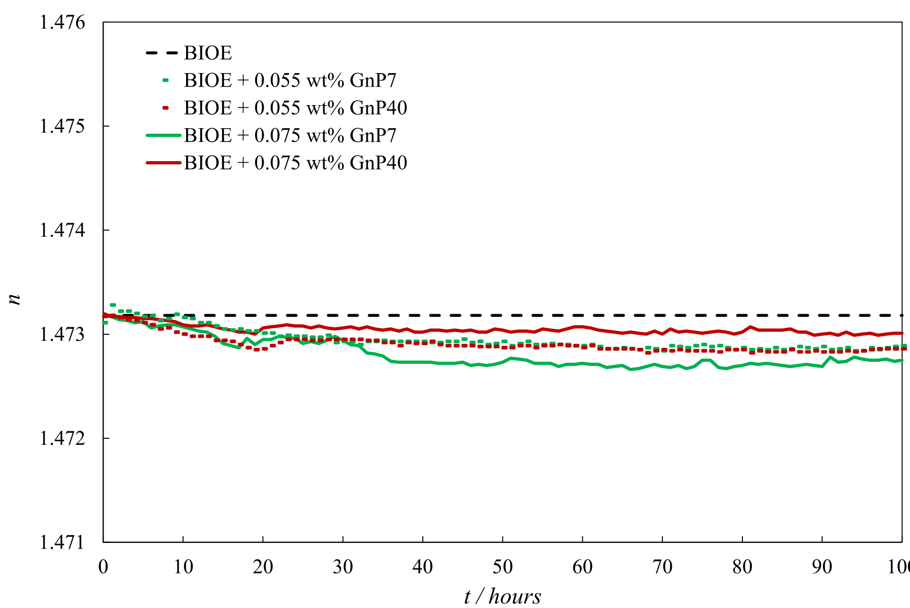

Fig. 6. Refractive index (n) evolution at 293.15 K for BIOE based nanolubricants.

Table 2
Average values of friction coefficients, μ, and of width, WTW, depth, WTD, area of the worn scar and their standard deviations, σ, for all tested BIOE nanolubricants.

Nanolubricant	μ	σ	WTW/μm	σ/μm	WTD/μm	σ/μm	Area/ $10^2 \mu m^2$	σ/ $10^2 \mu m^2$
BIOE + 0.015 wt% GnP7	0.0921	0.0026	256	15	1.26	0.11	1.10	0.17
BIOE + 0.035 wt% GnP7	0.0856	0.0040	239	12	0.88	0.12	1.21	0.20
BIOE + 0.055 wt% GnP7	0.0832	0.0017	224	11	0.80	0.11	0.87	0.11
BIOE + 0.075 wt% GnP7	0.0864	0.0018	255	13	1.06	0.14	1.65	0.16
BIOE + 0.015 wt% GnP40	0.0849	0.0059	247	12	0.91	0.12	1.24	0.18
BIOE + 0.035 wt% GnP40	0.0805	0.0031	249	11	0.95	0.10	1.24	0.14
BIOE + 0.055 wt% GnP40	0.0757	0.0030	249	11	0.98	0.13	1.37	0.17
BIOE + 0.075 wt% GnP40	0.0844	0.0053	250	13	0.92	0.11	1.21	0.15

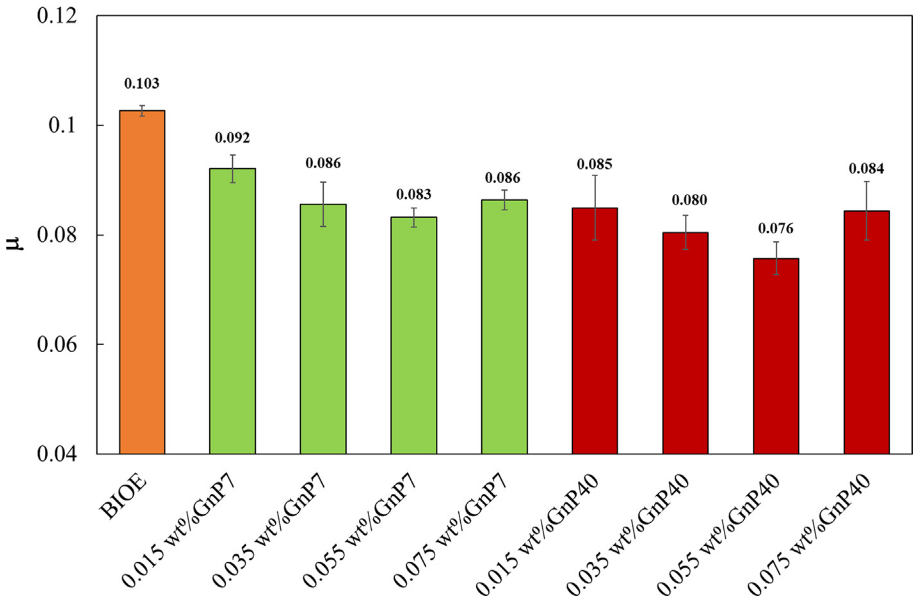

Fig. 7. Average coefficients of friction, μ, attained for all studied BIOE-based lubricants. The values for the neat oil (BIOE) were taken from [22].

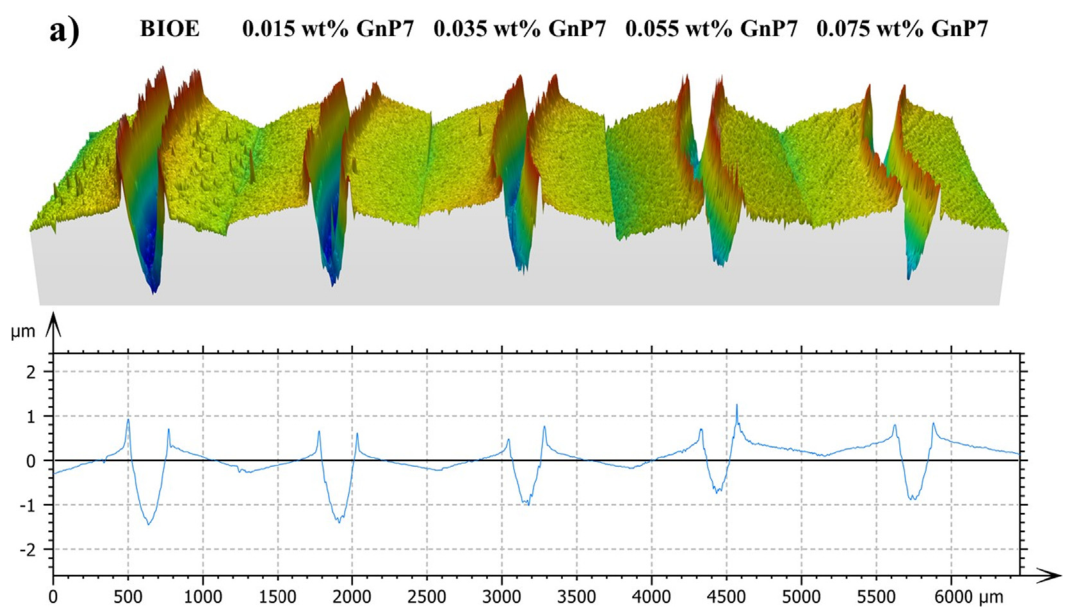

Fig. 8. 3D Surface topography and cross section profiles of worn tracks lubricated with BIOE [22] and a) GnP7 nanolubricants and b) GnP40 nanolubricants.

wear parameters are lesser than those for the unadditivated BIOE oil [22] (Fig. 8). Maximum wear reductions in WTW, WTD and area were obtained with the 0.055 wt% GnP7 nanolubricant. Hence, reductions of 17%, 42% and 58% were obtained, respectively. Regarding the GnP40 nanolubricants, wear hardly varies with the nanopowder load, the greatest anti-wear behaviour was reached for the 0.015 wt% GnP40 nanolubricant with decreases of 9% and 34% in terms of WTW and WTD, respectively. Then, the maximum wear parameter reductions were achieved adding 0.055 wt% GnP7 to BIOE. This can be explained by the larger surface area of this nanoadditive in relation with GnP40 (Table 1). A larger specific surface area favours the formation of protecting tribofilm in the tribo-contact surfaces through adsorption or chemical reactions, thereby preventing direct metal–metal contacts and reducing friction and wear [9,35].

Specific wear rates (Table 3 and Fig. 10) were calculated as follows [36]:

$$W = \frac{\Delta V}{F_n S_s} \quad (1)$$

where W is the specific wear rate ($mm^3\ N^{-1}\ m^{-1}$), ΔV is the volume loss (mm^3), F_n is the applied load (N), and S_s is the sliding distance (m). The volume loss can be determined from cross-section area (A) and the perimeter of the wear track (r):

$$\Delta V = 2\pi r A \quad (2)$$

Fig. 10 shows the specific wear rates on the worn disks tested during a 340 m sliding distance under 20 N load for the different lubricants used. A minimum specific wear rate value can be observed for the nanolubricant containing 0.055 wt% GnP7 which

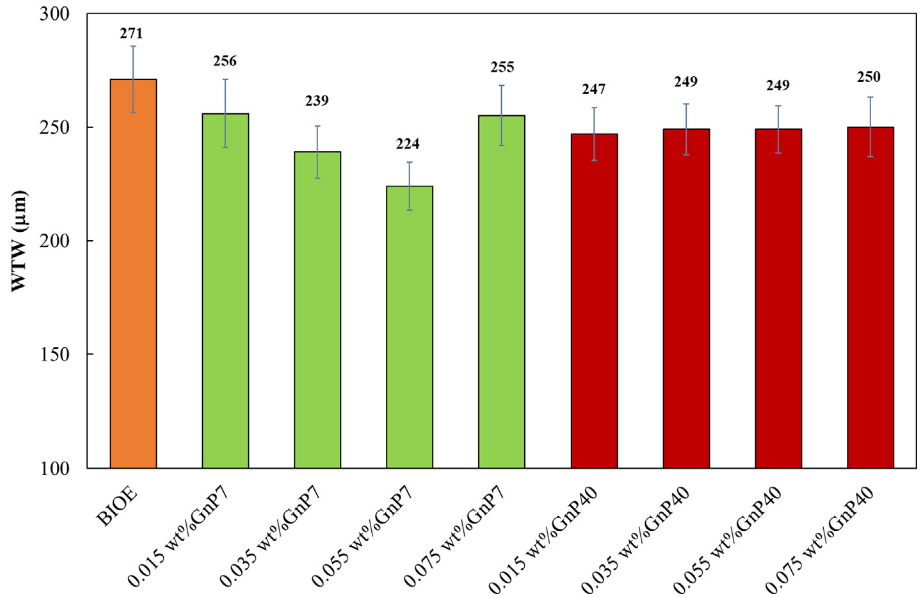

Fig. 9. Wear track width of disks lubricated with the BIOE-based lubricants. The values for the neat oil (BIOE) were taken from [22].

Table 3
Roughness, R_a, and specific wear rate, W, and their respective standard deviations, σ, of worn scars lubricated with the tested BIOE nanolubricants.

Nanolubricant	R_a/nm	σ/nm	W/10^{-11} mm^3 N^{-1} m^{-1}	σ/10^{-11} mm^3 N^{-1} m^{-1}
BIOE + 0.015 wt% GnP7	172	18	3.05	0.47
BIOE + 0.035 wt% GnP7	180	18	3.35	0.54
BIOE + 0.055 wt% GnP7	165	16	2.41	0.30
BIOE + 0.075 wt% GnP7	174	14	4.57	0.44
BIOE + 0.015 wt% GnP40	183	15	3.44	0.48
BIOE + 0.035 wt% GnP40	182	12	3.44	0.38
BIOE + 0.055 wt% GnP40	190	16	3.80	0.48
BIOE + 0.075 wt% GnP40	178	17	3.35	0.40

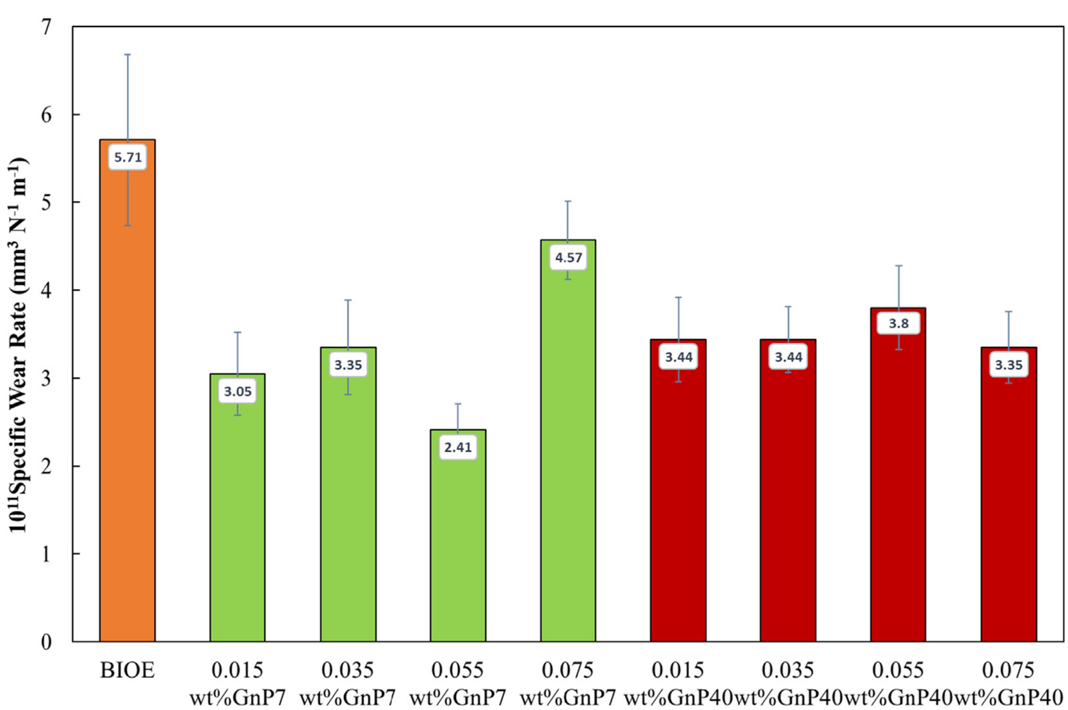

Fig. 10. Specific wear rate of disks lubricated with the BIOE-based lubricants.

significantly improves the wear resistance compared to engine oil, reaching a maximum improvement of 58%. The evolution of this wear parameter agrees with that obtained above for the wear track width (Fig. 9).

Roughness (R_a) of the worn tracks were also measured (Table 3) to compare the anti-wear nanolubricant ability. Lower roughness was obtained for the surfaces lubricated with each tested GnP nanolubricant than that lubricated with neat BIOE. Precisely, a R_a value of 210 nm was previously obtained for the lubricated BIOE worn track [22], whereas for the surface tested with the nanolubricant 0.055 wt% GnP7 the minimum R_a value was reached (165 nm) which implies a 21% roughness decrease.

In addition, analyzing wear results, all the wear parameters achieved from the wear tracks obtained using nanolubricants, are lower than those corresponding to neat BIOE. Thus, surface enhancement due to the presence of nanoadditives takes place.

From these results, in the case of nanolubricants containing GnP7, an optimal concentration of 0.055 wt% GnP7 in BIOE was found for friction coefficients and wear parameters. For the nanolubricants containing GnP40, the same optimal concentration (0.055 wt% GnP40 in BIOE) was found in the case of friction coefficients while the wear parameters barely varied with the nanoparticle loading. Optimal concentrations were also previously reported by other authors for nanodispersions containing different nanoadditives and base oils [37–39]. Thus, when the concentration is less than this optimal value, the amount of nanoadditives is insufficient to fully cover and protect the surface and beyond this optimum concentration an excess in nanomaterial loading could result in the formation of a discontinuous oil film [40]. On the other hand, we must consider that friction and wear are not material properties, but responses of the tribological system. It has been claimed that friction is strongly correlated with wear, but there is no simple relationship between both, and low friction does not always mean low wear [7,41–43]. So, when nanoadditive concentration increases, the number of particles in the contact increases, and, as a result, both the average particle/surface contact pressure and the plowing abrasive wear should decrease [44]. Thus, there are two competitive effects which may involve wear remains unaffected by nanoadditives loading as in the case of the nanodispersions containing GnP40.

Finally, with the aim of identifying the tribological mechanisms owing to the presence of nanoadditives, Raman microscopy and elemental mapping of the worn tracks of lubricated disks with neat BIOE and with the same concentrations of each carbon-based nanolubricant (0.055 wt% GnP7/BIOE and 0.055 wt% GnP40/BIOE) were performed through confocal Raman microscope at 532 nm wavelength. Raman spectrum of BIOE base oil was previously published [22]. Characteristic bands of each nanoadditive (Fig. 3) can be observed in the worn disks lubricated with nanolubricants. For instance, Fig. 11 reveals the unique presence of the biolubricant (green colour) in the form of stains deposited on the abrased surface. In the case of the steel surface lubricated with the 0.055 wt% GnP7/BIOE nanolubricant (Fig. 12), again the presence of the BIOE base oil is predominant, but the presence of

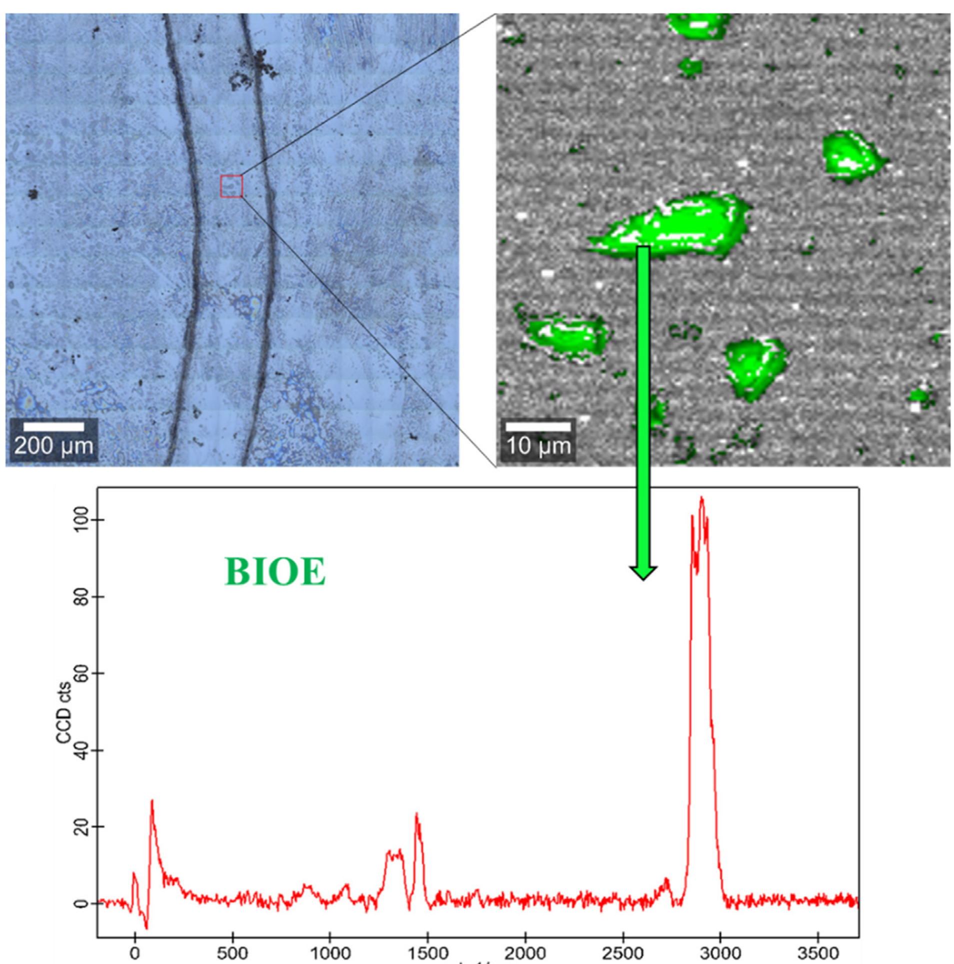

Fig. 11. Raman spectrum and elemental map of the worn track lubricated with BIOE oil.

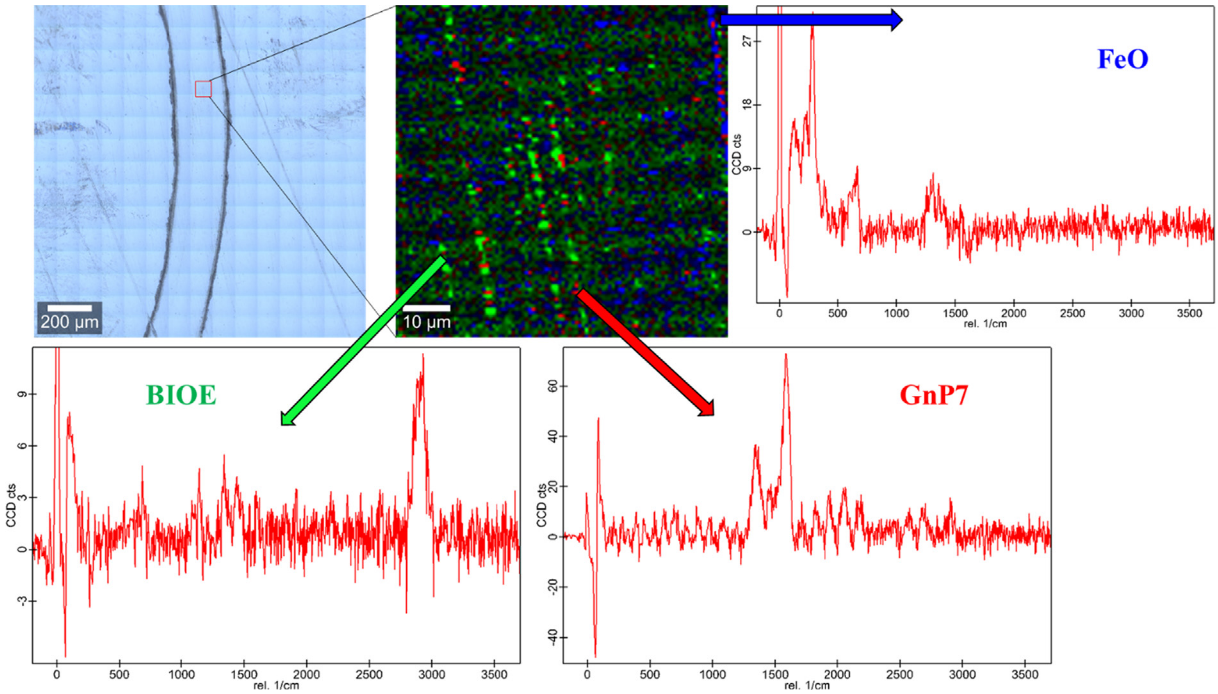

Fig. 12. Raman spectra and elemental map of the worn scar lubricated with 0.055 wt% GnP7/BIOE nanolubricant.

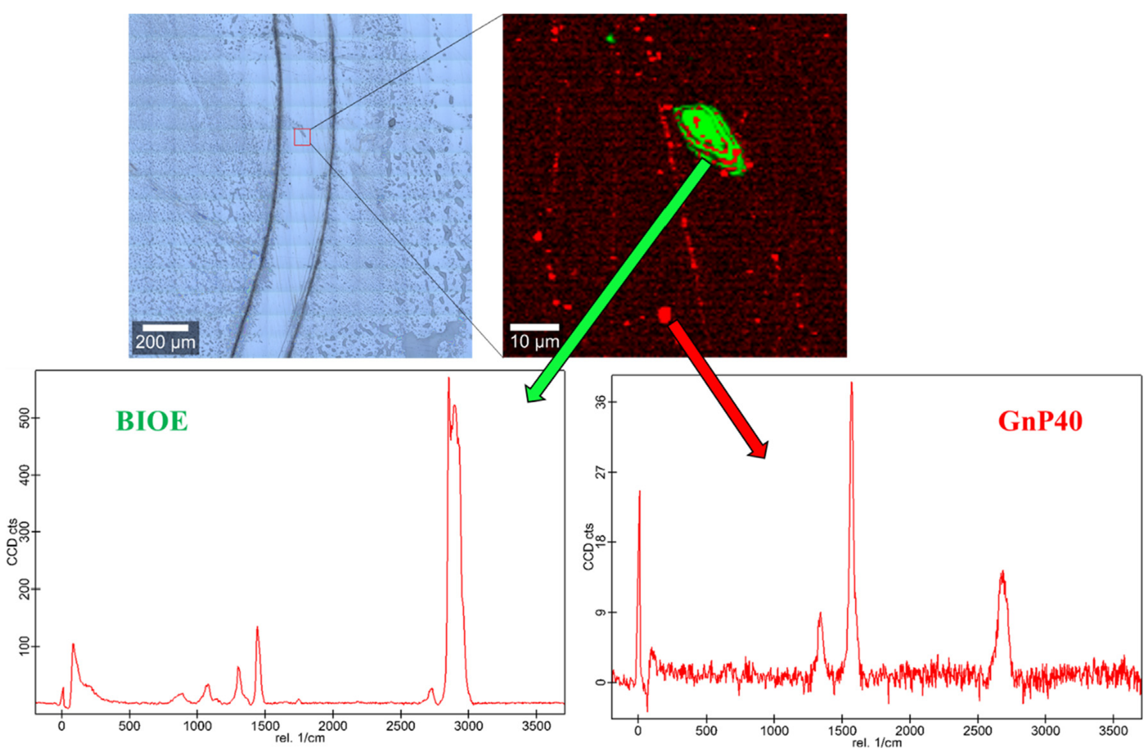

Fig. 13. Raman spectra and elemental map of the worn scar lubricated with 0.055 wt% GnP40/BIOE nanolubricant.

nanoadditive (GnP7) is also clear in form of spots (red colour). Traces of iron oxides were detected on the surface analysed (blue colour). Finally, Fig. 13 reveals again the existence of GnP40 nanoadditives deposited along the wear scars parallel to sliding direction (red colour), with a notable presence of BIOE (green colour). The detection of nanoadditives on worn tracks confirms their lubricating ability, improving the tribological properties (friction and wear) of the base oil through a) tribofilm formation which may be owing to the graphene overlapping with each other and general physical absorption at friction interfaces [12] and b) surface repairing mechanism, which consists of the deposition nanoparticles on the contact surface, forming a physical tribofilm that compensates for the loss of mass by reducing its surface roughness [3,45]. Another fact that supports the existence of this repair mechanism is the reduction in surface roughness (Table 3) obtained on the worn surfaces of the disks lubricated with nanolubricants compared to that when using the neat oil. Zhao et al. [16] have also reported reductions in wear and coefficients of friction due to the formation of tribofilms on interacting surfaces, detected by Raman analysis, when graphene with different degrees of exfoliation is used as a lubricant additive. These authors have concluded that graphene with a higher exfoliation degree can protect bigger surfaces than that with an inferior degree, hence enhancing the lubrication behaviour owing to a passivating effect [16].

4. Conclusions

In this work, the following findings were achieved:

- Good nanolubricant stabilities have been obtained dispersing, by the two-step method, commercial pristine graphene-based nanoadditives in a biodegradable oil, without the need of any additional functionalization.
- The results in terms of friction coefficient have been favourable for the eight designed nanolubricants. Friction reductions respect to that previously obtained with neat BIOE were obtained in all cases. The maximum reduction, $\sim$26%, has been achieved with the 0.055 wt% GnP40/BIOE nanolubricant.
- Wear parameters measured in the disks lubricated with the different nanolubricants were always lower than those found with the neat BIOE lubricant. The better wear behaviour was obtained with the GnP7/BIOE nanolubricant at 0.055 wt%, with reductions of 17%, 42% and 58% in WTW, WTD and worn area, respectively.
- Tribofilm formation and surface repairing lubrication mechanisms were noticed by Raman and roughness analyses.

CRediT authorship contribution statement

José M. Liñeira del Río: Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing. **María J.G. Guimarey:** Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Jose I. Prado:** Validation, Writing – review & editing. **Luis Lugo:** Supervision, Writing – review & editing. **Enriqueta R. López:** Supervision, Writing – review & editing. **María J.P. Comuñas:** Conceptualization, Supervision, Writing – review & editing.

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.

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