Review

Chemically modified nanomaterials as lubricant additive: Time stability, friction, and wear

Fátima Mariño [a], José M. Liñeira del Río [a,b], Enriqueta R. López [a], Josefa Fernández [a,*]

[a] *Laboratory of Thermophysical and Tribological Properties, Nafomat Group, Department of Applied Physics, Faculty of Physics, and Institute of Materials (iMATUS), Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain*
[b] *Unidade de tribologia, vibraçoes e manutençao industrial, INEGI, Universidade do Porto, Porto, Portugal*

A B S T R A C T

This work reviews the results on the temporal stability of nanodispersions containing chemically modified nanoadditives: carbon-based nanomaterials, metals, metal oxides, metal sulfides, nanocomposites, among others. Morphology, size, coating type and concentration of the NPs as well as the viscosity of the base oil are the main characteristics that affect stability. Coated spherical NPs with mean diameter lower than 20 nm are the most common among those which led to nanolubricants with stabilities longer than two months. The tribological results of the nanolubricants with stabilities higher than one month are also reviewed. Regardless the base oil, chemically modified nanoparticles reduced wear more than friction, reaching reductions of friction up to 75% and wear volume up to 99%. As for the tribological mechanisms involving chemically modified nanoparticles, the formation of adsorbed or tribochemical reaction films on worn surfaces were reported more often.

1. Introduction

At present, around 23% of the total energy consumed in the world is owing to friction and wear occurring in the tribological contacts of mechanical elements [1]. Of that, around 87% is used to overcome friction, and around 13% is used to remanufacture worn parts and spare equipment owing to the wear. According to Holmberg and Erdermir [1] calculations, worldwide, the overall economic costs due to tribological contacts in all societal sectors in 2017 were around $2500 \cdot 10^9$ euros/year of that around ¾ are owing to friction and ¼ is owing to wear. Furthermore, the amount of CO_2 emissions generated from friction and wear was estimated in more than 8,000 $MtCO_2$/year. The friction loss of the total energy used in the transportation sector is the greatest, being about 30% of the total energy use, in comparison with 20% in the manufacturing and power-generating industry and just 10% in the residential sector. Moreover, friction also causes severe problems such as surface corrosion and environmental contamination. Consequently, the reduction of friction and wear plays a crucial role in the extension of mechanical equipment service life, in saving energy and in emission decrease [1]. Lubrication is considered one of the most effective ways to save energy and increase the effectiveness of devices used in industries of different sectors [1,2]. Thus, lubrication is the procedure used to reduce friction and wear between two surfaces that move at a very short distance from each other, through the interposition of a substance called lubricant. A lubricant is a multicomponent mixture of different base oils and additives in a proportion around 90% and 10%, respectively. Many researchers considered diverse technologies to develop new procedures to substitute traditional environmentally harmful additives that cause adverse emissions and contain sulfur or phosphorous (for instance zinc dialkyldithiophosphate) studying environmentally friendly additives like many nanoparticles (NPs) [3,4]. Numerous studies show that several NPs used as additives have better tribological properties than traditional additives in lubricant bases used in different applications, such as wind turbines [5,6], automobile engines [7–11], transmission fluids for electric vehicles [12,13], cutting tools [14], among others. [1,3–5]. In fact, adding a small amount of NPs to a lubricant usually has favorable effects on both friction and wear reductions. Such improvement is owing to their small size, since nanoadditives can enter the contact area, causing a positive lubrication effect [11]. One of the main benefits of NPs as lubricant additive is their low volatility that prevents NP losses under high temperature conditions [15]. Furthermore, NPs are less chemically reactive than common additives, since their films are mechanically formed, so they do not react with other additives and, therefore, both the NPs and the other additives will be more durable [15].

Nomenclature

3-MPS	3-(Trimethoxysilyl)propyl methacrylate
AEAPS	3-(2-Aminoethylamino) propyldimethoxymethylsilane
APTES	(3-Aminopropyl)triethoxysilane
BA	Benzoic acid
CDs	Carbon dots
BHSN	Bifunctional hairy silica nanoparticles
COF	Coefficient of friction
CQDs	Carbon quantum dots
CNPs	Carbon nanoparticles
CTAB	Cetrimonium bromide
DDA	Dodecylamine
DDP	Dodecylphosphate
DETAS	N1-(3-trimethoxysilylpropyl) diethylenetriamine
DIOS	Dioctyl sebacate
DLS	Dynamic light scattering
DPA	Diphenylamine
DTS	Dodecyltrichlorosilane
GO	Graphene oxide
GOPS	3-Glycidoxypropyltrimethoxy silane
h-BN	Hexagonal boron nitride
HDA	Hexadecylamine
HSNs	Hairy silica nanoparticles
HTS	Hexyltrichlorosilane
IFs	Inorganic fullerene-like
IL	Ionic liquid
LA	Lauric acid
MADE	Maleic anhydride dodecyl ester
MTT	Montmorillonite
MWCNTs	Multi walled carbon nanotubes
NPs	Nanoparticles
OA	Oleic acid
ODA	Octadecylamine
OM	Oleylamine
OTES	Octadecyltriethoxysilane
OTS	Octadecyltrichlorosilane
PAA	Poly(acrylic acid) sodium salt
PAO	Polyalphaolefin
PEG	Polyethyleneglycol
PEI	Polyethylenimine
PLMA	Poly(lauryl methacrylate)
PSS	Poly(sodium 4-styrenesulfonate)
PVD	Physical vapor deposition
rGO	Reduced graphene oxide
SA	Stearic acid
ScA	Succinic acid
SPAN 80	Sorbitan monooleate
TMPTO	Trimethylolpropane trioleate
TOA	N,N-dioctyl-1-octanamine
UV–Vis	Ultraviolet–visible
W_{rate}	Wear rate
WSD	Wear scar diameter
WTW	Wear track width
W_{Vol}	Wear volume
ZDDP	Zinc dialkyldithiophosphate

Nevertheless, NPs still present several problems that limit their use in real applications in the industry. One of the main challenges of using NPs as additive is to achieve homogeneous and stable dispersions over time. The stability of a nanolubricant is the time that the NPs are suspended in the base oil without settling. Stability is a drawback that restricts both development and technical application of nanolubricants. Preparation of stable nanolubricants is a key step to achieve their use in industrial applications, such as in gearboxes or bearings of wind turbines or for lubrication of hybrid or electrical vehicles since long-term stability is needed [6,12,16–18]. After aggregation, sedimentation occurs. NPs tend to aggregate due to attractive van der Waals forces acting on each other [6,11]. To obtain a stable nanofluid, it is essential to overcome the attractive interaction between particles, which must be compensated with other types of forces [12]. A common solution is the addition of surfactants which work through two types of mechanisms: electrostatic stabilization with ionic surfactants that prevents agglomeration due to the presence of a double layer of electrical charges around the NPs, and steric stabilization in which surfactant molecules with long hydrocarbon
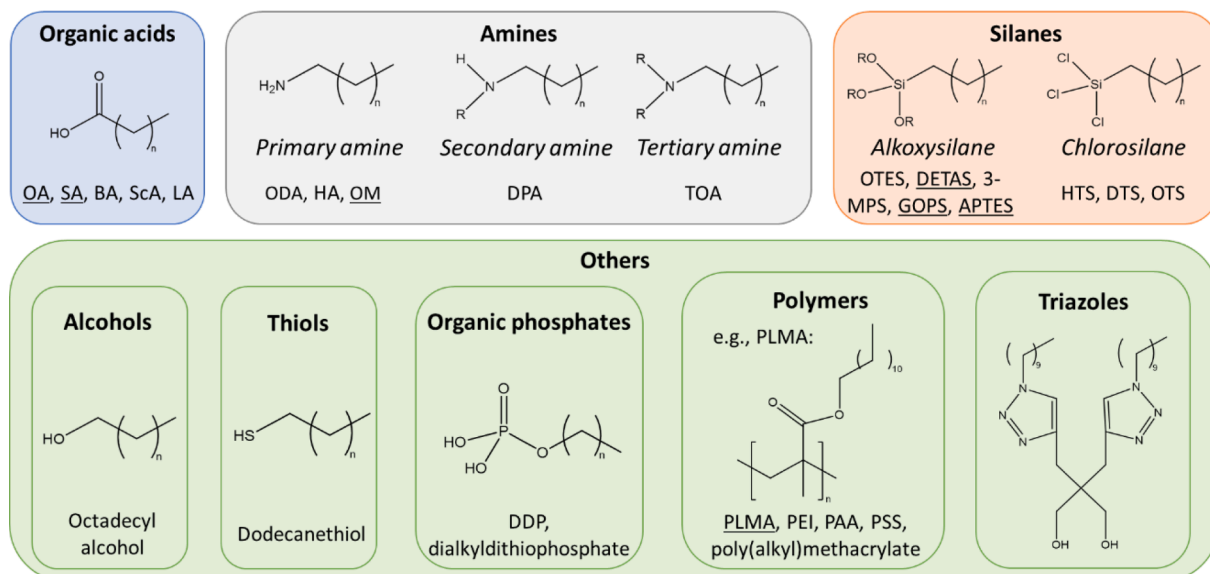

Fig. 1. Chemical structure of different NP modifying agents used in the literature. The names of the most common of each type are underlined.

chains surround the NPs create a steric barrier that separates the NPs from each other [19–22]. Electrostatic stabilization is the dominant mechanism of water-based dispersions. The use of surfactants may hinder the reduction of friction and wear produced by NPs [23], changes the formulation of the lubricant, and also does not usually lead to long-term stability (several months) [24]. Regarding oils, in addition to the use of non-ionic surfactants, there is another strategy to increase the stability time of the nanodispersions, which consists of the chemical modification of the NPs [25–27]. Of these two existing strategies [24], in this work we focus on the modification through covalent bonds of the surface of NPs with molecules of different type as organic acids, amines, silanes, organic phosphates, polymers, alcohols, among others (Fig. 1), the first three being the most common (Fig. 2). In all these cases, the molecules are chemically bonded to the surface of the NP and, in addition to their functional group that reacts with its surface, have long nonpolar chains at the other end of the molecule, which are capable of stabilizing the NPs in the oil [24]. Among the main conclusions of Chen et al. [24] review is that chemical coating with amphiphilic molecules is appropriate for stabilizing NPs with size smaller than 50 nm whereas for larger NPs, alkoxysilanes are better. These authors also indicate, based on theoretical analysis, that steric stabilization plays a more important role than other mechanisms because of the nonpolar nature of most of lubricating oils. On the other hand, the way most solvents perform is *like dissolves like,* thus it is generally agreed that a nonpolar compound will better solubilized in a nonpolar base fluid rather than in a polar one [19], although this is not exactly the case of nanomaterials, dispersing rather than dissolving in the base fluid. This rule has been modified to *like seeks like,* then including interactions with surfaces [28]. Thus, this rule, referred to nanomaterials, means that solvents will better disperse nanomaterials with similar surface chemistry [29].

This work is a review of published literature on non-aqueous lubricants containing chemical modified NPs. The article is organized in two parts. In the former, a review on the literature results of time stability of this type of nanolubricants for different types of base oils is presented. In the term chemical modified NPs, it is included not only surface-functionalized NPs but also oxygen reduction of nanomaterials [42,43]. Secondly, the tribological results (friction and wear) obtained with the nanolubricants with stabilities longer than four weeks are analyzed. According with the scarce literature [16,30–35], it seems that surface-functionalized NPs should have better tribological properties as additives than those of the corresponding bare NPs. The coating avoids material transfer, preventing direct contact and cold-welding between rubbing surfaces. Furthermore, the hybrid structure of functionalized NPs contains a rigid core and a soft shell which permits high load carrying capacities and has no negative effect on lubrication [30]. Thus, the functionalized NPs maintain the rigidity of the corresponding bare NPs thanks to the rigid core, whereas the soft shell is flexible and slippery

[33]. Therefore, compared to bare NPs, surface-modified NPs offer unique advantages. For instance, improvements in friction and wear properties were found by several authors [16,31–34] when functionalized NPs, compared to bare ones, were tested. Thus, Yegin et al. [33] examined how the addition of octadecyltrichlorosilane (OTS) functionalized silica NPs in an ionic liquid (IL, 1-butyl-3-methylimidazolium (trifluoromethysulfony)imide) affects the IL tribological properties under different lubrication conditions. Optimum concentrations of 0.05 wt% for uncoated silica NPs and at 0.10 wt% for OTS-functionalized silica NPs were found. These authors found that, at the optimum concentration, the IL additivated with functionalized NPs leads to a friction coefficient (COF) decrease of 37% compared to neat IL and of 17% compared to IL additivated with uncoated silica NPs. Srinivas et al. [32] modified multi walled carbon nanotubes (MWCNTs) with cetrimonium bromide (CTAB) or with sorbitan monooleate (SPAN 80) and tested them as additives for a diesel engine oil, finding that the surface modified nanoadditives improved the engine oil tribological properties whereas unmodified NPs lead to no improvements. Samanta et al. [31] functionalized graphene oxide (GO) with octadecylamine (ODA) finding that, when it is dispersed in heavy paraffin oil, hydrophobic GO-ODA NPs perform much better under low load conditions because of the presence of long hydrocarbon chains that act as a shield between the contact surfaces, while hydrophilic GO works better in the high load regime because it adheres onto surfaces when pressed under high pressure. Sade et al. [34] tested WS$_2$ nanotubes and two different grades of inorganic fullerene-like NPs (IFs), functionalized by a humin-like conformal shell, as additives for a polyalphaolefin (PAO4) oil. These authors found that the coating of WS$_2$ IFs leads to improvements in friction and wear comparing to the non-coated NPs, while they did not find any improvement in antifriction and antiwear capacity due to the functionalization of the WS$_2$ nanotubes. Saidi et al. [16], using octyl- and octadecyl- trichlorosilane as surface hydrophobization agents to improve the stability of MoS$_2$ nano-additives formulations in a wind turbine oil, found that both coated additives led to a strongly better antifriction and antiwear capacities than those of the corresponding bare MoS$_2$ NPs. Nevertheless, Viesca et al. [35] found that the addition of carbon-coated copper NPs decreases wear and increases the loading capacity of PAO6, but coated Cu NPs do not perform better than pristine Cu. Thus, the varied results indicate that this is an open field of research.

2. Nanolubricants stability

Long-term stability is a fundamental requirement for nanolubricants to be used in real applications. To obtain stable suspensions of NPs in lubricant oils, there are some strategies presented below. In addition, techniques for evaluating stability time are discussed.
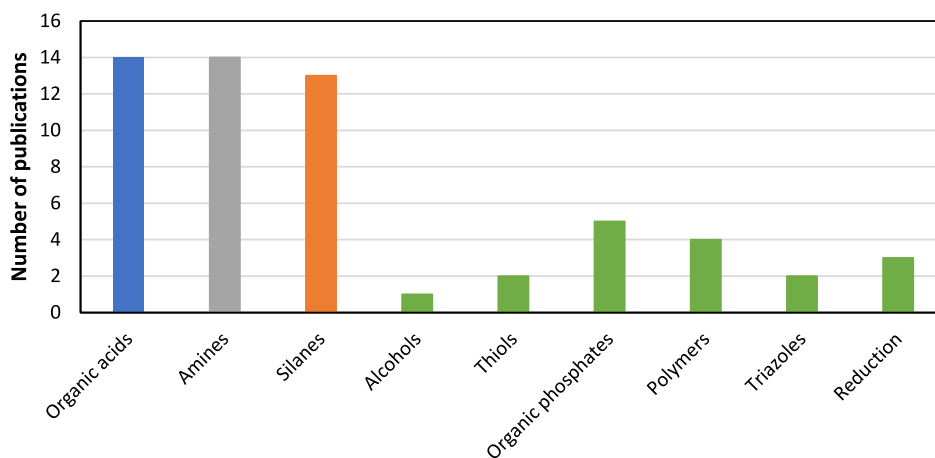

Fig. 2. Number of publications reviewed for each the type of modifying agent.

2.1. Techniques used to improve the nanolubricant stability

-*Preparation of nanodispersions:* It is generally considered that there are two main methods for preparing nanolubricants: single-step method and two-step method [36–38]. In the former, the production of NPs and their dispersion in the liquid occur simultaneously [11]. Vapor deposition is the single-step method most frequently used: the raw material is heated and evaporated in a resistively heated crucible, the vapor is condensed into NPs when it contacts with a flowing low vapor pressure liquid [36,39]. If the raw material is a liquid or solid this procedure is based in physical vapor deposition (PVD), and it is named one-step *physical* method. With this method only small amounts of NPs can be synthesized, which limits their application on an industrial scale. Zhu et al. [40] developed the one-step *chemical* method by preparing nanofluids under microwave irradiation. Mineral-oil-based nanofluids including silver NPs with a narrow size distribution (9.5 ± 0.7 nm) were prepared by one-step chemical method, but it was needed to use a surfactant to stabilize the nanofluid [41]. The one-step chemical method combines the synthesis of NPs with the preparation of nanofluids. With this method it is possible to control the particle size, reduce the agglomeration of NPs, and produce nanofluids containing metallic NPs [42]. However, it is difficult to prepare nanofluids with a high concentration of NPs using this last method. Nevertheless, with the single-step methods good stability results as well as a small agglomeration of the NPs are usually achieved but they are quite expensive and if the reactants are not completely transformed into products, there will be impurities in the nanofluid [38], making difficult to clarify the effect of NPs on the nanodispersion properties without removing impurities. In addition, these residues could negatively affect the tribological behavior and dispersion stability of the formulated lubricating oil.

Alternatively, in the two-step method, the NPs in dry powder form are incorporated into the base oil and the resulting dispersion is homogenized (Fig. 3). Such homogenization is usually carried out by ultrasonic stirring. For this purpose, an ultrasound tip or/and bath are used and different parameters such as power, shaking mode or sonication time are modified until the optimal conditions are found. An advantage of this method is the easy control of size of the NPs, since a wide variety of NPs with different sizes are commercially available. The two-step method is the most broadly used to formulate nanolubricants and thermal nanofluids as it is the most economical [19].

For nanodispersions containing ILs and NPs as hybrid additives of oils, Sanes et al. [43] designed a modified two-step method. In this case, nanopowders are added to the IL in an agate mortar being both mechanically mixed for 5 min and then mixed with the base oil. Finally, the nanodispersions are homogenized by means of an ultrasound bath. Using this method, Nasser et al. [44] obtained stabilities longer than eight months. Ali and Xianjun [45] proposed another method that includes mechanical stirring to mix the base oil and the IL with a magnetic stirrer and then adding the NPs to the liquid mixture using a probe sonicator and a ultrasonic vibration bath to disperse them. Stability

times up to 70 days were obtained for the lowest concentrations of NPs.

Another interesting method to improve the dispersion stability is the *four-step method* reported by Sui et al [25,46–48], which is based on an azeotropic distillation (Fig. 4). Firstly, a dispersion of ethanol and NPs is mixed with toluene and, after the evaporation of ethanol at 70 °C, PAO is added to the nanodispersion with fast stirring. Finally, the dispersion of the NPs in PAO is obtained by removing toluene by evaporation in an oven [48]. The stability results obtained through this method by Sui et al. [46] were better than those of the same dispersions prepared by the two-step method.

Recently, Liñeira del Río et al. [49] designed an efficient method to prepare nanodispersions (Fig. 5), in which superparamagnetic NPs, suspended in cyclohexane after the synthesis, are transferred to another highly volatile solvent by centrifugation. Subsequently, the NP concentration was obtained by thermogravimetry, and the dispersion was added to the base oil and blended with an ultrasonic bath and an ultrasonic probe sonicator for a total time of 15 min. Then, the solvent was evaporated with a rotary evaporator, obtaining the superparamagnetic nanolubricants. Finally, these nanolubricants were sonicated in the ultrasonic bath for 4 h. With this procedure, the nanodispersions are stable more than eleven months.

-*Use of dispersants:* As aforementioned to obtain more stable dispersions, surfactants are widely used. There are numerous different types such as oleic acid [49], alkyl phosphates [50], toluene [51,52], ionic liquids (ILs) [6,53,54], among others. Toluene modules the oil polarity of the nanodispersions, due to its small dipole moment, keeping the nonpolar base oil and NPs in a stable solution as a colloidal suspension [51]. Ionic liquids are considered outstanding dispersants for the stabilization of well-characterized nanomaterials [43,55–57], these compounds were also analyzed as hybrid lubricant additives in combination with NPs. For instance, Liñeira del Río et al. [54] examined the stability of a polyester base oil additivated with hybrid nanoadditives (hexagonal boron nitride, h-BN NPs and a phosphonium IL) obtaining temporal stabilities even longer than 3 weeks. Furthermore, Nasser et al. [44,53] studied the stability of h-BN NPs or GnP combined separately with three phosphonium ILs as hybrid nanoadditives in a polyalphaolefin (PAO32), finding stabilities higher than 150 days with the ILs based on the trihexyltetradecylphosphonium cation. It should be considered that surfactants can modify lubricant properties such as viscosity and antifriction and/or antiwear capabilities. For this reason, it is important to analyze the lubricants properties after the dispersant's addition.

-*Chemical modification of surface of NPs:* it is the most recent strategy to stabilize the NPs in the base oil [24], which was explained in the previous section. This type of stabilization is continuously developing. Usually, organic compounds with polar groups, among them dispersants, and compounds with long hydrocarbon chains and different polar functional groups (silanes, amines, carboxylic acids, alcohols, thiols, …) are used as modifying agents of the NP surface to have good dispersibilities in base oils [49,58,59]. There are other types of chemical modifications that improve the stability against sedimentation such as a
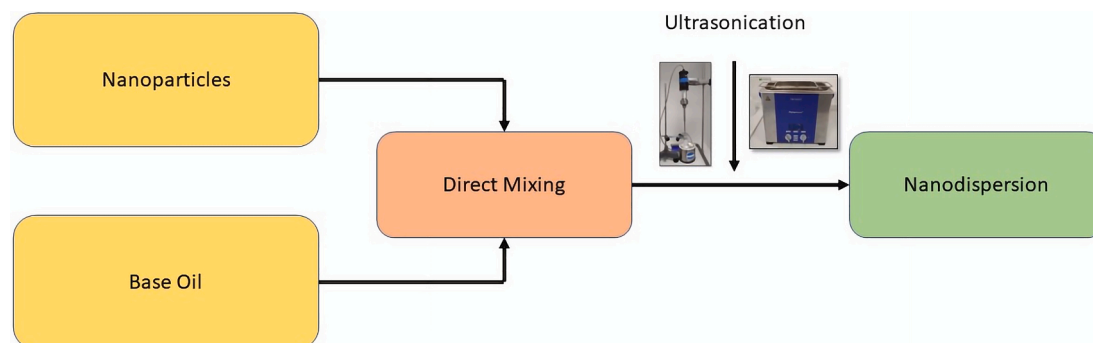

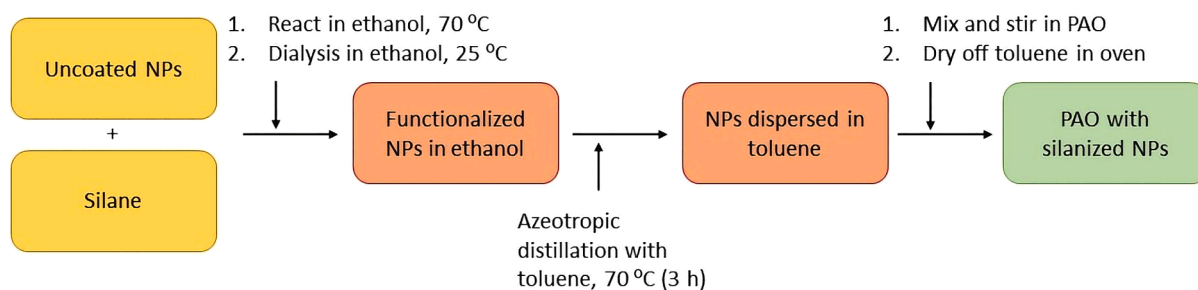**Fig. 3.** Two-step method for the preparation of nanodispersions.

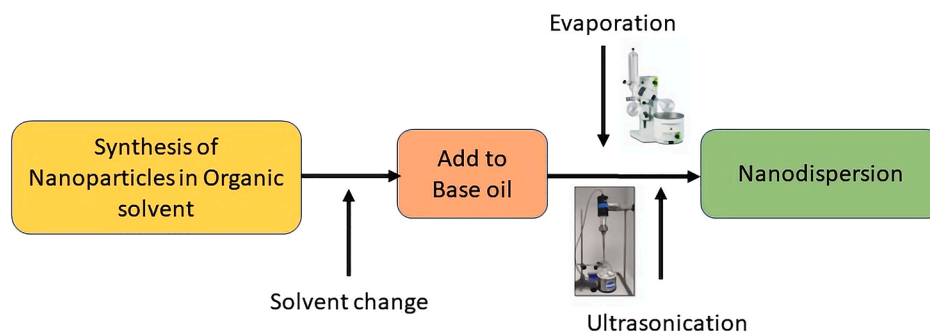**Fig. 4.** Scheme of four-step method based on azeotropic distillation.

Fig. 5. Preparation process of nanodispersions by Liñeira et al. method [49].

simple oxygen reduction [60,61].

2.2. Techniques to evaluate the nanolubricant stability

There are numerous techniques to analyze and quantify the stability of nanodispersions against sedimentation [19] such as sediment photograph capturing, refractometry, UV–Vis spectrophotometry, turbidimetry as well as dynamic light scattering (DLS). Nonetheless, most of them have some limitations due to some aspects as it is presented below.

Sediment photograph capturing: it is the easiest and most economical way to evaluate the stability of the nanolubricants. This process, also named visual inspection, is carried out taking photos of the nanodispersions over a period of time [62]. It is the most broadly used to have a qualitative notion of the stability of the nanolubricants [63]. In this evaluation technique, the nanodispersions must be kept under controlled conditions and without any alteration during analysis. It should be noted that the only limitation of this technique is that for dark nanodispersions it is sometimes difficult to see the sedimentation clearly. Usually, authors complement this procedure with other quantitative methods.

Dynamic light scattering (DLS): this technique is used to determine the size distribution of the aggregates of NPs in the lubricant [60,63,64]. The stability of nanodispersions is given by the evolution of the average size of the aggregates: if it increases over time, agglomeration occurs while if it decreases sedimentation takes place. In the case that the average size of the aggregates remains constant it can be considered that the nanolubricant is stable. However, this technique has a limitation for opaque nanolubricants because it is very difficult to obtain representative values of average particles size. Some authors analyze the size distribution of the aggregates of the nanoadditives of the formulated lubricants diluting them or transferring the NPs to a solvent in a very dilute concentration [65,66]. It is expected that the aggregate size distribution changes when both the base fluid and/or the concentration change [46,67].

Multiple Light Scattering technology consists of capturing and analyzing the intensity of the resulting light backscattered by the particles of a sample. When a liquid dispersion has a certain particle concentration, the light that hits one particle is scattered to hit nearby particles, finally being backscattered towards a backscattering detector. The intensity of light captured in this detector is directly related to the concentration, the average particle size, and the degree of dispersion of the sample. Turbiscan is a device that allows characterizing the stability of liquid dispersions, both at very low and at high concentrations, thanks to the Multiple Light Scattering technology and the two light transmission and backscattering detection systems [68,69]. It is common to use this device to characterize the coalescence, sedimentation, flotation, phase separation as well as to determine the average size of aggregates. Nevertheless, the use of this device to evaluate the stability of nanolubricants is quite scarce [69].

Evolution of refractive index is a stability characterization method developed by Guimarey et al. [70,71] based on the measurement of the refractive index of the nanodispersion over time. Nanodispersions are considered stable when the refractive index hardly varies with time, nonetheless when the NPs settle the refractive index changes [60,72].

UV–Vis spectroscopy is a conventional technique used to analyze the stability of nanodispersions. The decrease in the absorbance level indicates the sedimentation of NPs. Nevertheless, at the usual concentrations of NPs in nanolubricants for which wear and friction are considerably reduced, the signals from both devices show saturation because they are usually too opaque and absorbance is too strong [71]. To avoid this issue, some authors dilute the dispersion [19,65,73]; however, this method is not rigorous since the stability of the nanodispersions strongly depends on the concentration of NPs and the dilution will only give information about the stability of less concentrated nanodispersions [52].

2.3. Stability times of nanolubricants containing chemically modified NPs

In this section, the main literature results on the stability of lubricants containing chemical modified NPs are reviewed. In this regard, stability results with different types of functionalized NPs such as: carbon-based nanomaterials (Table 1), metals (Table 2), metal oxides (Table 3), metal sulfides (Table 4), other NPs (Table 5) and

Table 1

Stability of nanolubricants based on modified surface carbon-based nanomaterials.

Nanoadditive	Functionalization	Concentration	Base oil	Stability	Ref.
Graphene Nanosheets	Fluorine	NA	GTL-8	7 days	[90]
GO	DDA	0.1 wt%	5W30	32 days	[73]
GO	ODA	0.04 g L^{-1}	10W40	1 month	[83]
GO	DDP	0.1–0.5 g L^{-1}	Mineral oil	10 days	[91]
GO	OA	0.5–2 wt%	PAO12	7 days	[92]
rGO	ODA	0.04 g L^{-1}	10W40	>1 month	[58]
rGO	ODA	0.05 wt%+1 wt% IL	Ester Oil	28 days	[89]
rGO	PEI-PAA or PEI-PSS	1 g L^{-1}	Paraffin oil	2 months	[84]
rGO	OTS	0.04 wt%	Polyol ester	20 days	[81]
rGO	Octadecyl alcohol	0.01 wt%	Mineral oil	1 month	[85]
rGO	Triazole	0.01 wt%	500N	1 month	[93]
rGO	Reduction	0.01 wt%	Mineral oil	45 days	[74]
rGO	Reduction	0.50 wt%	PAO6	4 days	[61]
rGO	Reduction	0.25 wt%	TMPTO and PAO40	10 days	[60]
MWCNT (20–40 nm)	SA	0.45 wt%	Paraffin oil	6 months	[82]
CNPs (25–35 nm)	OM	1 wt%	PAO10	3 months	[94]
CDs (4.2 nm)	HDA	1 wt%	PAO4	3 months	[86]
CDs (4–12 nm)	N-OM	1 wt%	PAO	1 month	[87]
	N	1 wt%	PEG	1 month	
CQDs (2 nm)	DPA	0.2 wt%	Castor Oil	5 months	[88]
CQDs (4 nm)	DPA and OM	2 wt%	PAO6	<3 months	[88]

Table 2

Stability of nanolubricants based on modified metal NPs.

Nanoadditive	Functionalization	Concentration	Base oil	Stability	Ref.
Ag (4 nm)	Dialkyldithiophosphate	0.5 wt%	Paraffin oil	Several months (r.t.)* 3 days at 140 °C.	[95]
Ag (3–6 nm)	Dodecanethiol	0.5 wt%	PAO4	Several months	[96]
Ag (15 nm)	Dialkyldithiophosphate	0.5 wt%	Paraffin oil	5 days	[97]
Cu (5 nm)	Dialkyldithiophosphate	0.5 wt%	Paraffin oil	Several months (r.t.) 3 days at 140 °C.	[95]
Pd (2–4 nm)	Dodecanethiol	1.0 wt%	PAO4	Several months	[96]
Ni (7 nm)	OM and OA	0.025 wt%	PAO6	1 month	[98]

*r.t.: room temperature.

Table 3

Stability of nanolubricants based on modified metal oxide NPs.

Nanoadditive	Functionalization	Concentration	Base oil	Stability	Ref.
TiO$_2$ (15 nm)	PLMA	1.0 wt%	PAO4	56 days	[99]
TiO$_2$ (20–25 nm)	2-octyldodecyl gallate	1.0 wt%	PAO10 10 W30	3 days 5 days	[102]
Al$_2$O$_3$ (78 nm)	GOPS	0.05 wt%	N.A.**	50 days	[103]
ZnO (10–30 nm)	OA	0.5 wt%	60SN	12 h	[100]
ZnO (10 nm)	OA	0.25 wt%	PAO40	29 days	[101]
Fe$_3$O$_4$ (6.3, 10 nm)	OA	0.015 wt%	TMPTO	11 months	[49]
Nd alloy (19 nm)	OA	0.015 wt%	TMPTO	11 months	[49]

**Not available.

Table 4

Stability of nanolubricants based on modified metal sulfide NPs.

Nanoadditive	Functionalization	Concentration	Base oil	Stability	Ref.
IF-WS$_2$ (<150 nm)	OTS DTS HTS	1.0 wt%	Paraffin oil	4 days 14 days 8 days	[104]
WS$_2$ (6–8 nm)	OM	2.0 wt%	PAO6	6 months	[105]
WS$_2$ (6–8 nm)	OM and MADE	2.0 wt%	DIOS	6 months	[106]

nanocomposites (Table 6) are presented. The analyzed base oils include mineral (groups I, II, III), synthetic (polyalphaolefins, PAO; esters; polyethylene glycols, PEG) and vegetable oils. Fully formulated oils are included but aqueous lubricants are not considered here. Tables 1-6 also indicate the modifying agents of the NPs surface such as amines, organic acids, alcohols, thiols, organic phosphates, polymers, and silanes. In addition, several authors obtained remarkable stabilities by reducing carbon derivative nanomaterials [74]. Apart from the presence of "functionalities", the size, and shape of the nanoadditives as well as their concentration have a great impact on the stability of the dispersions. Thus, for the spherical NPs, their sedimentation velocity is proportional to the square of the radius according to the Stokes law [75]. The smaller the radius of the NP, the lower the sedimentation rate [24,75]. Another factor that affects the nanodispersion stability is the length/diameter

Table 5

Stability of nanolubricants based on other modified NPs.

Nanoadditive	Functionalization	Concentration	Base oil	Stability	Ref.
LaF$_3$ (8 nm)	Dialkyldithiophosphate	0.5 wt%	Paraffin oil	Several months (r.t.) 3 days (140 °C)	[95]
SiO$_2$ (15–20 nm)	APTES	0.3 wt%	Gas mobile oil	5 months	
	GOPS	0.3 wt%		5 months	[107]
	3-MPS	0.3 wt%		5 months	
SiO$_2$ (<100 nm)	DETAS	1.0 wt%	PAO100	2 months	[48]
SiO$_2$ (<200 nm)	DETAS	0.5 wt%	PAO100	< 2 months	
	DETAS-SA	0.5 wt%		> 2 months	[25,46]
	DETAS-BA	0.5 wt%		2 months	
	DETAS-ScA	0.5 wt%		< 2 months	
SiO$_2$ (100 nm)	DETAS and OTES	NA	PAO100	4 months	[47]
SiO$_2$ (24 nm)	PLMA	1.0 wt%	PAO4	55 days	[99]
SiO$_2$ (23 nm)	PLMA	1.0 wt%	PAO4	2 months	[66]
SiO$_2$ (58 nm)	OA	NA	Paraffin oil	30 days	[108]
h-BN	OA	NA	PAO8	3 days	[109]
h-BN (70 nm)	BA	NA	SN500	5 days	[110]
	ODA	NA		1 day	
	TOA	0.25 g L^{-1}		6 days	
ZnAl$_2$O$_4$ (95 nm)	OA	0.5 wt%	Lubricating oil	Several days (70 °C)	[111]

Table 6

Stability of nanolubricants based on modified nanocomposites.

Nanoadditive	Functionalization	Concentration	Base oil	Stability	Ref.
Al$_2$O$_3$/SiO$_2$ (70 nm)	GOPS	1 wt%	Lubricating oil	3 months	[112]
MoS$_2$ (50 nm)/rGO-T	Triazole	NA	Group II oil	1 month	[113]
ZnO/Al$_2$O$_3$ (63 nm)	OA	1 wt%	Mineral oil	28 days	[114]
Graphene/MTT	APTES	0.4 g/L	15W40	1 month	[115]
Cu (5 nm)/GO	SA	0.05 wt%	Paraffin oil	10 days	[116]
Cu/rGO (50 nm)	OA	0.5 wt%	PAO10	7 days	[117]

ratio (aspect ratio); the higher the aspect ratio of the NPs, the more likely they agglomerate [75]. However, it should be noted that some aggregation always occurs without a suitable dispersion method, regardless of the shape of the nanoadditive [24]. Furthermore, the higher the base oil viscosity, the longer the dispersion stability, according to the Stokes law.

As it was indicated, uncoated nanoadditives usually show low stabilities in nonpolar base oils due to the high Van der Waals interactions between bare NPs and their lipophobicity due to their high polarity. To coat the NPs with the modifying agents it is needed to chemically activate the surface of the NPs. In the case of metal oxide NPs and SiO$_2$, liquid or vapor water interacting with them can cause their hydration and hydroxylation leading to hydroxyl groups on the NPs surface [76]. Due to the similar chemical properties of metal oxides and metal sulfides, analogous behavior can be expected in metal sulfide NPs, which have thiol groups on their surface. In the case of metal NPs, surface oxidation may also occur due to the presence of gaseous species, water vapor, and other electrolytes in the air [77]; subsequently, the hydroxylation of the oxide coating can also lead to hydroxyl functionalities on those surfaces. Similarly, carbon based nanomaterials such as graphene nanoplatelets, which are hydrophobic, can be oxidized generating a highly defective graphene that is covered more or less uniformly with hydroxyl or carboxyl groups, which lead to a hydrophilic nanomaterial [78,79]. Even after chemical reduction of graphene oxide, obtaining reduced graphene oxide, some hydroxyl or carboxyl groups may remain [80]. Both graphene oxide and reduced graphene oxide can be further functionalized. Thus, some chemical reactions used in the functionalization of NPs occur with amphiphilic molecules, such as oleic acid, and happen through esterification reactions with the above-indicated surface groups (hydroxyl, carboxyl, thiol…). The presence of alkyl chains covalently bonded to the NPs can prevent agglomeration by reducing their surface energy, overcoming the Van der Waals interactions between NPs through steric hindrance, as well as the generation of Van der Waals interactions between the alkyl chains of the coating with those of the base oil [57,71]. If the alkyl chains of NPs slow down the

sedimentation rate enough, this can be counterbalanced by Brownian motion [72,73]. In fact, the longer the alkyl chains, the longer the stability time. It should be noted that the grafting density (number of chains per NP surface unit) vary with the number of available polar moieties and the type of synthesis [81]. Regarding the NPs size, Chen et al. [24] concluded that with the same surface coating, a decrease in the size of NPs reduce the attractive van der Waals interactions among NPs and rise the repulsive steric force.

Carbon and its derivatives: Different modifying agents were investigated, such as oleic acid, OA; stearic acid, SA; dodecylamine, DDA; hexadecylamine, HDA; 1-octadecylamine, ODA; diphenylamine, DPA; oleylamine, OM; octadecyl alcohol; dodecylphosphate, DDP; OTS; or triazole. Some polymers have been also used, such as polyethylenimine (PEI), poly(acrylic acid sodium salt) (PAA) and poly(sodium 4-styrenesulfonate) (PSS) (Table 1).

The best stability using carbon nanoadditives was achieved by Chen et al. [82] with SA functionalized MWCNTs in a paraffin oil, claiming a visual stability at ambient conditions for up to six months, meanwhile non-functionalized MWCNTs (outer diameter from 20 to 40 nm) are completely settled before two months. The alkyl chains of the coating lead to an increase of the outer diameter of 10 nm. Mungse et al. [83] achieved a slightly lower stability (1 month) with a less concentrated dispersion (0.04 g L^{-1}) of GO functionalized with ODA in a 10W40 mineral oil (104 cSt at 40 °C). Moreover, GO can also be modified by reduction reactions, obtaining rGO. Similar results were found by the same research group with rGO functionalized with ODA [58]. Samanta and Sahoo [84] obtained dispersions of rGO functionalized with a branched PEI and PSS or PAA at 1 g L^{-1} concentration in heavy paraffin oil (viscosity 64 cSt at 37 °C) with time stabilities of two months. In all the articles indicated in Table 1 the classical two-step method was used except in that of Zhu et al. [85] who used a rotary evaporator to transfer rGO functionalized with octadecyl alcohol from THF to a low viscosity mineral oil (13.2 cSt at 40 °C), reaching a month stability.

Another type of carbon-based NPs are CDs and QCDs. Liang et al.

[86] synthesized HDA modified carbon dots, CDs-HDA; their dispersions in PAO4 having stabilities of at least 3 months for the highest concentration (1 wt%). Furthermore, Shang et al. [87] synthetized hydrophilic N-doped carbon dots (4–12 nm), N-CDs and tuned to hydrophobic N-CDs through covalent grafting of OM on the surface of N-CDs, OM-N-CDs. Hydrophilic N-CDs were dispersed in a PEG meanwhile hydrophobic OM-N-CDs were dispersed in a PAO base oil, finding in both cases stabilities of 30 days for 1 wt% N-CDs or OM-N-CDs in the corresponding base oil. Finally, Ye et al. [88] synthetized N-doped carbon quantum dots uncoated and coated with OM (N-CQDs and OM-N-CQDs with 2 nm and 4.2 nm diameter, respectively), finding that the dispersion of a castor oil with 0.2 wt% N-CQDs was still stable after 5 months, whereas the dispersion stability of PAO with 2 wt% OM-N-CQDs showed little sedimentation after 3 months. The high stability of the first dispersion can be due to the small size of the NPs and the lowest concentration.

Functionalization of carbon nanomaterials leads to improve the stability of nanodispersions from days to months, mostly dispersed in mineral oils but also in ester oils, PAOs and some formulated oils. Furthermore, usually reducing GO the stability increases [60,89]. Chen et al. [82] reported the highest stability time of all the nanolubricants from Table 1 (6 months). Nevertheless, in their article [82] the photographs included were taken two months after preparation. However, those photographs evidence that the modification of MWCNTs leads to a more stable nanodispersion, although their length/diameter ratio. This improvement can be explained by the appearance of favorable steric hindrance force, due to the alkyl chains, which reduces the unfavorable van der Waals interaction between MWCNTs.

Functionalized metal NPs: these nanoadditives were functionalized with dialkyldithiophosphate, dodecanethiol, OM or OA (Table 2). Li et al. [95] synthetized surface modified Ag and Cu NPs, using dialkyldithiophosphate as a coating agent, indicating that their paraffin oil dispersions (0.5 wt%) kept unchanged for several months in ambient conditions or for 3 days at 140 °C (no images are reported). Kumara et al. [96] synthetized dodecanethiol coated silver and palladium NPs finding that the dispersions with 0.5 wt% concentration in PAO4 (17 cSt at 40 °C) are stable for several months, whereas at higher concentrations, up to 2 wt%, the time stability is only several days (no images are reported).

Briefly, all these authors got dispersions with stabilities of several months for the NPs with diameters lower than 7 nm [95,96] whereas for dialkyldithiophosphate functionalized Ag NPs (15 nm) dispersions in a paraffin oil the stability is only five days [97].

Functionalized metal oxide NPs: As concern these NPs, oleic acid is the most common functionalization although poly(lauryl methacrylate) (PLMA), 3-glycidoxypropyltrimethoxysilane (GOPS) or 2-octyldodecyl gallate are also used (Table 3). Wright et al. [99] studied three dispersions in PAO4 of hairy TiO$_2$ NPs densely grafted with PLMA which remained transparent and stable after 56 days at three different temperatures, −20, 22, and 100 °C, but the dispersion color at 100 °C changed, which was attributed by the authors to the oxidation of a residual catalyst used in the functionalization of the hairy NPs. The stability of ZnO NPs coated with oleic acid was analyzed by Ran et al. [100] in a mineral oil (viscosity 12 cSt at 40 °C) and by Mariño et al. [101] in PAO40 (viscosity 402 cSt at 40 °C). The later authors got a better stability (29 days against 12 h) likely due to the higher viscosity of oil and to the use of Liñeira del Río et al. [49] preparation method described in Fig. 2. In addition, these last authors [49] found the best stability among metal oxides, achieving stable TMPTO dispersions of OA modified Fe$_3$O$_4$ and a Nd alloy (Nd$_2$Fe$_{14}$B) for at least 11 months due to the mutual affinity of the base oil which contains three oleate groups and the OA coating as well as the preparation method of the nanodispersions (Fig. 2).

Functionalized metal sulfide NPs. Different dispersions of metal sulfides with some functionalities were studied, such as silanes (OTS; dodecyltrichlorosilane, DTS; hexyltrichlorosilane, HTS), and OM (Table 4). Shahar et al. [104] investigated the dispersibility in a paraffin

oil of inorganic fullerene-like tungsten disulfide (IF-WS$_2$) NPs with the three different alkylsilane surface modifiers: OTS, HTS and DTS. The different silanized IF-WS$_2$ NPs (size < 150 nm) were dispersed in a paraffin oil at 1 wt%. Surprisingly, the dispersion of IF-WS$_2$ functionalized with the silane with the longest alkyl chains, OTS (C$_{18}$ chain) is stable only for 4 days, whereas that of IF-WS$_2$ functionalized with DTS (C$_{12}$ chain) is stable for more than 14 days and that with HTS (C$_6$ chain) remained stable for 8 days. This could be due to differences in grafting-density. Jiang et al. [105] studied 2 wt% dispersions of OM modified WS$_2$ nanosheets (size 6–8 nm with 0.276 nm between nanosheets) in PAO6 (30.6 cSt at 40 °C), at ambient conditions the dispersions remain stable up to 6 months and, at 160 °C, up to 7 days. Another article from Jiang et al. [106] reports studies on ultrathin WS$_2$ nanosheets capped by OM and maleic anhydride dodecyl ester (MADE), being their 2 wt% dispersions in dioctyl sebacate (DIOS, 11.5 cSt at 40 °C) stable for 6 months at room temperature. Table 4 shows again the relevance of the size of the NPs in the stability of the nanodispersions.

Other functionalized NPs: other compounds used as nanoadditives for lubricants are silica (SiO$_2$) NPs, h-BN, rare-earth compounds like LaF$_3$ and mineral oxides like ZnAl$_2$O$_4$. Several modifying agents are used, such as organic acids (benzoic acid, BA; succinic acid, ScA or lauric acid, LA), amines (N,N-dioctyl-1-octanamine, TOA and ODA), OA, SA, polymers (PLMA, poly(alkyl)methacrylate) and silanes (octadecyltriethoxysilane, OTES; N1-(3-trimethoxysilylpropyl)diethylenetriamine, DETAS and 3-(trimethoxysilyl)propyl methacrylate, 3-MPS) (Table 5).

Li et al. [95] synthesized NPs of dialkyldithiophosphate modified lanthanum trifluoride, which were dispersed in a paraffin oil (viscosity 36 mPa·s at 40 °C) leading to a transparent lubricant with stabilities of several months in ambient conditions and for 3 days at 140 °C.

Li et al. [107] obtained a stability time even longer than 5 months for nanolubricants of three different silane-modified SiO$_2$ NPs (APTES, GOPS or 3-MPS) in a gas mobile oil (0.3 wt%). Sui et al. [48] reported the stability of a hairy SiO$_2$ NPs (HSNs) dispersed in PAO100 using an aminosilane ended in NH$_2$: DETAS. This aminosilane is not amphiphilic. After two months, the nanodispersion with HSNs remained stable but not that of unmodified SiO$_2$ NPs. Sui et al. [25,46] also investigated the effect of three different end modifications of DETAS HSNs adding BA, SA or ScA finding that their nanodispersions in PAO100 are also stable after 2 months standing. The nanodispersion of the DETAS HSNs modified with SA (18 C) presents the best optical transparency, which can be attributed to excellent affinity of the nonpolar functional groups of the NPs with PAO100. In addition, Sui et al. [47] analyzed the advantages of using silica NPs functionalized with both alkyl and amino terminated organic silanes (OTES and DETAS). The dispersibility characterized with DLS showed that as the amount of OTES increased, the dispersibility of these NPs in PAO100 improved.

Seymour et al. [66] studied a series of PLMA HSNs and the effect of alkyl pendant length (6, 8, 12, 13, 16 and 18 C atoms) on their stability in PAO4. The unmodified silica NPs were not stable in this PAO. All the HSNs with alkyl pendant length of more than eight carbons were readily dispersed in PAO and presented stability at room or high temperatures such as 80 °C for up to 60 days. However, C6- and C8-grafted silica NPs (1 wt%) are not readily dispersible in PAO4 at room temperature. The C8 HSNs suspensions in PAO4 became clear and homogeneous upon heating at 80 °C. Interestingly, this cloudy-to-clear transition is reversible. These changes in the stability behavior can be described in terms of favorable brush solvation forces, which increase with the alkyl pendant length of the HSNs as well as the unfavorable interactions a) between PAO4 and silica NPs and b) between hairy NPs.

Literature results, showed in Table 5, bring out that SiO$_2$ NPs with sizes from 15 to 200 nm led to quite stable nanodispersions when are functionalized with silanes or polymers. Generally, the longest the alkyl chain of the functionalization is, the most stable the nanodispersions. Furthermore, it is important to modulate the polarity of the coating depending on that of the base oil.

Functionalized nanocomposites: The modifying agents are organic

acids (OA, SA), silanes (GOPS and APTES), and triazole (Table 6). Jiao et al. [112] compared uncoated alumina/silica (Al_2O_3/SiO_2) composite NPs with GOPS modified Al_2O_3/SiO_2 NPs as additives of a mineral oil and after 3 months the uncoated nanocomposites were mostly precipitated, and the modified ones stayed homogenously dispersed in the oil. Two main factors affect the best time stability results corresponding to GOPS modified Al_2O_3/SiO_2 NPs: first the adequacy of the functionalization method (silanization) to the size of the NPs (70 nm) [24] and second, the fact that the surface properties of Al_2O_3/SiO_2 nanocomposite changed, after modification, from hydrophilicity to lipophilicity [112], showing affinity for nonpolar oils. Using click chemistry, Farsadi et al. [113] synthesized a novel friction modifier: a nanocomposite of MoS_2 NPs and a reduced graphene oxide functionalized with triazole (rGO-T). This nanocomposite was dispersed in a group II 500 N petroleum-based oil (viscosity 93 cSt at 40 °C) remaining uniformly dispersed for one month.

Regarding the lubricants containing nanocomposites, it should be pointed out that it has not broadly been investigated the stability of the nanodispersions with a given nanocomposite compared to that of the dispersions containing the corresponding separated NPs. Interestingly, Farsadi et al. [113] found that a MoS_2 nanodispersion shows sedimentation meanwhile the nanodispersion of MoS_2/FrGO nanocomposite remains stable, so, the triazole modified rGO, rGO-T, is capable of stabilizing the MoS_2 NPs.

Considering only those publications with information on the size of the NP, it is possible to relate the effect of their size, and the type of modifying agent with the stability time of the nanodispersions (Fig. 6). For this purpose, five types of modifying molecules were considered: organic acids, amines, silanes, combinations of two types and other modifying agents. Most nanodispersions included in Tables 1 to 6 show stability times longer than 4 weeks (28 days). Among the nanodispersions with lower stabilities, more than half have NPs with sizes above 50 nm. Silanes are the most effective modifying agents for increasing the stability times for nanodispersions of NPs above 70 nm, achieving a maximum stability of 120 days for a dispersion containing OTES and DETAS silanized SiO_2 NPs (100 nm) dispersed in PAO100 [47]. Despite the small size, some of the NPs with sizes below 30 nm have poor stability times, such as 2-octadecyl gallate modified TiO_2 NPs (20–25 nm) dispersed in PAO10 or 10W30 [102], and dialkyldithiophosphate modified Ag NPs (15 nm) dispersed in paraffin oil [97], all of them with <5 days of stability. It is very unlikely that the three close hydroxyl groups of the 2-octadecyl gallate react with the NP surface, so the formed coated NPs have OH groups, i.e., higher polarity than PAO10 and 10W30. The polar groups of 2-octadecyl gallate and dialkyldithiophosphate are bulkier than those of organic acids or amines, which can lead to lower grafting densities. Most of the nanodispersions with stability times greater than 4 weeks contain NPs with sizes smaller than 30 nm with organic acids or amines as modifying agents, reaching stabilities of 11 months (330 days), in the case of an ester oil containing OA modified Fe_3O_4 NPs (6.3 or 10 nm) or Nd alloy NPs (19 nm) [49]. Other nanolubricants with stability times higher than 5 months are: paraffin oil + (MWCNT-SA (20–40 nm), Ag-dialkyldithiophosphate (4 nm), Cu-dialkyldithiophosphate (5 nm)), castor oil + CQD-DPA (2 nm), PAO4 + (Ag-dodecanethiol (3–6 nm), Pd-dodecanethiol (2–4 nm)), PAO6 + WS_2-OM (6–8 nm) and DIOS + WS_2-OM-MADE (6–8 nm) and gas mobile oil + SiO_2-APTES, GOPS, or 3-MPS (15–20 nm). Except MWCNT-SA, all the last nanoadditives are spherical (Tables 1, 2, 4 and 5).
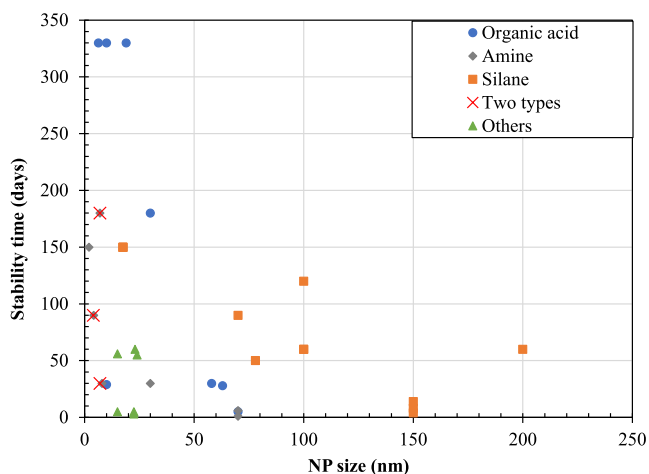
Other relevant factor to choose the appropriate modifying agent is the similarity in the polarities of the agent and of the base oil. For instance, an N-doped modification of CDs is more suitable for PEG (stability time of one month) meanwhile a further modification with OM to the N-doped CDs was needed for PAO4 (stability time of one month) [87]. Similarly, in the case of OM modified WS_2 NPs [105,106] with a non-polar base oil like PAO6 a stability time of 6 months was achieved. A further modification of OM-WS_2 NPs with MADE is needed to get the same stability time with a more polar ester base oil [106].

3. Tribological behavior using nanolubricants with functionalized NPs

The use of coated NPs not only affects the stability of the nanolubricants but also their tribological behavior, which is affected by many factors such as grafting density, size, shape, concentration, or composition [95,96,98,99] of the NPs. Furthermore, when the NP coating has polar groups at its external ends, tribochemical reactions can occur between those polar moieties and the positively charged metallic surface, facilitating the adsorption of the NPs onto the metallic surface [25,93,99]. In this section, the tribological results reported in the literature for nanolubricants, containing chemically modified NPs, with stabilities of at least four weeks, commented in section 2.3, are reviewed. Thus, the friction and wear reductions due to nanoadditives of carbon and its derivatives (Table 7), metals (Table 8), metal oxides (Table 9), metal sulfides (Table 10), nanocomposites (Table 11) and other NPs (Table 12) are summarized.

The different experimental conditions of the tribological experiments significantly affect both wear and friction values and highly difficult the comparison of the literature results. Standard measurement conditions should be defined by international associations of tribologists to better compare the antiwear and antifriction capabilities of the additives and lubricants from a global perspective. This issue can be partially arranged because in this paper friction and wear reductions respect to those of the base oils were used.

The dependence of the friction and wear reductions on the nanoparticle concentration, frequently shows a maximum at the usually named optimal concentration; for lower concentrations, the friction and wear reducing mechanisms due to NPs can partially (or even cannot) act since the quantity of NPs is insufficient, being the tribological behavior governed mainly by the base oil, while if the concentration is higher than the optimum one, the NPs can act as debris particles increasing friction and wear [93]. Wear can be characterized by different parameters such as wear volume (W_{Vol}), wear track width (WTW), wear scar diameter (WSD), or wear rate (W_{rate}). There are several tribological mechanisms by which nanoadditives improve lubrication [118], such as the formation of physical or chemical tribofilms leading to the protection of the tribopair from wear and a reduction of the coefficient of friction (COF) [27,99,106]. The other mechanisms that reduce friction and wear are rolling effect, which only occurs when the NPs are spherical or cylindrical, mending effect, which consists in the introduction of NPs in micro-pits and grooves present on the metallic surface, and polishing effect, through which the lubricated surface roughness is

Fig. 6. Effect of the size of the NPs and their modifying agent on the stability of their nanodispersions.

Table 7
Friction and wear reduction of nanolubricants based on modified carbon NPs.

Nanoparticle	Functionalization	Best concentration	Base oil	Friction reduction	Wear reduction	Ref.
GO	DDA	0.1 wt%	5 W30	40%	~50% WTW	[73]
GO	ODA	0.02 g L^{-1}	10 W40	25%	25% WTW	[83]
rGO	ODA	0.05 wt% + 1 wt% IL	Ester Oil	34%	34% WTW	[89]
rGO	PEI-PSS	0.5 wt%	Paraffin oil	75%	69% W$_{Vol}$	[84]
	PEI-PAA	0.5 wt%	Paraffin oil	50%	53% W$_{Vol}$	
rGO	Octadecyl alcohol	0.005 wt%	Hydraulic oil	10%	44% W$_{Vol}$	[85]
rGO	Triazole	0.01 wt%	Group II oil	16%	30% WSD	[93]
rGO	Reduction	0.050 wt%	Group II oil	40%	52 % W$_{rate}$	[74]
MWCNT (20–40 nm)	Stearic acid	0.45 wt%	Paraffin oil	4%	45% wear loss	[82]
CNPs (25–35 nm)	OM	1 wt%	PAO10	47%	30% WSD	[94]
CDs (4.2 nm)	HDA	1 wt%	PAO4	27%	46% W$_{Vol}$	[86]
CDs (4–12 nm)	N	1 wt%	PEG	72 %	83% W$_{Vol}$	[87]
CDs (4–12 nm)	N-OM	1 wt%	PAO	23%	46% W$_{Vol}$	[87]
CQDs (2 nm)	DPA	0.2 wt%	Castor Oil	COF increases	45% WSD	[88]
CQDs (4 nm)	DPA and OM	0.5 wt%	PAO6	COF increases	29% WSD	[88]

Table 8
Friction and wear reduction of nanolubricants based on modified metal NPs.

Nanoparticle	Functionalization	Best concentration	Base oil	Friction reduction	Wear reduction	Ref.
Ag (4 nm)	Dialkyldithiophosphate	0.5 wt%	Paraffin oil	N/A	59%WSD	[95]
Ag (15 nm)	Dodecanethiol	1.0 wt%	PAO4	37%	95% W$_{Vol}$	[96]
Cu (5 nm)	Dialkyldithiophosphate	0.5 wt%	Paraffin oil	N/A	58%WSD	[95]
Pd (2–4 nm)	Dodecanethiol	1.0 wt%	PAO4	~40%	98% W$_{Vol}$	[96]
Ni (7 nm)	OM and OA	0.05 wt%	PAO6	COF increases	30% WSD	[98]

Table 9
Friction and wear reduction of nanolubricants based on modified metal oxide NPs.

Nanoparticle	Functionalization	Best concentration	Base oil	Friction reduction	Wear reduction	Ref.
Al$_2$O$_3$ (78 nm)	GOPS	0.1 wt%	Machine oil	18%	42% WSD	[103]
TiO$_2$ (15 nm)	PLMA	1.0 wt%	PAO4	~40%	91% W$_{Vol}$	[99]
Fe$_3$O$_4$ (6.3, 10 nm)	OA	0.015 wt%	TMPTO	18%	76% W$_{Vol}$	[49]
Nd alloy (19 nm)	OA	0.015 wt%	TMPTO	29%	99% W$_{Vol}$	[49]

Table 10
Friction and wear reduction of nanolubricants based on modified metal sulfide NPs.

Nanoparticle	Functionalization	Best concentration	Base oil	Friction reduction	Wear reduction	Ref.
WS$_2$ (6–8 nm)	OM	2.0 wt%	PAO6	Load 392 N: r.t.: 0% 75 °C: 44% 150 °C: 37% 200 °C: 39%	W$_{Vol}$: r.t.: 77%, 75 °C: 96%, 150 °C: 97%, 200 °C: 96%	[105]
WS$_2$ (6–8 nm)	OM and MADE	2.0 wt%	DIOS	Load 392 N: 20 °C 50%, 75 °C: 56%, 150 °C 15%	W$_{Vol}$: 20 °C 68%, 75 °C 83%, 150 °C 52%	[106]

Table 11
Friction and wear reduction of nanolubricants based on other modified NPs.

Nanoparticle	Functionalization	Best concentration	Base oil	Friction reduction	Wear reduction	Ref.
LaF$_3$ (8 nm)	Dialkyldithiophosphate	0.5 wt%	Paraffin oil	N/A	WSD: 48%	[95]
SiO$_2$ (15–20 nm)	APTES	0.3 wt%	Gas mobile oil	42.8%	30.9% WSD	[107]
	GOPS	0.3 wt%		25.3%	22% WSD	
	3-MPS	0.3 wt%		40.6%	23.4% WSD	
SiO$_2$ (20, 50, 100 nm)	DETAS	1.0 wt%	PAO100	40%	60% WSD	[48]
SiO$_2$ (100 nm)	DETAS	1.0 wt%	PAO100	43%	N/A	[25]
SiO$_2$ (100 nm)	DETAS and OTES	1.0 wt%	PAO100	40%	60% WSD	[47]
SiO$_2$ (24 nm)	PLMA	1.0 wt%	PAO4	~30%	W$_{Vol}$: 92% plate 95% ball	[99]
SiO$_2$ (23 nm)	PLMA	1.0 wt%	PAO4	38%	90% W$_{Vol}$	[66]
SiO$_2$ (54 nm)	OA	0.05 wt%	Paraffin oil	28%	34% WSD	[108]

Table 12

Friction and wear reduction of nanolubricants based on modified nanocomposites.

Nanoparticle	Functionalization	Best concentration	Base oil	Friction reduction	Wear reduction	Ref.
Al$_2$O$_3$/SiO$_2$ (70 nm)	GOPS	0.5 wt%	Machine oil	20%	22% WSD	[112]
MoS$_2$ (50 nm)/rGO-T	Triazole	0.8 wt%	Group II oil	16%	29% WSD	[113]
Graphene/MTT	APTES	0.4 g L^{-1}	15W40	50%	13% WSD	[115]

reduced by abrasion due to NPs [4].

Carbon and its derivatives (Table 7): Sun and Du [119] studied the mechanisms by which graphene derivatives with two-dimensional structures, as GO or rGO, act as antifriction and antiwear nano-additives. According to these authors, these NPs 1) can easily enter the friction pair contact region, being able to be effectively involved in lubrication because they easily shear; 2) can form friction transfer films and 3) can both fill the surface concave area, and adsorb at the roughness peaks, thus reducing the friction between the rubbing surfaces. The tribological performance of the lubricants containing this type of additives not only depends on the morphology and the type of coating but also on number of layers, and their size [120].

Paul et al. [73] analyzed the effect of applied load for a 5W30 oil and three of its nanodispersions containing DDA functionalized GO (0.01, 0.05, 0.10 wt%) obtaining the optimal concentration 0.10 wt% with reductions of 40% in friction coefficient and 50% in WTW under a load of 10 N, the lowest load analyzed.

Mungse et al. [83] studied the antifriction and antiwear properties of GO functionalized with ODA as an additive for a 10W40 oil, presenting a 25% reduction in both COF and WTW compared to those of pristine 10W40 oil. Several articles shown the tribological properties of lubricants using rGO as additives. Samanta and Sahoo [84] examined the effect of a polymer-grafted rGO on the tribological behavior at different contact pressures and on load-bearing capacity of a paraffin oil. The highest COF reductions achieved under 147 N were 75% and 50% for rGO-PEI-PSS and rGO-PEI-PAA respectively being the wear volume reductions 69% and 53% compared to that obtained with the paraffin oil additivated with GO. Due to the higher packing density and the dispersion stability, the rGO modified with polymer brushes can more effectively reduce stress, compression, and shear than unmodified rGO, leading to improvements in antifriction, antiwear and load-bearing capacities.

Ismail et al. [93] studied the tribological behavior of a base oil (group II 500 N petroleum-based oil) containing triazole ring-decorated rGO, FrGO, at three different concentrations, by means of four-ball tests. The nanodispersion with 0.01 wt% of FrGO led to the greatest COF and wear reductions, being respectively 16% and 30% (WSD) when compared to those of neat base oil. The aforementioned results show that several functionalities (ODA, PEI-PSS, octadecyl alcohol and triazole) of GO or rGO, enhance the stability of the nanoadditives in the oil and also lead to excellent tribological properties. On the other hand, Patel et al. [74] used a ball-on-disc instrument to measure the wear preventive characteristics of rGO dispersed at three different concentrations in a group II oil; the nanolubricant containing 0.05 wt% rGO nanoplatelets showed the greatest wear reduction, 52% compared to the group base oil, as well as a reduction in friction of around 40% at 60 rpm.

Chen et al. [82] modified MWCNTs with SA (20–40 nm), dispersed them in a liquid paraffin (being the concentration 0.45 wt%), and studied the effect of the mass ratio of SA to MWCNTs (SA:MWCNTs) on tribological properties under a load of 1000 N, finding 2:1 as the optimum ratio to improve the friction reduction and antiwear capacity of base lubricant. These could be explained because SA is also a good lubricant; during the wear test, SA forms an effective film, but, due to the high temperature reached during the tests, for high SA concentrations it is decomposed and oxidized easily, increasing COF and wear. Furthermore, these authors also examined the effect of load on tribological properties using modified and unmodified MWCNTs nanodispersions

(0.45 wt% and a SA:MWCNT mass ratio 2:1) obtaining the highest friction reductions and the best antiwear capacities with the modified MWCNTs. This fact can be explained by the better dispersibility of modified MWCNTs; the tribopair surfaces were easily filled with the dispersed modified MWCNTs during the tribological tests, and then the NPs on the wear surface could help as spacers, avoiding rough contact between the two mating surfaces, thus greatly reducing the wear loss significantly (45% at 1000 N). Nevertheless, the friction reductions are quite small: 9% at 500 N and 4% at 1000 N.

Liang et al. [74] analyzed the tribological behavior of CDs-HDA (4.2 nm) as additives of PAO4, observing that for the load of 20 N and the nanolubricant with the optimal concentration (1 wt%), the COF and wear volume decreased by 27% and 46%, respectively. These authors proposed that boundary lubrication films containing iron oxides and CDs-HDA are formed on rubbing surfaces by absorption and deposition but also act through rolling, mending and polishing mechanisms. Furthermore, Shang et al. [75] analyzed the tribological behavior of dispersions of N-CDs in a PEG as well as OM-N-CDs in a PAO finding that the COF and wear volumes of PEG with 1.0 wt% N-CDs are reduced up to 76% and 83%, respectively. In addition, for the OM-N-CDs (1.0 wt% in PAO) 23% and 46% reductions in COF and wear were achieved. These authors suggested that N-CDs act as rolling ball bearings and could be irregularly deposited on the worn surface with mending effect and the formation of a tribochemical film which contains also Fe$_2$O$_3$ and nitrogen element, which prevented direct contact of the metal surfaces.

Likewise, Lu et al. [76] studied the mass concentration effect of OM-CDs on tribological properties of PAO10, concluding that the 1.0 wt% OM-CDs nanolubricant showed the best friction-reducing and antiwear properties. Specifically, the COF and diameter of the worn scar were reduced by 47 and 30%, respectively. These authors suggested that the synergistic effect of a formed tribofilm which includes PAO and the OM-CDs might account for the good antiwear and antifriction capabilities under boundary lubrication. Finally, Ye et al. [88] evaluated the tribological performance of castor oil and PAO nanooils containing N-CQDs as additives, finding that for both oils the COF is not improved by adding these nanoadditives. Nevertheless, the wear is reduced by 45% for the optimal concentration of 0.2 wt% N-CQDs (in comparison to the CO base oil) and 29% for optimal addition of 0.5 wt% OM-N-CQDs (in comparison to PAO). These authors proposed that CQDs are deposited unevenly on the worn surface and form a thin protective film also containing iron oxides and nitrogen.

In conclusion, it can be inferred that nanolubricants based on functionalized carbon derivatives act as contact mitigators between rubbing surfaces through the formation of effective tribofilms, which reduce friction and protects the surfaces against undesirable wear, especially when their coating contains polar groups, which promote tribochemical reactions with the positively charged metal surfaces.

Functionalized metal NPs (Table 8): Li et al. [95] found improvements in the antiwear properties of a paraffin oil through the addition of dialkyldithiophosphate-coated copper or silver NPs. Wear analysis showed significant reductions with the addition of these NPs compared to that obtained using the base oil, especially at high loads. Specifically, paraffin oil nanodispersions containing 0.5 wt% dialkyldithiophosphate coated copper or silver NPs lead to WSD reductions of 58% or 59%, respectively. Antiwear properties of the dispersions containing dialkyldithiophosphate coated Cu NPs are better than those containing only zinc dialkyldithiophosphate (ZDDP), especially at lower concentrations. Moreover, Kumara et al. [96] performed tribological tests with

dodecanethiol-modified silver or palladium NPs (Ag and Pd NPs) dispersed in PAO4 for a contact formed by a steel ball and a cast iron plate. Both Pd and Ag NPs led to substantial reductions of the COF (25–40%) and wear of the cast iron plate (90–97%) with the best reductions in both properties being obtained with Pd NPs, especially with the 1.0 wt% concentration. Chen et al. [98] studied the effect of OM and OA modified Ni NPs of controlled sizes on tribological performance of PAO6, using a four-ball friction and wear tester. The authors concluded that the smallest NPs (7 nm) are more effective than the larger ones, specifically in reducing WSD, with a maximum reduction of 30%. Nevertheless, no reduction was found in the COF for any coated Ni NPs.

The sizes of NPs contained in Table 8 are lower than 15 nm. For three of the five nanodispersions, friction data are not available or get worse. Nevertheless, in terms of wear, substantial reductions are achieved by using nanolubricants instead of neat oils; the most sensitive wear parameter is the worn track volume, with reductions of up to 98%. Furthermore, in this case, under mixed and boundary lubrication conditions, the nanoadditives could easily form boundary lubricating films on the sliding surfaces. In addition, smaller NPs (high surface activity) can generate protective tribofilms through an *in situ* deposition mechanism.

Functionalized metal oxide NPs (Table 9): Wright et al. [99] studied the lubricating performances of PLMA brush-grafted titania NPs, as additives of PAO4 for different molecular mass of the coating (8–21 kDa of PLMA). The modified TiO_2 NPs were not regular in shape with plate and rod-like nanostructures. For all the studied nanodispersions, the COF decreased, obtaining with the lowest molecular mass NPs the highest friction reduction (40%) respect to that obtained with PAO4. Meanwhile, wear was also significantly reduced (91%) in terms of worn volume of iron plates.

Liñeira del Río et al. [49] characterized the tribological performance of three nanolubricants composed by TMPTO base oil with superparamagnetic NPs: Fe_3O_4 (6.3 nm), Fe_3O_4 (10 nm) and a Nd alloy (19 nm), all of them coated with OA, being the NP concentration 0.015 wt%. For the tribological tests performed under pure sliding conditions, COFs for the three nanolubricants are lower than that achieved with the base oil, with the best friction performance achieved for the Nd alloy nanolubricant with a friction decrease of 29 % in comparison to TMPTO base oil. All the nanolubricants also improved wear, with the Nd alloy nanolubricant also achieving the highest wear reduction 99 % in terms of W_{Vol}. A smoother surface was found when the pins are lubricated with each one of the nanolubricants instead of with the base oil, being the biggest roughness reduction for Nd alloy nanolubricant, 54%. Boundary tribofilm, polishing and mending effects happen owing to the presence of NPs.

In general, tribological results with nanolubricants based on modified metal oxide NPs are meaningful, highlighting those related to nanolubricants containing oil-soluble polymer brush-grafted TiO_2 NPs, improving the results when the brush molecular mass reduces. Reductions up to 40% in friction and 91% in wear volumes were found. Regarding the lubrication mechanisms, protective tribofilms formed on the friction surfaces were suggested in all the cases. Furthermore, rolling mechanism was identified for nanolubricants including spherical Al_2O_3 NPs [103]. Finally, the mechanisms due to the presence of superparamagnetic NPs also include mending and polishing effects. It must be noted that NPs with different shapes lead to excellent tribological properties: in the case of the brush-grafted TiO_2 NPs they are irregularly shaped with rod-like nanostructures and those superparamagnetic NPs showed spherical and cubical shapes.

Functionalized metal sulfide NPs (Table 10): Jiang et al. [105] prepared dispersions of OM-modified ultrathin tungsten disulfide nanosheets in PAO6 base oil and evaluated their tribological performance with a four-ball machine. The best antiwear and friction-reducing ability was obtained at 75 °C with the 2.0% mass fraction nanodispersion, resulting in 96% and 44% reductions, respectively. Moreover, the tribological behavior of modified WS_2 nanosheets as additives of PAO6

is better than that of OM as additive. These authors [105] also evaluated the effect of temperature and load on the tribological behavior of the later nanolubricant, obtaining that WSD and COF increased with increasing temperature (or load), remaining better than those of PAO6 base oil. These reductions are because stable suspensions can effectively transfer the NPs onto the contact zone of rubbing steel surfaces, forming a surface protective layer. In a later work, Jiang et al. [106] also studied the tribological behavior of OM and MADE capped WS_2 NPs in an ester oil (DIOS) at different temperatures and loads, finding wear and friction reductions in all the conditions. The best tribological results were at 75 °C with reductions of 56% and 83% for COF and W_{Vol}, respectively. The tribological behavior with NP concentration followed the same trend as in their previous work [105].

Considering the aforementioned results, it is clear that modified WS_2 nanoplatelets exhibit significant tribological performance over a broad range of temperatures, because of the nanoadditives are capable to form on the worn surfaces both adsorbed films with a low shear force and tribochemical reaction films [105,106].

Other functionalized NPs (Table 11): Li et al. [95] examined the enhancement of the antiwear properties of a paraffin oil by the addition of dialkyldithiophosphate coated LaF_3. WSD is highly reduced with the addition of NPs compared to that of neat paraffin oil, especially at higher loads.

As regards to SiO_2 NPs, Li et al. [107] studied the tribological behavior of ST5W/30 gas mobile oil with three different silane modified silica NPs (APTES, GOPS or 3-MPS) as separately additives with a reciprocating tribotester and a four-ball tester. In both cases 3-MPS modified SiO_2 NPs lead to the best friction and wear reductions.

Sui et al. [48] used HSNs tethering separately three different amino functionalized silanes (APTES, AEAPS or DETAS) onto silica NPs with different sizes. The tribological properties of these HSNs dispersed in PAO100 were measured on a four-ball tester. Among the three HSNs of 20 nm size, the NPs coated with AEAPS leads to the best tribological behavior. Regarding the 50 and 100 nm HSNs, DETAS HSNs showed the best friction reduction and antiwear properties, being in both cases the COF lower than that of 20 nm AEAPS HSNs. For 100 nm DETAS HSNs the maximum reductions in WSD and COF were found, being 60% and 40%, respectively, comparing to neat PAO100. In a later article, Sui et al. [25] studied the effect of different functional groups (amino, carboxyl, phenyl, and alkyl groups) tethered on DETAS HSNs on their tribological performance. The best antiwear and friction reductions (40%) correspond to the NH_2 terminated HSNs at the optimum concentration of 1 wt%, but showed concentration sensitive behavior, due to the hydrogen bonding between the primary NH_2 groups leads to aggregation. The CH_3 and C_6H_5 terminated HSNs improved the tribological performance and the stability of the HSNs. Sui et al. [47] also modified silica NPs with DETAS and OTES in different ratios to obtain bifunctional hairy silica NPs (BHSN). The optimal DETAS:OTES ratio in BHSNs was investigated, obtaining the best tribological properties with the 2:1 ratio, specifically, reductions of 40% in COF and 60% in WSD compared to those of the neat PAO100.

Wright et al. [99] studied the lubricating performances of PLMA brush-grafted silica NPs with different average molecular weights as additives for PAO4 using a tribotester in a ball-on-plate reciprocating configuration. Modified SiO_2 with the lower molecular weights (4.1 kDa) as PAO additives (at 1 wt%) showed a noticeable reduction in COF (30%) and important reductions in W_{Vol} (up to ~90% for both plate and ball). Free polymer PLMA (38 kDa) dispersed in PAO4 was tested for comparison with modified SiO_2 and performed similarly to neat PAO4. To investigate the concentration effect, three additional dispersions of PLMA brush-grafted silica (21.7 kDa) were dispersed in PAO4, decreasing the COF when the NP concentration increases, until achieving a concentration of 4.0 wt% in the lubricant.

Moreover, Seymour et al. [66] studied the effect of alkyl pendant chain length (6, 8, 12, 13, 16 and 18 C atoms) of a series of PLMA brush-grafted HSNs, using a ball-on-plate reciprocating tribotester. All the

dispersions led to lower COFs than those of ZDDP in PAO and of neat PAO, being the maximum friction reduction 38% with the HSNs with alkyl pendant chain length of 16 C atoms. Nevertheless, the antifriction behavior showed by the HSNs with different alkyl pendant chains is similar, which indicates the relevance of the core silica NPs in the efficacy as lubricant additives. Likewise, W_{Vol} values of the iron plates tested with HSN dispersions were found to be similar reducing up to 90% compared to that of neat PAO, but are slightly higher than that of ZDDP in PAO.

Regarding the tribological mechanisms that take place when using other modified NPs (Table 11), which are all nearly spherical, most authors describe that these NPs are embedded in the nanogrooves on the wear surface and can form protective films that reduce friction and wear.

Functionalized nanocomposites (Table 12): Jiao et al. [112] tested Al_2O_3/SiO_2 nanocomposites modified with GOPS coupling agent as additives of a lubricating oil with a four-ball tribometer, obtaining the best tribological performance at 0.5 wt%, reducing COF by 20% and WSD by 22%. In addition, thrust-ring tests led to a 50% COF reduction, which was better than those obtained with single Al_2O_3 or SiO_2 dispersions. Li et al. [115] dispersed functionalized graphene/montmorillonite (FG/MTT) nanosheets, in a 15W40 engine oil, evaluating the tribological properties in a four-ball tribometer. At the optimal concentration, COF and WSD were improved by 50% and 13%, respectively, compared with those obtained with the neat oil, being the friction reduction notably higher than those obtained using as additives FGO or MTT separately. Regarding the tribological mechanisms, two situations must be distinguished, considering the shape of the NPs: one that involves nanocomposites with the two types of NPs almost spherical and other in which at least one type of NPs is laminar. The first is the case of Al_2O_3/SiO_2 nanocomposite, which can form a thin lubricating layer between the contact surfaces and act as bearings changing the sliding friction to rolling friction. The latter is the case of functionalized Graphene/MTT, where the lamellar structure of graphene is combined with smaller nanoplatelets of MTT, filling the asperities on the contact surface with sheets of different sizes and also reacting with this surface to form a repairing tribolayer.

The effect of the size of the NPs and their modifying agents on reductions of the friction coefficient and wear has been analyzed (Fig. 7), in a similar way to the analysis carried out with the stability time of the nanodispersions (Fig. 6). The same five categories of the modifying agents were considered. Only the tribological behavior of those nanodispersions with more than 4 weeks of stability were analyzed. Most of the NPs (83%) that appear in Fig. 7 have sizes smaller than 40 nm, being all the NPs with sizes greater than 60 nm silanized. For most nanodispersions, the wear reductions are higher than the COF reductions. In

Fig. 7. Effect of the size of the nanoparticle and its modifying agent on the reduction of friction (**blue**) and wear (**red**).

fact, the COF can increase while the wear decreases due to the NPs [88,98]. The highest friction reduction in Fig. 7 is 72% for N-doped CDs (8 nm) dispersed in PEG [87], followed by WS$_2$-(OM + MADE) (6–8 nm) dispersed in a ester, CNP-OM (25–35 nm) dispersed in PAO10 with reductions of 56% and 47%, respectively. These last nanoadditives are spherical. Nevertheless, the highest friction reduction (75%) was obtained with rGO-PEI-PSS (unknown size) dispersed in a paraffin oil. On the other hand, the highest wear reduction reaches a 99% for an OA modified Nd alloy NP (19 nm) in an ester [49], followed by Pd-Dodecanethiol (2–4 nm) in PAO4, WS$_2$-OM (6–8 nm) in PAO6, Ag-Dodecanethiol (15 nm) in PAO4 and SiO$_2$-PLMA (24 nm) in PAO4 with 98%, 97%, 95% and 95%, respectively. All these nanoadditives are spherical except the coated Nd alloy NPs which are cubic. Notably, there are ten nanodispersions with wear reductions higher than 75%, none of them contains silanized NPs, for which the highest wear reduction is 60% for a DETAS silanized SiO$_2$ NPs (100 nm) dispersed in PAO100 [48].

Apart from the size, modifying agent and chemical structure of the NPs, as well as the polarity of the base oil, the viscosity of the oil should be taken into account. In general, the NPs led to higher friction and wear reductions dispersed in low viscosity oils (as PAO4, PAO6, DIOS) [96,105,106] than in high viscosity oils [25,115].

4. Conclusions

Although the two-step method is the most widely used to prepare nanolubricants, the dispersion methods involving evaporation of a volatile solvent lead to greater stability results compared to the former. To determine the stability time of the nanolubricants, the sediment photograph capturing is the most common method. This technique should be accompanied by a more quantitative method; however, some of them, like DLS or UV–Vis, show important limitations when the nanodispersions are dark, opaque, or highly concentrated.

Several parameters affect the stability of the nanodispersions, such as the morphology, size and concentration of the NPs, or the viscosity of the base oil and the type of coating. Analyzing the results with higher stabilities (several months), the most common morphology was spherical with a NP size lower than 20 nm (CQDs, Ag, Cu, Pd, Fe$_3$O$_4$, SiO$_2$, WS$_2$). These nanodispersions have concentrations between 0.015 wt% and 1 wt% in most cases, being the highest stability (longer than 11 months) for the lowest NP concentration. Regarding the type of chemical modifier, the most important factors for a good stabilizing performance in nonpolar base oils is the length of the alkyl chain, which should be of at least 12 carbon atoms, such as stearic acid (C18), oleic acid (C18), oleylamine (C18), dodecanethiol (C12), and the presence of a nonpolar CH$_3$ termination, whereas the type of polar functional group linked to the bare NPs hardly has influence. Nevertheless, for spherical NPs (SiO$_2$, Al$_2$O$_3$) with diameters higher than 70 nm, silane modifiers seem to be more appropriate (Table 3 and 5). Polymer functionalization gives rise to nanodispersions with stabilities of two months with excellent tribological properties. Studies on the effect of the length of the polymer coatings of the NPs on the stabilities of the nanodispersions are scarce. Respect to the effect of the functionalized NPs on the tribological performance, in most cases the nanolubricants reduce more effectively the wear than the friction.

Concerning the viscosity of the base oils, higher values lead to better stabilities, although, some of the more stable nanodispersions are based on low viscosity oils such as PAO4 or PAO6 proving that the chemical modification and other parameters (such as the NP size) play an important role in stabilizing the nanolubricants. Low viscosity oils (viscosity at 100 °C lower than 10 cSt) should be developed as transmission fluids for electrical vehicles, among other applications. In this regard, Tables 1-12 allow to identify the following candidates for low viscosity nanolubricants: a) Nd alloy NPs (19 nm) functionalized with OA dispersed in TMPTO (viscosity at 100 °C 8.45 cSt) which are stable more than 11 months and provide reductions up to 29 % for friction and
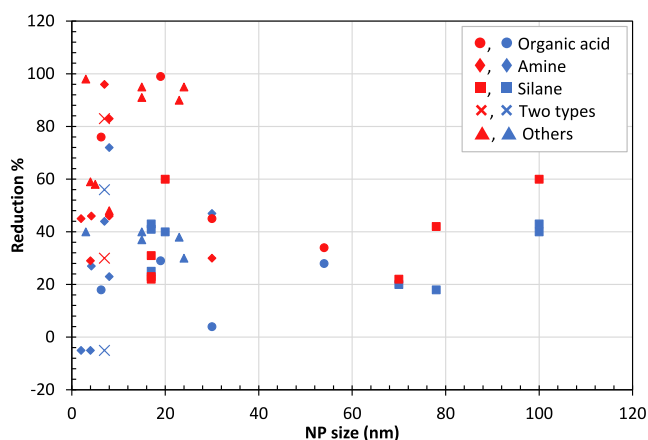
99 % for W$_{Vol}$, b) WS$_2$ NPs functionalized with OM or OM and MADE (6–8 nm) dispersed in PAO6 or DIOS: six months stability, friction and W$_{Vol}$ reductions of up to 50% and 97% and c) Ag (15 nm) or Pd (2–4 nm) NPs functionalized with dodecanethiol, dispersed in PAO4: several months stability, friction and W$_{Vol}$ reductions around 40% 95% respectively. Tribofilm, mending, polishing and rolling effects can explain this tribological behavior.

CRediT authorship contribution statement

Fátima Mariño: Data curation, Writing – original draft, Writing – review & editing, Methodology, Investigation, Formal analysis. **José M. Liñeira del Río:** Writing – review & editing, Methodology, Investigation. **Enriqueta R. López:** Writing – review & editing, Validation, Supervision, Formal analysis. **Josefa Fernández:** Conceptualization, Writing – review & editing, Supervision, Project administration.

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

The data used in this review have been published in the cited articles

Acknowledgements

References

[1] K. Holmberg, A. Erdemir, Influence of tribology on global energy consumption, costs and emissions, Friction 5 (2017) 263–284, https://doi.org/10.1007/s40544-017-0183-5.
[2] K. Holmberg, A. Erdemir, The impact of tribology on energy use and CO$_2$ emission globally and in combustion engine and electric cars, Tribol. Int. 135 (2019) 389–396, https://doi.org/10.1016/j.triboint.2019.03.024.
[3] M.K. Ahmed Ali, H. Xianjun, F. Essa, M.A. Abdelkareem, A. Elagouz, S. Sharshir, Friction and wear reduction mechanisms of the reciprocating contact interfaces using nanolubricant under different loads and speeds, J. Tribol. 140 (2018), https://doi.org/10.1115/1.4039720.
[4] W. Dai, B. Kheireddin, H. Gao, H. Liang, Roles of nanoparticles in oil lubrication, Tribol. Int. 102 (2016) 88–98, https://doi.org/10.1016/j.triboint.2016.05.020.
[5] R. Xia, D. Lou, H. Younes, J. Haiston, H. Chen, H. Hong, Synergistic effect of hexagonal boron nitride and carbon nanofibers on tribological behavior of nanolubricant, Tribol. Int. 177 (2023), 107957, https://doi.org/10.1016/j.triboint.2022.107957.
[6] K.I. Nasser, J.M. Liñeira del Río, F. Mariño, E.R. López, J. Fernández, Double hybrid lubricant additives consisting of a phosphonium ionic liquid and graphene nanoplatelets/hexagonal boron nitride nanoparticles, Tribol. Int. 163 (2021), 107189, https://doi.org/10.1016/j.triboint.2021.107189.
[7] M.K.A. Ali, H. Xianjun, M.A. Abdelkareem, M. Gulzar, A. Elsheikh, Novel approach of the graphene nanolubricant for energy saving via anti-friction/wear in automobile engines, Tribol. Int. 124 (2018) 209–229, https://doi.org/10.1016/j.triboint.2018.04.004.
[8] J. Kałużny, M. Waligorski, G.M. Szymański, J. Merkisz, J. Różański, M. Nowicki, M. Al Karawi, K. Kempa, Reducing friction and engine vibrations with trace amounts of carbon nanotubes in the lubricating oil, Tribology International 151 (2020) 106484, 10.1016/j.triboint.2020.106484.
[9] S.C. Tung, M.L. McMillan, Automotive tribology overview of current advances and challenges for the future, Tribol. Int. 37 (2004) 517–536, https://doi.org/10.1016/j.triboint.2004.01.013.
[10] A. Rasheed, M. Khalid, A. Javeed, W. Rashmi, T. Gupta, A. Chan, Heat transfer and tribological performance of graphene nanolubricant in an internal combustion engine, Tribol. Int. 103 (2016) 504–515, https://doi.org/10.1016/j.triboint.2016.08.007.
[11] N.G. Demas, E.V. Timofeeva, J.L. Routbort, G.R. Fenske, Tribological effects of BN and MoS$_2$ nanoparticles added to polyalphaolefin oil in piston skirt/cylinder liner tests, Tribol. Lett. 47 (2012) 91–102, https://doi.org/10.1007/s11249-012-9965-0.
[12] W.A.A. Mustafa, F. Dassenoy, M. Sarno, A. Senatore, A review on potentials and challenges of nanolubricants as promising lubricants for electric vehicles, Lubr. Sci. 34 (2022) 1–29, https://doi.org/10.1002/ls.1568.
[13] Y. Chen, S. Jha, A. Raut, W. Zhang, H. Liang, Performance characteristics of lubricants in electric and hybrid vehicles: a review of current and future needs, Front. Mech. Eng. 6 (2020), 571464, https://doi.org/10.3389/fmech.2020.571464.
[14] M.A.M. Ali, A.I. Azmi, M.N. Murad, M.Z.M. Zain, A.N.M. Khalil, N.A. Shuaib, Roles of new bio-based nanolubricants towards eco-friendly and improved machinability of Inconel 718 alloys, Tribol. Int. 144 (2020), 106106, https://doi.org/10.1016/j.triboint.2019.106106.
[15] H. Spikes, Friction modifier additives, Tribol. Lett. 60 (2015) 5, https://doi.org/10.1007/s11249-015-0589-z.
[16] M.Z. Saidi, C. El Moujahid, A. Pasc, N. Canilho, C. Delgado-Sanchez, A. Celzard, V. Fierro, R. Kouitat-Njiwa, T. Chafik, Enhanced tribological properties of wind turbine engine oil formulated with flower-shaped MoS$_2$ nano-additives, Colloids Surf. A Physicochem. Eng. Asp. 620 (2021), 126509, https://doi.org/10.1016/j.colsurfa.2021.126509.
[17] S.C. Tung, M. Woydt, R. Shah, Global insights on future trends of Hybrid/EV driveline lubrication and thermal management, Front. Mech. Eng. 6 (2020) 74, https://doi.org/10.3389/fmech.2020.571786.
[18] N. Nyholm, N. Espallargas, Functionalized carbon nanostructures as lubricant additives – a review, Carbon 201 (2023) 1200–1228, https://doi.org/10.1016/j.carbon.2022.10.035.
[19] N.F. Azman, S. Samion, Dispersion stability and lubrication mechanism of nanolubricants: a review, Int. J. Precision Eng. Manuf.-Green Technol. 6 (2019) 393–414, https://doi.org/10.1007/s40684-019-00080-x.
[20] V. Zin, F. Agresti, S. Barison, L. Colla, E. Mercadelli, M. Fabrizio, C. Pagura, Tribological properties of engine oil with carbon nano-horns as nano-additives, Tribol. Lett. 55 (2014) 45–53, https://doi.org/10.1007/s11249-014-0330-3.
[21] V.N. Bakunin, G.N. Kuzmina, O.P. Parenago, G.M. Bancroft, Tribological behavior and tribofilm composition in lubricated systems containing surface-capped molybdenum sulfide nanoparticles, Tribol. Lett. 22 (2006) 289–296, https://doi.org/10.1007/s11249-006-9095-7.
[22] N. Nunn, Z. Mahbooba, M.G. Ivanov, D.M. Ivanov, D.W. Brenner, O. Shenderova, Tribological properties of polyalphaolefin oil modified with nanocarbon additives, Diam. Relat. Mater. 54 (2015) 97–102, https://doi.org/10.1016/j.diamond.2014.09.003.
[23] P. Rabaso, F. Dassenoy, F. Ville, M. Diaby, B. Vacher, T. Le Mogne, M. Belin, J. Cavoret, An investigation on the reduced ability of IF-MoS$_2$ nanoparticles to reduce friction and wear in the presence of dispersants, Tribol. Lett. 55 (2014) 503–516, https://doi.org/10.1007/s11249-014-0381-5.
[24] Y. Chen, P. Renner, H. Liang, Dispersion of nanoparticles in lubricating oil: a critical review, Lubricants 7 (2019) 7, https://doi.org/10.3390/lubricants7010007.
[25] T. Sui, B. Song, F. Zhang, Q. Yang, Effects of functional groups on the tribological properties of hairy silica nanoparticles as an additive to polyalphaolefin, RSC Adv. 6 (2016) 393–402, https://doi.org/10.1039/C5RA22932D.
[26] C. Kumara, H. Luo, D.N. Leonard, H.M. Meyer, J. Qu, Organic-modified silver nanoparticles as lubricant additives, ACS Appl. Mater. Interfaces 9 (2017) 37227–37237, https://doi.org/10.1021/acsami.7b13683.
[27] X. Wu, K. Gong, G. Zhao, W. Lou, X. Wang, W. Liu, Surface modification of MoS$_2$ nanosheets as effective lubricant additives for reducing friction and wear in poly-α-olefin, Ind. Eng. Chem. Res. 57 (2018) 8105–8114, https://doi.org/10.1021/acs.iecr.8b00454.
[28] E. Burello, A.P. Worth, QSAR modeling of nanomaterials, Wiley Interdiscip. Rev. Nanomed. Nanobiotechnol. 3 (2011) 298–306, https://doi.org/10.1002/wnan.137.
[29] C.S. Torres Castillo, C. Bruel, J.R. Tavares, Chemical affinity and dispersibility of boron nitride nanotubes, Nanoscale, Advances 2 (2020) 2497–2506, https://doi.org/10.1039/D0NA00136H.
[30] I.E. Uflyand, V.A. Zhinzhilo, V.E. Burlakova, Metal-containing nanomaterials as lubricant additives: state-of-the-art and future development, Friction 7 (2019) 93–116, https://doi.org/10.1007/s40544-019-0261-y.
[31] S. Samanta, S. Singh, R.R. Sahoo, Simultaneous chemical reduction and surface functionalization of graphene oxide for efficient lubrication of steel–steel contact, RSC Adv. 5 (2015) 61888–61899, https://doi.org/10.1039/C5RA10696F.
[32] V. Srinivas, K.R.R. Chebattina, N. Mohan Rao, Lubricating and physico-chemical properties of CI- 4 plus engine oil dispersed with surface modified multi-walled carbon nanotubes, Tribol. Mater. Surf. Interfaces 12 (2018) 107–114, https://doi.org/10.1080/17515831.2018.1452847.
[33] C. Yegin, W. Lu, B. Kheireddin, M. Zhang, P. Li, Y. Min, H.-J. Sue, M. Sari, M. Akbulut, The effect of nanoparticle functionalization on lubrication performance of nanofluids dispersing silica nanoparticles in an ionic liquid, J. Tribol. 139 (2016), 041802, https://doi.org/10.1115/1.4035342.
[34] H. Sade, A. Moshkovich, J.-P. Lellouche, L. Rapoport, Testing of WS$_2$ nanoparticles functionalized by a humin-like shell as lubricant additives, Lubricants 6 (2018) 3, https://doi.org/10.3390/lubricants6010003.
[35] J.L. Viesca, A. Hernández Battez, R. González, R. Chou, J.J. Cabello, Antiwear properties of carbon-coated copper nanoparticles used as an additive to a polyalphaolefin, Tribol. Int. 44 (2011) 829–833, https://doi.org/10.1016/j.triboint.2011.02.006.

[36] L. Kong, J. Sun, Y. Bao, Preparation, characterization and tribological mechanism of nanofluids, RSC Adv. 7 (2017) 12599–12609, https://doi.org/10.1039/C6RA28243A.

[37] S.U. Ilyas, R. Pendyala, N. Marneni, Preparation, sedimentation, and agglomeration of nanofluids, Chem. Eng. Technol. 37 (2014) 2011–2021, https://doi.org/10.1002/ceat.201400268.

[38] W. Yu, H. Xie, A review on nanofluids: preparation, stability mechanisms, and applications, Nanomaterials 2012 (2012) 1–17, https://doi.org/10.1155/2012/435873.

[39] J.A. Eastman, S. Choi, S. Li, W. Yu, L. Thompson, Anomalously increased effective thermal conductivities of ethylene glycol-based nanofluids containing copper nanoparticles, Appl. Phys. Lett. 78 (2001) 718–720, https://doi.org/10.1063/1.1341218.

[40] H.-T. Zhu, Y.-S. Lin, Y.-S. Yin, A novel one-step chemical method for preparation of copper nanofluids, J. Colloid Interface Sci. 277 (2004) 100–103, https://doi.org/10.1016/j.jcis.2004.04.026.

[41] H. Bönnemann, S.S. Botha, B. Bladergroen, V.M. Linkov, Monodisperse copper- and silver-nanocolloids suitable for heat-conductive fluids, Appl. Organomet. Chem. 19 (2005) 768–773, https://doi.org/10.1002/aoc.889.

[42] D. Wu, H. Zhu, L. Wang, L. Liu, Critical issues in nanofluids preparation, characterization and thermal conductivity, Curr. Nanosci. 5 (2009) 103–112, https://doi.org/10.2174/157341309787314548.

[43] J. Sanes, M.-D. Avilés, N. Saurín, T. Espinosa, F.-J. Carrión, M.-D. Bermúdez, Synergy between graphene and ionic liquid lubricant additives, Tribol. Int. 116 (2017) 371–382, https://doi.org/10.1016/j.triboint.2017.07.030.

[44] K.I. Nasser, J.M. Liñeira del Río, E.R. López, J. Fernández, Hybrid combinations of graphene nanoplatelets and phosphonium ionic liquids as lubricant additives for a polyalphaolefin, J. Mol. Liq. 336 (2021) 116266, https://doi.org/10.1016/j.molliq.2021.116266.

[45] M.K.A. Ali, H. Xianjun, Colloidal stability mechanism of copper nanomaterials modified by bis(2-ethylhexyl) phosphate dispersed in polyalphaolefin oil as green nanolubricants, J. Colloid Interface Sci. 578 (2020) 24–36, https://doi.org/10.1016/j.jcis.2020.05.092.

[46] T. Sui, M. Ding, C. Ji, S. Yan, J. Wei, A. Wang, F. Zhao, J. Fei, Dispersibility and rheological behavior of functionalized silica nanoparticles as lubricant additives, Ceram. Int. 44 (2018) 18438–18443, https://doi.org/10.1016/j.ceramint.2018.07.061.

[47] T. Sui, B. Song, Y.-H. Wen, F. Zhang, Bifunctional hairy silica nanoparticles as high-performance additives for lubricant, Sci. Rep. 6 (2016) 22696, https://doi.org/10.1038/srep22696.

[48] T. Sui, B. Song, F. Zhang, Q. Yang, Effect of particle size and ligand on the tribological properties of amino functionalized hairy silica nanoparticles as an additive to polyalphaolefin, J. Nanomater. 2015 (2015) 492401, https://doi.org/10.1155/2015/492401.

[49] J.M. Liñeira del Río, E.R. López, M. González Gómez, S. Yañez Vilar, Y. Piñeiro, J. Rivas, D.E.P. Gonçalves, J.H.O. Seabra, J. Fernández, Tribological behavior of nanolubricants based on coated magnetic nanoparticles and trimethylolpropane trioleate base oil, Nanomaterials 10 (2020) 683, https://doi.org/10.3390/nano10040683.

[50] M.K.A. Ali, H. Xianjun, Role of bis (2-ethylhexyl) phosphate and Al₂O₃/TiO₂ hybrid nanomaterials in improving the dispersion stability of nanolubricants, Tribol. Int. 155 (2021) 106767, https://doi.org/10.1016/j.triboint.2020.106767.

[51] V.S. Mello, E.A. Faria, S.M. Alves, C. Scandian, Enhancing CuO nanolubricant performance using dispersing agents, Tribol. Int. 150 (2020) 106338, https://doi.org/10.1016/j.triboint.2020.106338.

[52] S.M. Alves, V.S. Mello, E.A. Faria, A.P.P. Camargo, Nanolubricants developed from tiny CuO nanoparticles, Tribol. Int. 100 (2016) 263–271, https://doi.org/10.1016/j.triboint.2016.01.050.

[53] K.I. Nasser, J.M. Liñeira del Río, E.R. López, J. Fernández, Synergistic effects of hexagonal boron nitride nanoparticles and phosphonium ionic liquids as hybrid lubricant additives, J. Mol. Liq. 311 (2020) 113343, https://doi.org/10.1016/j.molliq.2020.113343.

[54] J.M. Liñeira del Río, E.R. López, J. Fernández, Synergy between boron nitride or graphene nanoplatelets and tri(butyl)ethylphosphonium diethylphosphate ionic liquid as lubricant additives of triisotridecyltrimellitate oil, J. Mol. Liq. 301 (2020) 112442, https://doi.org/10.1016/j.molliq.2020.112442.

[55] V. Khare, M.-Q. Pham, N. Kumari, H.-S. Yoon, C.-S. Kim, J.-I.-L. Park, S.-H. Ahn, Graphene–ionic liquid based hybrid nanomaterials as novel lubricant for low friction and wear, ACS Appl. Mater. Interfaces 5 (2013) 4063–4075, https://doi.org/10.1021/am302761c.

[56] J.M. Liñeira del Río, M.J.G. Guimarey, M.J.P. Comuñas, E.R. López, A. Amigo, J. Fernández, Thermophysical and tribological properties of dispersions based on graphene and a trimethylolpropane trioleate oil, J. Mol. Liq. 268 (2018) 854–866, https://doi.org/10.1016/j.molliq.2018.07.107.

[57] B.T. Seymour, W. Fu, R.A.E. Wright, H. Luo, J. Qu, S. Dai, B. Zhao, Improved lubricating performance by combining oil-soluble hairy silica nanoparticles and an ionic liquid as an additive for a synthetic base oil, ACS Appl. Mater. Interfaces 10 (2018) 15129–15139, https://doi.org/10.1021/acsami.8b01579.

[58] H.P. Mungse, O.P. Khatri, Chemically functionalized reduced graphene oxide as a novel material for reduction of friction and wear, J. Phys. Chem. C 118 (2014) 14394–14402, https://doi.org/10.1021/jp5033614.

[59] J.C. Sánchez-López, M.D. Abad, L. Kolodziejczyk, E. Guerrero, A. Fernández, Surface-modified Pd and Au nanoparticles for anti-wear applications, Tribol. Int. 44 (2011) 720–726, https://doi.org/10.1016/j.triboint.2009.12.013.

[60] J.M. Liñeira del Río, E.R. López, J. Fernández, F. García, Tribological properties of dispersions based on reduced graphene oxide sheets and trimethylolpropane trioleate or PAO 40 oils, J. Mol. Liq. 274 (2019) 568–576, https://doi.org/10.1016/j.molliq.2018.10.107.

[61] Y. Li, J. Zhao, C. Tang, Y. He, Y. Wang, J. Chen, J. Mao, Q. Zhou, B. Wang, F. Wei, J. Luo, G. Shi, Highly exfoliated reduced graphene oxide powders as efficient lubricant oil additives, Adv. Mater. Interfaces 3 (2016) 1600700, https://doi.org/10.1002/admi.201600700.

[62] D. Zheng, Z.-B. Cai, M.-X. Shen, Z.-Y. Li, M-H. Zhu, Investigation of the tribology behaviour of the graphene nanosheets as oil additives on textured alloy cast iron surface, Appl. Surf. Sci. 387 (2016) 66–75, https://doi.org/10.1016/j.apsusc.2016.06.080.

[63] J.M. Liñeira del Río, M.J.G. Guimarey, M.J.P. Comuñas, E.R. López, J.I. Prado, L. Lugo, J. Fernández, Tribological and thermophysical properties of environmentally-friendly lubricants based on trimethylolpropane trioleate with hexagonal boron nitride nanoparticles as an additive, Coatings 9 (2019) 509, https://doi.org/10.3390/coatings9080509.

[64] J. Lee, Y.-J. Yoon, J. Eaton, K. Goodson, S. Bai, Analysis of Oxide (Al₂O₃, CuO, and ZnO) and CNT Nanoparticles Disaggregation Effect on the Thermal Conductivity and the Viscosity of Nanofluids, Int. J. Precis. Eng. Manuf. 15 (2014) 703–710, https://doi.org/10.1007/s12541-014-0390-1.

[65] V. Saini, J. Bijwe, S. Seth, S.S.V. Ramakumar, Interfacial interaction of PTFE sub-micron particles in oil with steel surfaces as excellent extreme-pressure additive, J. Mol. Liq. 325 (2021) 115238, https://doi.org/10.1016/j.molliq.2020.115238.

[66] B.T. Seymour, R.A.E. Wright, A.C. Parrott, H. Gao, A. Martini, J. Qu, S. Dai, B. Zhao, Poly(alkyl methacrylate) brush-grafted silica nanoparticles as oil lubricant additives: effects of alkyl pendant groups on oil dispersibility, stability, and lubrication property, ACS Appl. Mater. Interfaces 9 (2017) 25038–25048, https://doi.org/10.1021/acsami.7b06714.

[67] J.-F. Lou, H. Zhang, R. Wang, Experimental investigation of graphite nanolubricant used in a domestic refrigerator, Adv. Mech. Eng. 7 (2015), https://doi.org/10.1177/1687814015571011.

[68] N. Rivera, D. Blanco, J.L. Viesca, A. Fernández-González, R. González, A. H. Battez, Tribological performance of three fatty acid anion-based ionic liquids (FAILs) used as lubricant additive, J. Mol. Liq. 296 (2019) 111881, https://doi.org/10.1016/j.molliq.2019.111881.

[69] M.Z. Saidi, A. Pasc, C. El Moujahid, N. Canilho, M. Badawi, C. Delgado-Sanchez, A. Celzard, V. Fierro, R. Peignier, R. Kouitat-Njiwa, H. Akram, T. Chafik, Improved tribological properties, thermal and colloidal stability of poly-α-olefins based lubricants with hydrophobic MoS₂ submicron additives, J. Colloid Interface Sci. 562 (2020) 91–101, https://doi.org/10.1016/j.jcis.2019.12.007.

[70] M.J.G. Guimarey, M.J.P. Comuñas, E.R. López, A. Amigo, J. Fernández, Thermophysical properties of polyalphaolefin oil modified with nanoadditives, J. Chem. Thermodyn. 131 (2019) 192–205, https://doi.org/10.1016/j.jct.2018.10.035.

[71] M.J.G. Guimarey, M.R. Salgado, M.J.P. Comuñas, E.R. López, A. Amigo, D. Cabaleiro, L. Lugo, J. Fernández, Effect of ZrO₂ nanoparticles on thermophysical and rheological properties of three synthetic oils, J. Mol. Liq. 262 (2018) 126–138, https://doi.org/10.1016/j.molliq.2018.04.027.

[72] M.J.G. Guimarey, J.M. Liñeira del Río, J. Fernández, Improvement of the lubrication performance of an ester base oil with coated ferrite additives for different material pairs, J. Mol. Liq. 118550 (2022), https://doi.org/10.1016/j.molliq.2022.118550.

[73] G. Paul, S. Shit, H. Hirani, T. Kuila, N. Murmu, Tribological behavior of dodecylamine functionalized graphene nanosheets dispersed engine oil nanolubricants, Tribol. Int. 131 (2019) 605–619, https://doi.org/10.1016/j.triboint.2018.11.012.

[74] J. Patel, A. Kiani, Effects of reduced graphene oxide (rGO) at different concentrations on tribological properties of liquid base lubricants, Lubricants 7 (2019) 11, https://doi.org/10.3390/lubricants7020011.

[75] J. Zhao, Y. Huang, Y. He, Y. Shi, Nanolubricant additives: a review, Friction 9 (2021) 891–917, https://doi.org/10.1007/s40544-020-0450-8.

[76] H. Tamura, K. Mita, A. Tanaka, M. Ito, Mechanism of hydroxylation of metal oxide surfaces, J. Colloid Interface Sci. 243 (2001) 202–207, https://doi.org/10.1006/jcis.2001.7864.

[77] X. Phung, J. Groza, E.A. Stach, L.N. Williams, S.B. Ritchey, Surface characterization of metal nanoparticles, Mater. Sci. Eng.: A 359 (2003) 261–268, https://doi.org/10.1016/S0921-5093(03)00348-4.

[78] G. Wang, J. Yang, J. Park, X. Gou, B. Wang, H. Liu, J. Yao, Facile synthesis and characterization of graphene nanosheets, J. Phys. Chem. C 112 (2008) 8192–8195, https://doi.org/10.1021/jp710931h.

[79] L. Liu, M. Qing, Y. Wang, S. Chen, Defects in graphene: generation, healing, and their effects on the properties of graphene: a review, J. Mater. Sci. Technol. 31 (2015) 599–606, https://doi.org/10.1016/j.jmst.2014.11.019.

[80] L. Stobinski, B. Lesiak, A. Malolepszy, M. Mazurkiewicz, B. Mierzwa, J. Zemek, P. Jiricek, I. Bieloshapka, Graphene oxide and reduced graphene oxide studied by the XRD, TEM and electron spectroscopy methods, J. Electron Spectrosc. Related Phenomena 195 (2014) 145–154, https://doi.org/10.1016/j.elspec.2014.07.003.

[81] H.P. Mungse, K. Gupta, R. Singh, O.P. Sharma, H. Sugimura, O.P. Khatri, Alkylated graphene oxide and reduced graphene oxide: Grafting density, dispersion stability to enhancement of lubrication properties, J. Colloid Interface Sci. 541 (2019) 150–162, https://doi.org/10.1016/j.jcis.2019.01.064.

[82] C.S. Chen, X.H. Chen, L.S. Xu, Z. Yang, W.H. Li, Modification of multi-walled carbon nanotubes with fatty acid and their tribological properties as lubricant additive, Carbon 43 (2005) 1660–1666, https://doi.org/10.1016/j.carbon.2005.01.044.

[83] H.P. Mungse, N. Kumar, O.P. Khatri, Synthesis, dispersion and lubrication potential of basal plane functionalized alkylated graphene nanosheets, RSC Adv. 5 (2015) 25565–25571, https://doi.org/10.1039/C4RA16975A.

[84] S. Samanta, R.R. Sahoo, Layer by layer assembled functionalized graphene oxide-based polymer brushes for superlubricity on steel–steel tribocontact, J. Soft Matter 17 (2021) 7014–7031, https://doi.org/10.1039/D1SM00690H.

[85] C. Zhu, Y. Yan, F. Wang, J. Cui, S. Zhao, A. Gao, G. Zhang, Facile fabrication of long-chain alkyl functionalized ultrafine reduced graphene oxide nanocomposites for enhanced tribological performance, RSC Adv. 9 (2019) 7324–7333, https://doi.org/10.1039/C9RA00433E.

[86] Z. Liang, B. Wang, M. Luo, H. Lu, Synthesis of hexadecylamine modified carbon dots and their friction-reducing and anti-wear performance in polyalphaolefin, Diam. Relat. Mater. 112 (2021), 108238, https://doi.org/10.1016/j.diamond.2021.108238.

[87] W. Shang, M. Ye, T. Cai, L. Zhao, Y. Zhang, D. Liu, S. Liu, Tuning of the hydrophilicity and hydrophobicity of nitrogen doped carbon dots: A facile approach towards high efficient lubricant nanoadditives, J. Mol. Liq. 266 (2018) 65–74, https://doi.org/10.1016/j.molliq.2018.06.042.

[88] M. Ye, T. Cai, L. Zhao, D. Liu, S. Liu, Covalently attached strategy to modulate surface of carbon quantum dots: towards effectively multifunctional lubricant additives in polar and apolar base fluids, Tribol. Int. 136 (2019) 349–359, https://doi.org/10.1016/j.triboint.2019.03.045.

[89] J.M. Liñeira del Río, E.R. López, F. García, J. Fernández, Tribological synergies among chemical-modified graphene oxide nanomaterials and a phosphonium ionic liquid as additives of a biolubricant, J. Mol. Liq. 336 (2021), 116885, https://doi.org/10.1016/j.molliq.2021.116885.

[90] X. Ci, W. Zhao, J. Luo, Y. Wu, T. Ge, L. Shen, X. Gao, Z. Fang, Revealing the lubrication mechanism of fluorographene nanosheets enhanced GTL-8 based nanolubricant oil, Tribol. Int. 138 (2019) 174–183, https://doi.org/10.1016/j.triboint.2019.05.044.

[91] L. Zhang, Y. He, L. Zhu, Z. Jiao, W. Deng, C. Pu, C. Han, S. Tang, Alkyl phosphate modified graphene oxide as friction and wear reduction additives in oil, J. Mater. Sci. 54 (2019) 4626–4636, https://doi.org/10.1007/s10853-018-03216-7.

[92] T. Chen, Y. Xia, Z. Jia, Z. Liu, H. Zhang, Synthesis, characterization, and tribological behavior of oleic acid capped graphene oxide, J. Nanomater. 2014 (2014), 654145, https://doi.org/10.1155/2014/654145.

[93] N.A. Ismail, S. Bagheri, Highly oil-dispersed functionalized reduced graphene oxide nanosheets as lube oil friction modifier, Mater. Sci. Eng. B 222 (2017) 34–42, https://doi.org/10.1016/j.mseb.2017.04.010.

[94] H. Lu, W. Tang, X. Liu, B. Wang, Z. Huang, Oleylamine-modified carbon nanoparticles as a kind of efficient lubricating additive of polyalphaolefin, J. Mater. Sci. 52 (2017) 4483–4492, https://doi.org/10.1007/s10853-016-0694-x.

[95] B. Li, X. Wang, W. Liu, Q. Xue, Tribochemistry and antiwear mechanism of organic–inorganic nanoparticles as lubricant additives, Tribol. Lett. 22 (2006) 79–84, https://doi.org/10.1007/s11249-005-9002-7.

[96] C. Kumara, D.N. Leonard, H.M. Meyer, H. Luo, B.L. Armstrong, J. Qu, Palladium nanoparticle-enabled ultrathick tribofilm with unique composition, ACS Appl. Mater. Interfaces 10 (2018) 31804–31812, https://doi.org/10.1021/acsami.8b11213.

[97] L. Sun, Z.J. Zhang, Z.S. Wu, H.X. Dang, Synthesis and characterization of DDP coated Ag nanoparticles, Mater. Sci. Eng. A 379 (2004) 378–383, https://doi.org/10.1016/j.msea.2004.03.002.

[98] Y. Chen, Y. Zhang, S. Zhang, L. Yu, P. Zhang, Z. Zhang, Preparation of nickel-based nanolubricants via a facile in situ one-step route and investigation of their tribological properties, Tribol. Lett. 51 (2013) 73–83, https://doi.org/10.1007/s11249-013-0148-4.

[99] R.A. Wright, K. Wang, J. Qu, B. Zhao, Oil-soluble polymer brush grafted nanoparticles as effective lubricant additives for friction and wear reduction, Angew. Chem. 128 (2016) 8798–8802, https://doi.org/10.1002/ange.201603663.

[100] X. Ran, X. Yu, Q. Zou, Effect of particle concentration on tribological properties of ZnO nanofluids, Tribol. Trans. 60 (2017) 154–158, https://doi.org/10.1080/10402004.2016.1154233.

[101] F. Mariño, E.R. López, Á. Arnosa, M.A. González Gómez, Y. Piñeiro, J. Rivas, C. Alvarez-Lorenzo, J. Fernández, ZnO nanoparticles coated with oleic acid as additives for a polyalphaolefin lubricant, J. Mol. Liq. 348 (2022) 118401, https://doi.org/10.1016/j.molliq.2021.118401.

[102] F.T. Hong, A. Schneider, S.M. Sarathy, Enhanced lubrication by core-shell TiO₂ nanoparticles modified with gallic acid ester, Tribol. Int. 146 (2020), 106263, https://doi.org/10.1016/j.triboint.2020.106263.

[103] T. Luo, X. Wei, X. Huang, L. Huang, F. Yang, Tribological properties of Al₂O₃ nanoparticles as lubricating oil additives, Ceram. Int. 40 (2014) 7143–7149, https://doi.org/10.1016/j.ceramint.2013.12.050.

[104] C. Shahar, D. Zbaida, L. Rapoport, H. Cohen, T. Bendikov, J. Tannous, F. Dassenoy, R. Tenne, Surface functionalization of WS₂ fullerene-like nanoparticles, Langmuir 26 (2010) 4409–4414, https://doi.org/10.1021/la903459t.

[105] Z. Jiang, Y. Zhang, G. Yang, K. Yang, S. Zhang, L. Yu, P. Zhang, Tribological properties of oleylamine-modified ultrathin WS₂ nanosheets as the additive in polyalpha olefin over a wide temperature range, Tribol. Lett. 61 (2016) 24, https://doi.org/10.1007/s11249-016-0643-5.

[106] Z. Jiang, Y. Zhang, G. Yang, J. Ma, S. Zhang, L. Yu, P. Zhang, Tribological properties of tungsten disulfide nanoparticles surface-capped by oleylamine and maleic anhydride dodecyl ester as additive in diisooctylsebacate, Ind. Eng. Chem. Res. 56 (2017) 1365–1375, https://doi.org/10.1021/acs.iecr.6b04074.

[107] X. Li, Z. Cao, Z. Zhang, H. Dang, Surface-modification in situ of nano-SiO₂ and its structure and tribological properties, Appl. Surf. Sci. 252 (2006) 7856–7861, https://doi.org/10.1016/j.apsusc.2005.09.068.

[108] D.X. Peng, C.H. Chen, Y. Kang, Y.P. Chang, S.Y. Chang, Size effects of SiO₂ nanoparticles as oil additives on tribology of lubricant, Ind. Lubricat. Tribol. 62 (2010) 111–120, https://doi.org/10.1108/00368791011025656.

[109] G. Wen, X. Wen, P. Bai, Y. Meng, L. Ma, Y. Tian, Effect of mixing procedure of oleic acid and BN nanoparticles as additives on lubricant performance of PAO8, Tribol. Int. 175 (2022), 107842, https://doi.org/10.1016/j.triboint.2022.107842.

[110] S. Kumari, O.P. Sharma, O.P. Khatri, Alkylamine-functionalized hexagonal boron nitride nanoplatelets as a novel material for the reduction of friction and wear, PCCP 18 (2016) 22879–22888, https://doi.org/10.1039/C6CP04741F.

[111] X. Song, S. Zheng, J. Zhang, W. Li, Q. Chen, B. Cao, Synthesis of monodispersed ZnAl₂O₄ nanoparticles and their tribology properties as lubricant additives, Mater. Res. Bull. 47 (2012) 4305–4310, https://doi.org/10.1016/j.materresbull.2012.09.013.

[112] D. Jiao, S. Zheng, Y. Wang, R. Guan, B. Cao, The tribology properties of alumina/silica composite nanoparticles as lubricant additives, Appl. Surf. Sci. 257 (2011) 5720–5725, https://doi.org/10.1016/j.apsusc.2011.01.084.

[113] M. Farsadi, S. Bagheri, N.A. Ismail, Nanocomposite of functionalized graphene and molybdenum disulfide as friction modifier additive for lubricant, J. Mol. Liq. 244 (2017) 304–308, https://doi.org/10.1016/j.molliq.2017.09.008.

[114] Q. Chen, S. Zheng, S. Yang, W. Li, X. Song, B. Cao, Enhanced tribology properties of ZnO/Al₂O₃ composite nanoparticles as liquid lubricating additives, J. Sol-Gel Sci. Technol. 61 (2012) 501–508, https://doi.org/10.1007/s10971-011-2651-0.

[115] Y. Li, R. Yang, Q. Hao, W. Lei, Tribological properties of the functionalized graphene/montmorillonite nanosheets as a lubricant additive, Tribol. Lett. 69 (2021) 1–13, https://doi.org/10.1007/s11249-021-01495-x.

[116] Y. Meng, F. Su, Y. Chen, Synthesis of nano-Cu/graphene oxide composites by supercritical CO₂-assisted deposition as a novel material for reducing friction and wear, Chem. Eng. J. 281 (2015) 11–19, https://doi.org/10.1016/j.cej.2015.06.073.

[117] Z. Jia, T. Chen, J. Wang, J. Ni, H. Li, X. Shao, Synthesis, characterization and tribological properties of Cu/reduced graphene oxide composites, Tribol. Int. 88 (2015) 17–24, https://doi.org/10.1016/j.triboint.2015.02.028.

[118] W.K. Shafi, M.S. Charoo, An overall review on the tribological, thermal and rheological properties of nanolubricants, Tribol. Mater. Surf. Interfaces 15 (2021) 20–54, https://doi.org/10.1080/17515831.2020.1785233.

[119] J. Sun, S. Du, Application of graphene derivatives and their nanocomposites in tribology and lubrication: a review, RSC Adv. 9 (2019) 40642–40661, https://doi.org/10.1039/C9RA05679C.

[120] J. Zhao, T. Gao, Y. Li, Y. He, Y. Shi, Two-dimensional (2D) graphene nanosheets as advanced lubricant additives: a critical review and prospect, Mater. Today Commun. 29 (2021), 102755, https://doi.org/10.1016/j.mtcomm.2021.102755.