Moringa oil with graphite and hexagonal boron nitride particles as additives for lubrication

Manuella Vitulin, Henry Joseph, Philippe Thomas, Nadiège Nomède-Martyr

To cite this version:

Manuella Vitulin, Henry Joseph, Philippe Thomas, Nadiège Nomède-Martyr. Moringa oil with graphite and hexagonal boron nitride particles as additives for lubrication. Diamond and Related Materials, 2022, 124, pp.108930. 10.1016/j.diamond.2022.108930 . hal-03603399

Version of Record: https://www.sciencedirect.com/science/article/pii/S0925963522001121
Manuscript_64b7c7f9691b506729c60d96cdf1c271

Moringa oil with graphite and hexagonal boron nitride particles as additives for lubrication

Nadiège Nomède-Martyr*[1], Manuella Vitulin[1], Henry Joseph[2] and Philippe Thomas[1]

[1]Groupe de Technologie des Surfaces et Interfaces (GTSI) EA 2432, Faculté des Sciences Exactes et Naturelles, Université des Antilles, 97159 Pointe à Pitre Cedex, France
[2]Laboratoire Phytobokaz, Chemin de Gros Morne, Dolé, 97113 Gourbeyre

Correspondence: nadiege.nomede-martyr@univ-antilles.fr

Abstract:

Tribological behaviour of bio-lubricants is constantly evolving to be improved. Vegetable and synthetic oils owing the increasing interest of the environmental impact constitute a suitable alternative for lubrication. The addition of particles as additive show a great potential to improve the tribological properties of bio-lubricants. This paper overviewed the effect of graphite and hexagonal boron nitride (hBN) particles as additives on the tribological properties of different lubricating base oils such as mineral oil (dodecane), vegetable oil (moringa oil) and vegetable/dodecane blends. The addition of particles (0.5 and 1 w%) has indicated an improvement of the mineral base oil. At the addition of small amounts of moringa oil (MO), a reduction of about 55% of friction and wear performances of dodecane. We showed that the more promising results were obtained for the blend containing 3 w% of MO with hBN particles. These new formulations lubricant represent an excellent alternation for lubrication environmentally friendly.

Keywords: vegetable oil; additives; graphite; hexagonal boron nitride; mixed lubrication

1. Introduction

Lubrication consists in controlling friction and wear by the introduction of friction reducing film between moving surfaces in contact. The role of lubricant is to reduce friction, prevent wear, protect the equipment from corrosion, control temperature…during different lubrication regimes. Mixed lubrication regime is characterized by a thin lubricating film, the asperities of the surfaces remaining in contact. Friction reduction additives have to ensure lubricating properties. Researches have proved that lubricants composed of petroleum and synthetic-based oil with various additives affect negatively the environment and human health. The main objective is to reduce both dependence on petroleum and anthropogenic impact on the environment by using vegetable oil-based lubricants. Indeed, due to their high biodegradability, low toxicity, renewability and excellent lubricating performances, vegetable oils show a potential to deem a suitable substitute or improve petroleum oils performances for lubricants [1–5]. « Biolubricants » are still not widely used due to several challenges and difficulties regarding their performances and production such as feed-stock reliability and consistency as well as industry acceptance [6–9].

Composition of fatty acid in triglyceride structures have an important influence on tribological properties of vegetable oils [10–14]. Such molecules present a strong adsorption capability which contributes to good lubricating effects. Carboxyl groups are chemically bonded to metal surfaces while alkyls tail sticking away from the metal surface forming a monolayer film [15]. Natural fatty acids present in vegetable oils are saturated, polyunsaturated and monounsaturated molecules. Lundgren et al showed that friction increases with increasing unsaturation due to multi-layered structure of U-shaped molecules adsorbed film [16]. Reeves et al studies that natural oils with high oleic acid concentrations improve friction and wear performance by establishing densely packed monolayers on surfaces [17]. Moringa oil mainly composed of unsaturated fatty acid molecules presents a potential source for bio-fuel [18–20]. Sharma et al have showed the good potential of moringa oil to be used as lubricant base oil due to excellent thermal and oxidative stability [21]. Various types of nanoparticles from solid lubricant were used as additives to increase the efficiency, physical, chemical properties of lubrication oils [22–26]. Graphite and hexagonal boron nitride present lamellar structure, well known for good anti-wear and anti-friction ability resultant in low tribological performances [27–29]. Kerni et al revealed that the addition of 0.5 w% concentration of CuO and hBN nanoparticles in olive oil improves the friction properties [26].

The objective of this paper is to study the effect of graphite and hexagonal boron nitride (hBN) particle as friction reduction additives on the tribological properties of different lubricating base oils such as mineral oil (dodecane), vegetable oil (moringa) and vegetable/dodecane blends. Tribological properties of blends with 0.5 and 1 w% of particles in oils were determined at ambient atmosphere using ball-on-plane tribometer in mixed lubrication tribological regime. Physicochemical characterisations of the different base-oil lubricant formulations were performed using infrared spectroscopy, viscosimeter. Raman and SEM investigations were carried out on resulting tribological films.

2. Materials and Methods

Dodecane ReagentPlus 99% used in this study as mineral base oil was provided by Sigma-Aldrich. Vegetable oil is local moringa oil (MO) extracted by Phytobokaz Laboratory (Guadeloupe, France). It is used either as vegetable base-oil or as additive in dodecane base-oil. The fatty acids composition of moringa oil is presented in Table 1 (industrial analysis from Phytobokaz). MO is mainly composed of monounsaturated fatty acid. Exfoliated graphite particles were used as a solid friction reduction additive (Timcal Society). Graphite particles thickness is about 100 nm with an average size of 40 µm. The ratio between size and thickness is about 400. Hexagonal boron nitride particles are commercialized by Sigma Aldrich society. The particles present rounded and flattened shapes. The average thickness is 0.2 µm and length and width are about 2 µm and 1.5 µm respectively.

In a first part, blends containing 0.5 and 1 w% of particles in base oils were prepared. The mixture preparation consists in simply weighing with a precision of 0.01 mg. Two types of lubricants were prepared using dodecane base-oil and moringa base-oil. The dispersion of the different blends was obtained in ultrasonically bath during 5 min. In a second part, blends containing 0.5, 1, 1.5, 2 and 3 w% of moringa oil in dodecane were prepared. Three lubricant compositions were obtained with 1 w% of graphite and 0.5 w% of hBN in base oil composed of 1, 2 and 3 w% of MO in dodecane by the same weighing technique.

Fatty Acid Methyl Ester		**% Mole Fraction**
Palmitic	C16:0	6.09
Palmitoleic	C16:0	1.94
Stearic	C18:0	3.77
Oleic	C18:1	75.33
Linoleic	C18:2	0.90
Linolenic	C18:3	0.29
Arachidic	C20:0	2.47
Behenic	C22:0	5.67
Lignoceric	C24:0	1.01

Table 1: Composition of moringa oil

The friction properties of materials were measured at room temperature (25 °C) with a reciprocating ball-on-plane tribometer consisting of a AISI 52100 steel ball rubbing against a static AISI 52100 steel plane (Figure 1). The ball with a diameter of 1 cm was brought in contact of the plane with a normal load of 10 N. The alternative motion of the ball was performed with a sliding speed of 4 mm/s. The frequency is 1 Hz. The tangential force F_T was estimated with a computer-based data acquisition system. The friction coefficient value was calculated as $\mu = {}^{F_T}/_{F_N}$. 2000 friction cycles were performed, a cycle corresponding to an alternative motion of the ball. According to Hertz theory, such tribological conditions lead to maximum contact pressure of 1 GPa and a contact diameter of 140 µm.

The steel planes were unpolished with abrasive discs up to reach a roughness close to 350 nm. The generation of multidirectional stripes favours the adherence of particles on the sliding surfaces (Figure 1c). For all experiments, the initial roughness of the steel ball was about 50 nm. Before friction experiments, both steel materials were successively cleaned in ultrasonic acetone and ethanol baths. First the tribological properties of pure particles were evaluated. The corresponds friction coefficient are noted $\mu_{particles}$. The influence of dodecane was evaluated by the addition of a drop during friction experiment of pure particles; $\mu_{particles+dodecane}$. In the case of the mixtures, a drop of the solution was deposed on the plane before the friction experiment. The blends were manually agitated before each friction experiments to collect the drop. The blends composed with particles as additives are noted $\mu_{w\%\,particles+dodecane}$ and $\mu_{w\%\,particles+MO}$. The blends with MO and dodecane are noted $\mu_{w\%MO+dodecane}$ and for mixtures containing particles, the notation is $\mu_{w\%\,particles+w\%\,MO+dodecane}$.

The viscosity parameter of the blends without particles was measured by a modular compact rheometer (Anton Paar) at ambient temperature with a cone/plane contact. The cone presents a diameter of 50 mm and angle of 2°. The plane diameter is 50 mm. The share rate is 0.01 to 1000 s^{-1}. Fourier transform infrared spectroscopy (FTIR) analyses were performed to identify the functional groups in the blends using a PerkiElmer Spectrum Two spectrometer with a range of 4000 to 50 cm^{-1} wave numbers and a resolution of 4 cm^{-1}. Scanning electron microscopy (SEM) investigations using secondary electron imaging are performed to characterize the particles and their corresponding tribofilms with a FEI Quanta 250 microscope. Both samples were analysed by Raman spectroscopy performed with a HR 800 Horiba multi-channel spectrometer using a Peltier-cooled CCD detector for signal recording. The exciting line was 532 nm wavelength line (ND YAG laser). The steel planes were rinsed before Raman analysis in order to eliminate the residual particles.

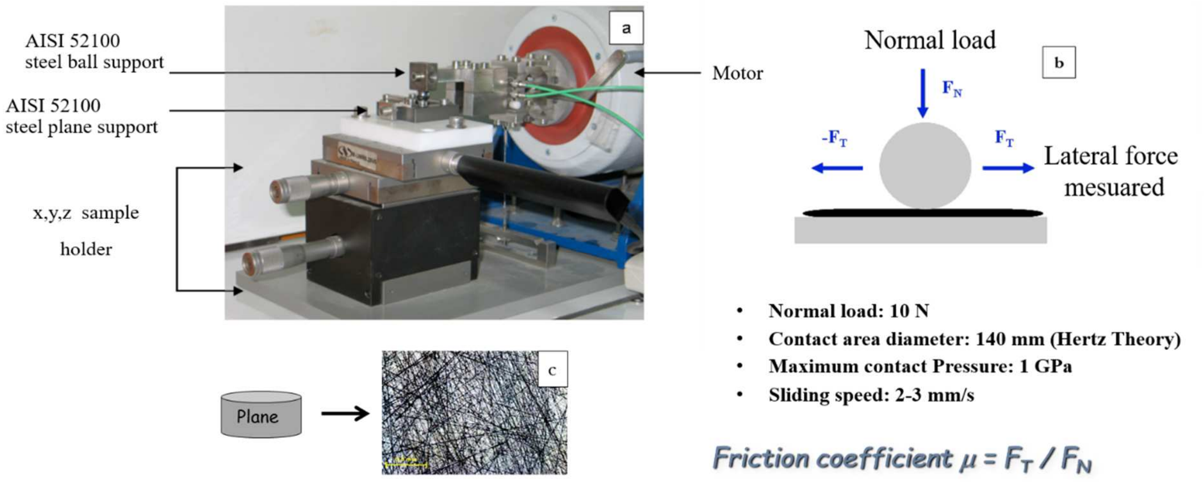


Figure 1: Picture of reciprocating ball on plan tribometer **(a)** with a schematization of friction experiment **(b)** and SEM image of the multidirectional stripes generated on the steel plane in order to a the presence of solid particles in the sliding contact **(c)**.

3. Results

3.1. Friction properties of solid particles

Figure 2a presents the evolution of the friction coefficient as a function of cycles number of both graphite and hexagonal boron nitride pure particles in dry conditions. The graphite friction curve starts with an induction period characterized by a high friction value and then decreases continuously during 30 cycles down to reach an asymptotic value $\mu_{graphite} = 0.09 \pm 0.01$. This induction period is associated to the built-up of the tribofilm. For hBN, this period corresponds to 20 cycles with a higher starting friction coefficient value. The stable friction value is higher than graphite one; $\mu_{hBN} = 0.42 \pm 0.01$. In the case of hBN, after 50 cycles, the coefficient increases up to the steel coefficient value indicating a progressive degradation of the hBN tribofilm during the friction experiment. In dry conditions, graphite and hBN particles present different tribological performances. In previous studies, we showed the beneficial influence of the presence of liquid on the tribological properties of graphite and hBN particles [29]. Figure 2b reports the friction curves obtained at the addition of dodecane during the friction experiments of graphite and hBN. The friction experiments start in dry conditions with respective friction coefficient values. In both cases, an immediate and drastic reduction of the friction coefficients is observed when dodecane is added. For both cases, it is important to note that the friction values are similar and remain stable until the end of the experiments.

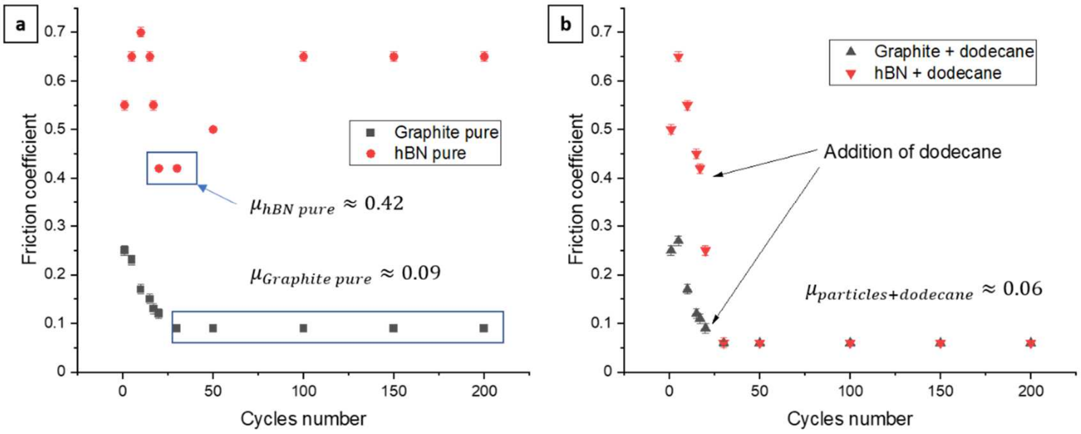


Figure 2: Friction coefficient as a function of cycles number of pure graphite and hBN in dry conditions **(a)**. and when dodecane is added **(b)**.

Raman spectroscopy investigations were used to evaluate the degradation of the particles structure in the presence of dodecane after friction experiments (Figure 3). The typical Raman spectra recorded on the initial graphite particles presents three bands. The G band at 1575 cm^{-1} is associated to relative elongation vibration of carbon atoms in the graphene planes. The D band at 1350 cm^{-1} and D' band at 1620 cm^{-1} are attributed to disorder. Similar Raman bands are observed on the tribofilm built from the mixture graphite/dodecane (Figure 3a). Tunistra and Koeing have shown a relation between the coherence length of graphite crystallites L_a and the intensity of Raman bands associated to D and G modes; $L_a(\dot{A}) = C(\lambda)\,{}^{I_G}\!/_{I_D}$ with $C(\lambda = 514\,nm) = 44$ [30]. Figure 3b displays the coherence length calculated as a function of cycles number constituting the tribofilms built with graphite/dodecane blend. The initial crystallite size (before friction) is about $70 \pm 5\,\dot{A}$ and decreases down to $30 \pm 3\dot{A}$ after 200 cycles. In the case of hBN (Figure 3c), Raman spectra is characterized by a band at 1368 cm^{-1} with a width of 19 cm^{-1} associated to the intra-plane vibrations [31]. Nemanich et al have shown that the band characterizing the intra-plane vibration mode is shifted towards high frequencies and widens with decrease of the size of crystallites; $L_a = {}^{1417}\!/_{\Gamma_{1/2}} - 8.70$ with $\Gamma_{1/2}$ the half-width value of the intra plane vibration band [32]. As for graphite, Raman spectra obtained on initial powder and on the tribofilm built with hBN/dodecane mixture are similar. The initial value is about $130 \pm 17\dot{A}$ and after 200 cycles $L_a = 127 \pm 5\dot{A}$ (Figure 3b). These results show that the presence of dodecane limits the crystallite size reduction of the solid particles.

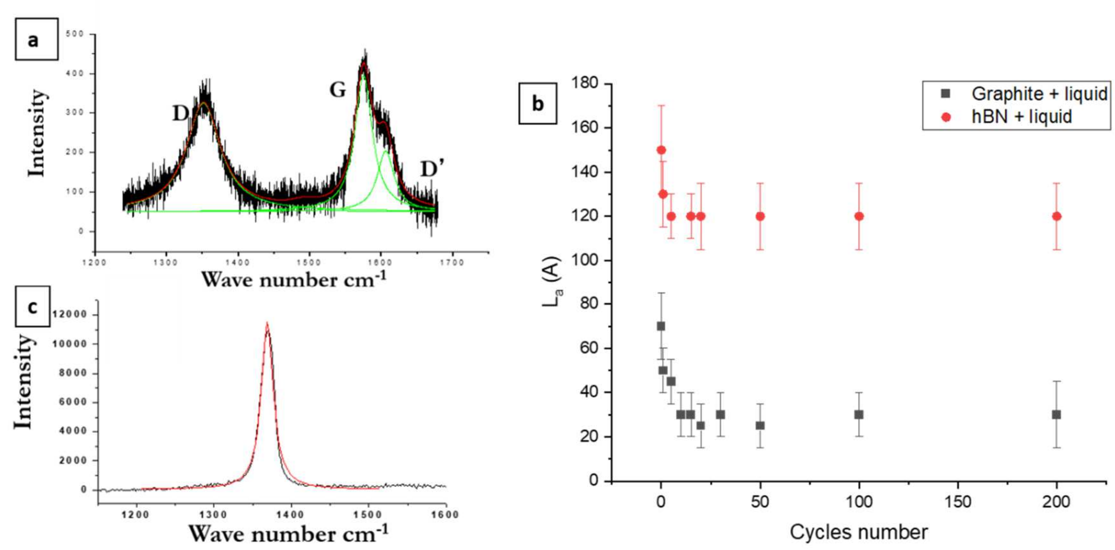


Figure 3: Raman spectra recording on tribofilms built in the presence of liquid for graphite particles **(a)** and hBN **(c)**. Corresponding length coherence calculated as a function of cycles number for both crystallites **(b)**.

In order to evaluate the effiency of graphite and hBN particles as friction reduction additives to mineral oil (dodecane) and vegetable oil (moringa oil), blends containing 0.5 and 1 w% of particles were prepared. It is important to note that the friction and wear values obtained for pure dodecane are high; $\mu_{pure\ dodecane} = 0.18 \pm 0.02$ and a contact diameter $\emptyset_{pure\ dodecane} = 280 \pm 10$ μm characterizing severe tribological conditions. In comparison, friction and wear performances of pure moringa oil are weak; $\mu_{pure\ MO} = 0.07 \pm 0.005$ and $\emptyset_{pure\ MO} = 150 \pm 10$ μm. Figure 4 displays the friction coefficients values obtained with the different mixtures containing particles as additives in dodecane (a) and in MO base-oil (b) at 2000 cycles. According to the percentage of particles as additives in both base oils, the friction coefficient values are modified. The presence of particles in mineral base-oil leads to an improvement about 50% of the tribological properties of dodecane. The best results are obtained with 1 w% of graphite and 0.5 w% of hBN in dodecane. The friction coefficient values are similar $\mu_{1w\%\ graphite+dodecane} = \mu_{0.5w\%\ hBN+dodecane} = 0.06 \pm 0.005$. In comparison, no reduction is observed for blends containing particles as additive in moringa oil base. Despite the significant increase of the coefficient, an influence of the amount and the type of particles can be noted. The friction coefficient values are higher than the friction coefficient of pure MO but the lowest values are obtained for blends with 1 w% of graphite and 0.5 w% of hBN in MO. These results confirm an influence of the viscosity parameter on friction performances of particles. Indeed, we are measured for dodecane, $\nu_{Pure\ dodecane} \approx 1.383\ mPa.s$ and MO, $\nu_{Pure\ moringa\ oil} \approx 87\ mPa.s$. Moreover, an important effect of percentage of solid additives is evidenced. For both mineral and vegetable base-oils, the best results are obtained for the blends composed with 1 w% of graphite and 0.5 w% of hBN.

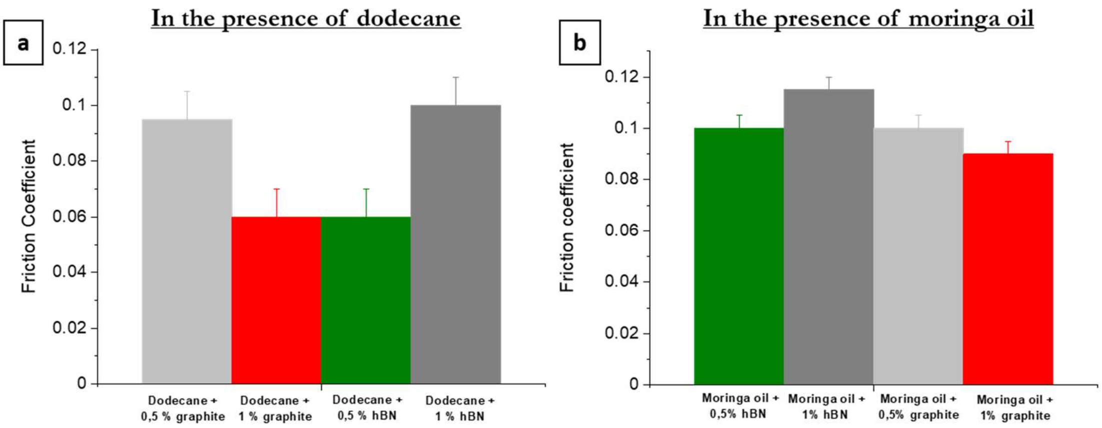


Figure 4: Friction coefficient of blends with dodecane as base-oil **(a)** and moringa base-oil **(b)**. The values are obtained after 2000 cycles.

3.2. Moringa oil and particles as additives in lubricants

Blends composed with small amounts of moringa oil in dodecane were investigated. The friction coefficient values obtained at 1000 cycles and wear scar diameters measured on the ball for pure MO and as a function of the percentage of MO added in dodecane are presented in Figure 5. The friction coefficient values obtained for MO/dodecane are higher than the one obtained for pure MO, but lower than pure dodecane. A progressive decreasing of the values according to the percentage of MO added in dodecane is noticed. A stabilisation of the friction coefficient from 1 w% of MO until 3 w% added is observed; $\mu = 0.1 \pm 0.005$. The wear scar diameter decreases from 180 to 145 ± 5 µm from the blend with 0.5 w% of MO to 1.5 w% and then stabilizes until 3 w% of MO. The addition of MO improves the friction reduction properties of dodecane and enhances the anti-wear performances of the lubricant.

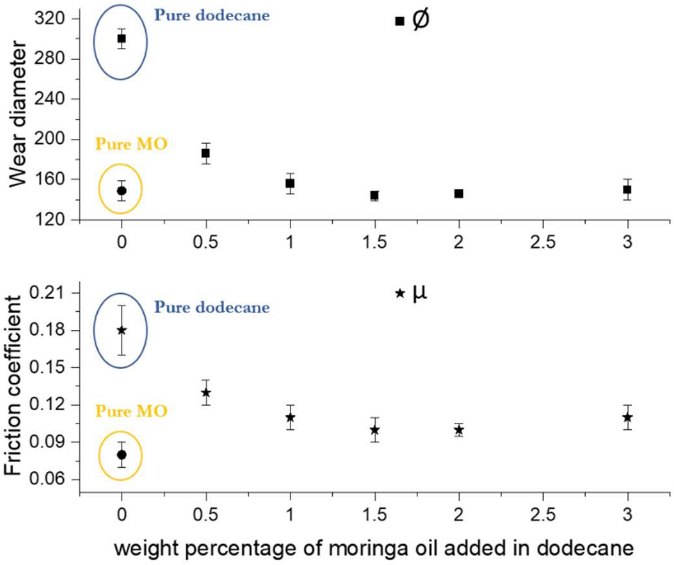


Figure 5: Friction coefficient values and diameter of wear tracks on the ball after friction experiments as a function of percentage of MO added in dodecane base oil.

According to previous results, different mixtures were prepared containing 1 w% of graphite and 0.5 w% of hBN with 1, 2 and 3 w% of MO in the mineral base-oil. Figure 6a displays the friction coefficient values obtained after 2000 cycles from the different blends containing graphite particles. An influence of the percentage of vegetable oil added is evidenced. Higher and similar friction coefficient values are obtained for the graphite/MO and graphite/3w% MO/dodecane blends. For mixture containing graphite with 1 w% of MO, the friction coefficient is weaker but greater than graphite/dodecane blend. The best result is obtained with 2 w% of MO added in graphite/dodecane blend. In the case of mixtures with hBN, higher friction coefficient is obtained with pure MO. We observe a progressive reduction of the friction values according to the percentage of MO added. With 1 w% of MO, the value is higher than hBN/dodecane blend but from 2 w% of MO, friction values are weaker. The best result with hBN mixtures has been obtained with 3 w% of MO/dodecane blend.

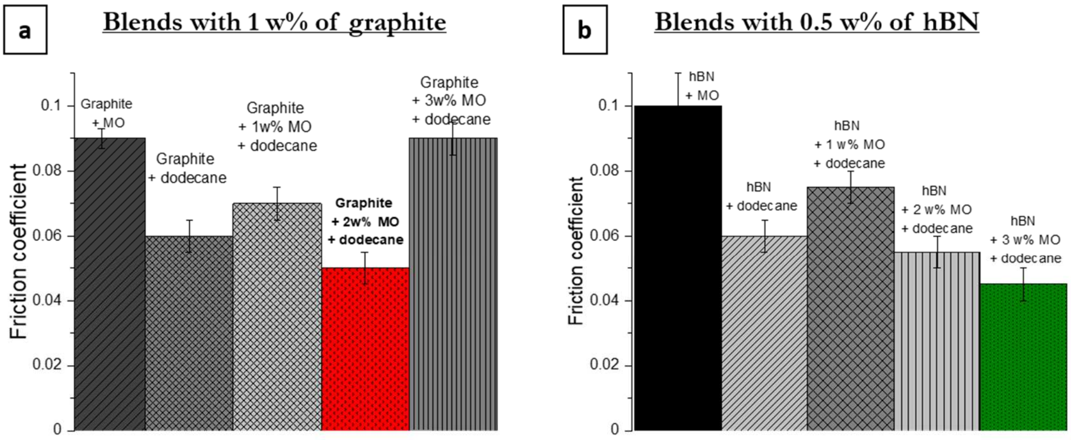


Figure 6: Friction coefficient values obtained after 2000 cycles with blends containing graphite **(a)** and hexagonal boron nitride **(b)** particles

In order to evaluate the physicochemical difference between the %w MO/dodecane blends, viscosity parameter and FTIR have been investigated. Pure dodecane has a weak viscosity compare to pure moringa; $\nu_{pure\ dodecane} = 1.383\ mPas$ and $\nu_{pure\ MO} = 87\ mPas$. In the case of the blends, no significant differences have been noted $\nu_{1w\%MO/dodecane} = \nu_{2w\%MO/dodecane} \approx \nu_{3w\%MO/dodecane} \approx 2.37 mPas$. Figure 7 presents a comparison between the FTIR spectra obtained for pure dodecane, pure MO and the MO/dodecane blends. FTIR measurement uncertainty is approximately ± 3 cm^{-1}. FTIR technique allows to identify important functional groups which are capable to absorb metal ions. Table 2 recapitulates FTIR peaks composed MO and dodecane. No difference has been observed between dodecane and the blends. The low amount of MO characterized by carboxylic peaks of fatty acid molecules have not been detected. FTIR spectra for 3w% MO/dodecane blend is not represented due to its similarity.

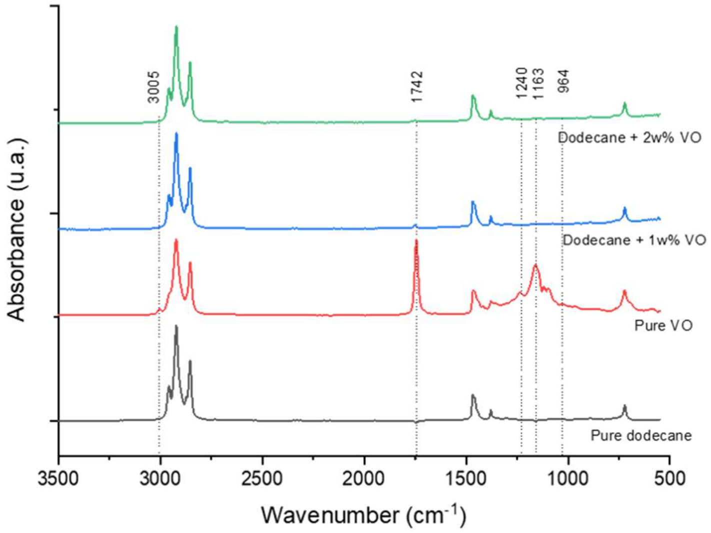
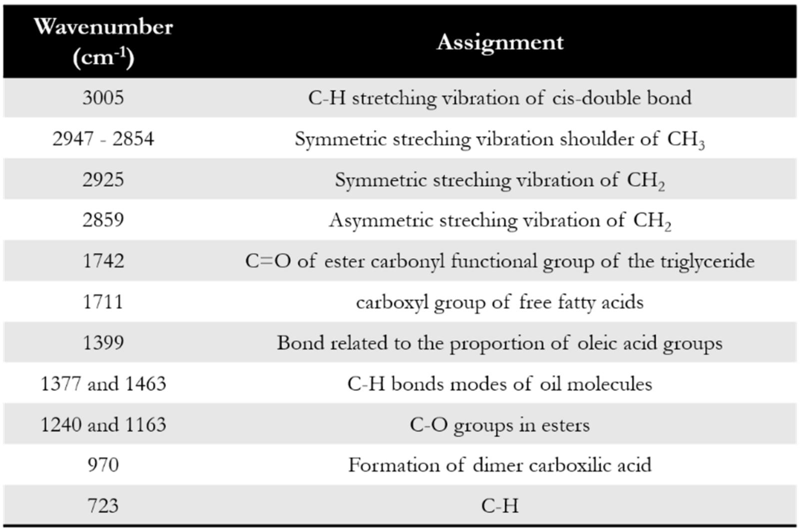


Figure 7: Comparison between different FTIR spectra obtained



Wavenumber (cm^{-1})	Assignment
3005	C-H stretching vibration of cis-double bond
2947 - 2854	Symmetric streching vibration shoulder of CH$_3$
2925	Symmetric streching vibration of CH$_2$
2859	Asymmetric streching vibration of CH$_2$
1742	C=O of ester carbonyl functional group of the triglyceride
1711	carboxyl group of free fatty acids
1399	Bond related to the proportion of oleic acid groups
1377 and 1463	C-H bonds modes of oil molecules
1240 and 1163	C-O groups in esters
970	Formation of dimer carboxilic acid
723	C-H

Table 2: FTIR peaks characterizing functional groups in dodecane and moringa oil

The tribological film built with graphite/2w% MO/dodecane blend was analysed by SEM and Raman spectroscopy. Figure 8a presents a SEM micrograph of the tribofilm obtained after 2000 cycles. Near to the wear track, some initial graphite particles are visible. The initial stripes of steel plane are visible in the wear track confirming a weak thickness of the tribofilm. Moreover, the tribofilm is not homogenous along the wear track indicating a weak adhesion of the particles on the steel plane. These observations show excellent antiwear properties of this lubricant formulation. Raman spectra recorded on graphite particles near the wear trace and on the tribofilm are presented in Figure 8b and 8c. The three Raman bands corresponding to graphite (as previously described) are detected. No significant difference between both spectra are noticed characterizing no significant evolution of the crystalline structure after the friction experiments. Same observations have been realized with tribofilm built with hBN/w% MO/dodecane blends. The presence of fatty acid and dodecane seems to limit the mechanical constraints during the sliding experiments.

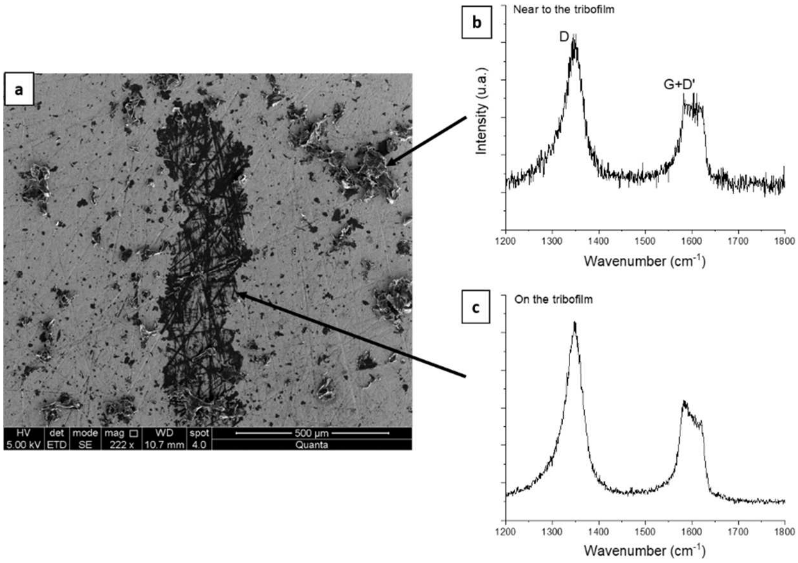


Figure 8: SEM micrograph of graphite/2w% MO/dodecane blend **(a)** – Raman spectrum recorded on graphite particles near to the tribofilm **(b)** and Raman spectrum, obtained on the tribofilm **(c)**

4. Discussion

Graphite and hexagonal boron nitride present good lubrication properties due to their lamellar structure characterized by covalent bands within basal layers and weak van der Waals interaction between the sheets, resulting in interplanar mechanical weakness [33,34]. Indeed, lamellar lubricants, due to the weak Van der Waals forces during the sliding process can adhere to the surface forming a protective layer that minimize contact between opposite surfaces asperities and prevent from wear. Moreover, the basal planes are parallel to the sliding direction minimizing friction. However, hBN particles are considered less efficient except for high-temperature applications. At ambient atmosphere, we have showed an important difference between the friction performances of both particles; $\mu_{graphite} = 0.09 \pm 0.01$ whereas $\mu_{hBN} = 0.42 \pm 0.01$ (Figure1). After the formation of the tribological film, a deterioration is noted during the sliding of hBN whereas the performances are stable for graphite particles. Severe friction and wear are confirmed for hBN at ambient atmosphere. In previous study, we have shown the effect of the presence of liquid on tribological performances of graphite and hBN particle at ambient atmosphere [29]. An important and drastic reduction of the friction coefficient is observed at the addition of liquid; $\mu_{Graphite+liquid} \approx \mu_{hBN+liquid} = 0.06 \pm 0.01$ except in the presence of high-viscosity liquid. These values are stable until the end of friction experiments (Figure 3). We have demonstrated that this reduction is not due to intercalation or hydrogen lubrication process, and that adsorption mechanism on particles and on metallic surfaces cannot explain this improvement. The selected friction mechanism points out that the simultaneous presence of particles and low-viscosity liquid in the sliding contact under pressure improves friction performances and allows significant reduction of the mechanical constraints undergone by the solid particles in the presence of liquid.

In order to evaluate the performances of graphite and hBN particles as additives in mineral base (dodecane) and in vegetable base (moringa oil), the tribological properties of two different blends with 0.5 and 1w% have been analysed. In good agreement with previous results, the best friction coefficient values are obtained for blends using dodecane as base oil due to viscosity parameter measured for both base-oils; $\nu_{Pure\ dodecane} \approx 1.383\ mPa.s$ and $\nu_{Pure\ moringa\ oil} \approx 87\ mPa.s.$ Whatever was the percentage of particles, an important reduction was observed compared to friction and wear performances of pure dodecane whereas no improvement can be noted in moringa base-oil. Moreover, an effect of the percentage of solid additives is obtained for both base-oils. The lowest friction coefficient values are attained with blends containing 1 w% of graphite and 0.5 w% of hBN. It is important to note that similar friction coefficients are obtained in the presence of dodecane base oil characterizing an effect of the percentage and the shape of particles on tribological performances. Numerous studies on friction-reducing and antiwear properties of vegetable based oil using graphite or hBN particles as additives have been performed [27,35–38]. Reeves et al have evaluated the effect of boron nitride particle size on the tribological performance of canola oil-based lubricant mixtures at 5% by weight [39]. They show that the nano-sized particles were able to better coalesce in the asperity valleys of surfaces due to their small size and spherical shape resulting enhanced tribological properties. Su et al investigated the tribological properties and lubrication mechanism of graphite as vegetable based oil additive [28]. Same conclusion has been observed a same nanoparticles mass fraction, the smaller the particles, the lower the friction coefficient and wear volume due to the formation of physical deposition film on the friction surfaces. Our results are in accordance with literature, hBN particles are smaller than graphite ones and consequently the tribofilm covers the roughness of metallic surfaces. We can deduce an effect on the thickness of the tribofilm on the tribological properties of the mixtures. This is the reason why the next lubricant formulations were carried out with 1 w% of graphite and 0.5 w% of hBN.

The third part of this review is about the tribological performances of moringa oil (MO) and solid particles as additives on dodecane lubricant base-oil. Friction and wear performances of blends containing different percentage of MO in dodecane base oil have been analysed. At the addition of small amount of MO an improvement about 50 % of dodecane properties was observed. A progressive reduction then a stabilization according to the percentage of added MO is noted. These results are in good agreement with literature. Singh et al showed that the addition of 5 and 8 % moringa-oil-based biodiesel with the base lubricant SAE 20W40 acted as a very good lubricant additive [20]. Bahari et al showed that when palm oil and soybean oil are blended with mineral engine oil, the performance of the blend is influenced by its vegetable oil component and that tribological characteristics of vegetable oils are dominant [40]. We found that $\mu_{Pure\,MO} = 0.08 \pm 0.01$ and $\mu_{2w\%\,MO+dodecane} = 0.1 \pm 0.01$ whereas $\mu_{Pure\,dodecane} = 0.18 \pm 0.01$ allowing us to confirm an excellent influence of MO physicochemical properties as bio-additive for lubrication. Different mixtures containing 1w% of graphite and 0.5 w% of hBN in 1, 2 and 3 w% of MO/dodecane were investigated. An evolution of the friction coefficient values according to the percentage of MO added shows an effect of fatty acid molecules on the tribological performances of the mixtures. In the case of graphite, a critical value of the quantity of MO was observed, the friction coefficient increases with 3 w% of MO added. While, the coefficient decreases with 3 w% MO with hBN blend confirming an important action of the thickness of fatty acid adsorbed on the particles surface. Indeed, no difference about the viscosity parameter can be noted; $\upsilon_{1w\%\,MO/dodecane} \approx \upsilon_{2w\%\,MO/dodecance} \approx \upsilon_{3w\%\,MO/dodecane} \approx 2.37\,mPa.s$. In previous study, we had shown an influence of the thickness of fatty acid cekanoic acid, CK8) molecules adsorbed at the hBN' surfaces on their tribological properties [29]. The coefficient value is high for a low thickness fatty acid molecule adsorbed. The best lubricant formulations are 1w% graphite + 2 w% of MO + dodecane, $\mu_{1w\%\,graphite+2w\%MO+dodecane} = 0.05 \pm 0.005$ and 0.5 w% of hBN + 3 w% of MO + dodecane, $\mu_{0.5w\%\,hBN+3w\%MO+dodecane} = 0.045 \pm 0.005$. These results evidenced an action of surface properties 'influencing the tribological properties of lubricants.

5. Conclusion

Lubricating properties of moringa oil as base-oil and as friction reducer additive have been determined at ambient atmosphere in mixed lubricating regime. Graphite and hexagonal boron nitride are the solid particles using as friction reducer additives used for lubricants. The major quantitative results are as follows.

(1) Under ambient atmosphere, the friction performances of graphite are better than those of hexagonal boron nitride. Friction curve shows a rapid deterioration of the hBN tribofilm whereas in the case of graphite a stabilisation is noted until the end of friction experiment.

(2) At the addition of dodecane, an immediate and drastic reduction of the friction coefficient values for graphite and hBN is showed. The friction values are similar and stable. During the friction experiment, the presence of dodecane limits the degradation of crystallites structure of particles.

(3) Graphite and hBN particles are excellent performances as friction reducer additive in mineral base-oil compare to vegetable base-oil due to the viscosity difference between both base-oils. In agreement with previous studies, these results confirm the excellent influence of the presence of liquid on tribological properties of solid particles.

(4) Similar friction coefficient values have been obtained with blends containing 1 w% of graphite and 0.5 w% of hBN in dodecane evidencing an action of particles size on tribological properties of lubricant formulations.

(5) Moringa oil have excellent friction reducer and also antiwear properties as additive in mineral base-oil. The presence of weak amount of MO in dodecane allows an important improvement of dodecane tribological performances. Moringa as additive for mineral base oil could be interesting for “bio-lubricant” field.

(6) An adsorption effect of fatty acid molecules on tribological properties of the different lubricant formulations have been demonstrated. The surface properties of solid particles are an important parameter for tribological performances of lubricants; the best results have been obtained to lubricant 1 w% of graphite + 2 w% of MO + dodecane and 0.5 w% of hBN + 3 w% of MO + dodecane mixtures.

(7) The lubricants formulated present excellent friction performances and also antiwear performances. Tribofilms formed have excellent protective properties for metallic surfaces in sliding.

6. Reference

[1] K.M. Talkit, D.T. Mahajan, V.H. Masand, Study on physicochemical properties of vegetable oils and their blends use as possible ecological lubricant, J. Chem. Pharm. Res. 4 (2012) 5139–5144.

[2] M. Ruths, S. Lundgren, K. Danerlöv, K. Persson, Friction of fatty acids in nanometer-sized contacts of different adhesive strength, Langmuir. 24 (2008) 1509–1516. https://doi.org/10.1021/la7023633.

[3] A.G. Ponomarenko, T.G. Boiko, A.A. Bicherov, A. V. Bicherov, T.A. Shiryaeva, D. V. Kulemzin, Improving the lubricating properties of transmission oils by activating the processes of boundary films formation, IOP Conf. Ser. Mater. Sci. Eng. 1029 (2021). https://doi.org/10.1088/1757-899X/1029/1/012002.

[4] L.I. Farfan-Cabrera, E.A. Gallardo-Hernández, M. Gómez-Guarneros, J. Pérez-González, J.G. Godínez-Salcedo, Alteration of lubricity of Jatropha oil used as bio-lubricant for engines due to thermal ageing, Renew. Energy. 149 (2020) 1197–1204. https://doi.org/10.1016/j.renene.2019.10.116.

[5] A.S. Kalhapure, V.M. Mhaske, S. Bajaj, Tribological Evaluation of Vegetable oils as a Multi-cylinder Engine lubricant, Int. Adv. Res. J. Sci. 3 (2016) 68–72. https://doi.org/10.17148/IARJSET/ICAME.14.

[6] R. Kreivaitis, J. Padgurskas, M. Gumbyte, V. Makarevičiene, B. Spruogis, The influence of oxidation on tribological properties of rapeseed oil, Transport. 26 (2011) 121–127. https://doi.org/10.3846/16484142.2011.586109.

[7] R. Singh, Progress of environment friendly cutting fluids/solid lubricants in turning-A review, Mater. Today Proc. 37 (2020) 3577–3580. https://doi.org/10.1016/j.matpr.2020.09.585.

[8] N. M, A. A, J. H.M.A., T. Manzoor, Q. M. M., I. T., Z.M. Zulfattah, K. M., F. I. M.R., Friendly Machining Using Biodegradable Cutting Fluids, (2021).

[9] N. Salih, J. Salimon, E. Yousif, The physicochemical and tribological properties of oleic acid based triester biolubricants, Ind. Crops Prod. 34 (2011) 1089–1096. https://doi.org/10.1016/j.indcrop.2011.03.025.

[10] N. Salih, J. Salimon, A review on eco-friendly green biolubricants from renewable and

sustainable plant oil sources, Biointerface Res. Appl. Chem. 11 (2021) 13303–13327. https://doi.org/10.33263/BRIAC115.1330313327.

[11] A. Ruggiero, R. D'Amato, M. Merola, P. Valašek, M. Müller, Tribological characterization of vegetal lubricants: Comparative experimental investigation on Jatropha curcas L. oil, Rapeseed Methyl Ester oil, Hydrotreated Rapeseed oil, Tribol. Int. 109 (2017) 529–540. https://doi.org/10.1016/j.triboint.2017.01.030.

[12] S. Loehle, C. Matta, C. Minfray, Mixed Lubrication with C18 Fatty Acids : Effect of Unsaturation, (2014) 319–328. https://doi.org/10.1007/s11249-013-0270-3.

[13] F. Cyriac, X.Y. Tee, S.K. Poornachary, P.S. Chow, Influence of structural factors on the tribological performance of organic friction modifiers, Friction. 9 (2021) 380–400. https://doi.org/10.1007/s40544-020-0385-0.

[14] K. Chowdary, A. Kotia, V. Lakshmanan, A.H. Elsheikh, M.K.A. Ali, A review of the tribological and thermophysical mechanisms of bio-lubricants based nanomaterials in automotive applications, J. Mol. Liq. 339 (2021) 116717. https://doi.org/10.1016/j.molliq.2021.116717.

[15] C.H. Chan, S.W. Tang, N.K. Mohd, W.H. Lim, S.K. Yeong, Z. Idris, Tribological behavior of biolubricant base stocks and additives, Renew. Sustain. Energy Rev. 93 (2018) 145–157. https://doi.org/10.1016/j.rser.2018.05.024.

[16] S.M. Lundgren, M. Ruths, K. Danerlöv, K. Persson, Effects of unsaturation on film structure and friction of fatty acids in a model base oil, J. Colloid Interface Sci. 326 (2008) 530–536. https://doi.org/10.1016/j.jcis.2008.05.068.

[17] C.J. Reeves, P.L. Menezes, T. Jen, M.R. Lovell, The influence of fatty acids on tribological and thermal properties of natural oils as sustainable biolubricants, Tribiology Int. 90 (2015) 123–134. https://doi.org/10.1016/j.triboint.2015.04.021.

[18] C.S.T. Araújo, V.N. Alves, H.C. Rezende, I.L.S. Almeida, R.M.N. De Assunção, C.R.T. Tarley, M.G. Segatelli, N.M.M. Coelho, Characterization and use of Moringa oleifera seeds as biosorbent for removing metal ions from aqueous effluents, Water Sci. Technol. 62 (2010) 2198–2203. https://doi.org/10.2166/wst.2010.419.

[19] S.K. Tulashie, F. Kotoka, Kinetics and thermodynamic studies on Moringa oleifera oil extraction for biodiesel production via transesterification, Biofuels. 0 (2019) 1–9.

https://doi.org/10.1080/17597269.2019.1697041.

[20] Y. Singh, A. Singla, A. Upadhyay, A.K. Singh, Sustainability of Moringa-oil–based biodiesel blended lubricant, Energy Sources, Part A Recover. Util. Environ. Eff. 39 (2017) 313–319. https://doi.org/10.1080/15567036.2016.1179360.

[21] B.K. Sharma, U. Rashid, F. Anwar, S.Z. Erhan, Lubricant properties of Moringa oil using thermal and tribological techniques, J. Therm. Anal. Calorim. 96 (2009) 999–1008. https://doi.org/10.1007/s10973-009-0066-8.

[22] N.A. Masripan, M.A. Salim, G. Omar, M.R. Mansor, A.M. Saad, N.A. Hamid, M.I. Syakir, F. Dai, Vegetable oil as bio-lubricant and natural additive in lubrication: A review, Int. J. Nanoelectron. Mater. 13 (2020) 161–176. http://dspace.unimap.edu.my/bitstream/handle/123456789/68830/Vegetable Oil as Bio-Lubricant and Natural Additive in Lubrication.pdf?sequence=1.

[23] A. Yadav, Y. Singh, P. Negi, A review on the characterization of bio based lubricants from vegetable oils and role of nanoparticles as additives, Mater. Today Proc. (2021). https://doi.org/10.1016/j.matpr.2021.01.046.

[24] V. Cortes, K. Sanchez, R. Gonzalez, M. Alcoutlabi, J.A. Ortega, The performance of SiO2 and TiO2 nanoparticles as lubricant additives in sunflower oil, Lubricants. 8 (2020). https://doi.org/10.3390/lubricants8010010.

[25] N.H. Jayadas, K.P. Nair, Coconut oil as base oil for industrial lubricants-evaluation and modification of thermal, oxidative and low temperature properties, Tribol. Int. 39 (2006) 873–878. https://doi.org/10.1016/j.triboint.2005.06.006.

[26] L. Kerni, A. Raina, M.I.U. Haq, Friction and wear performance of olive oil containing nanoparticles in boundary and mixed lubrication regimes, Wear. 426–427 (2019) 819–827. https://doi.org/10.1016/j.wear.2019.01.022.

[27] Q. Wan, Y. Jin, P. Sun, Y. Ding, Tribological behaviour of a lubricant oil containing boron nitride nanoparticles, in: Procedia Eng., 2015. https://doi.org/10.1016/j.proeng.2015.01.226.

[28] Y. Su, L. Gong, D. Chen, An Investigation on Tribological Properties and Lubrication Mechanism of Graphite Nanoparticles as Vegetable Based Oil Additive, 2015 (2015).

[29] N. Nomede-Martyr, B. Philippe, T. Philippe, M. Georges, R. Laurence, Tribological

performances of graphite and hexagonal boron nitride particles in the presence of liquid, J. Tribol. (2021) 1–29. https://doi.org/https://doi.org/10.1115/1.4048550.

[30] F. Tunistra, J.L. Koening, Raman spectrum of graphite, J. Chem. Physic. 53 (1970). https://doi.org/https://doi.org/10.1063/1.1674108.

[31] R. Geick, C.. Perry, G. Rupprecht, Normal Modes in Hexagonal Boron Nitride, Phys. Rev. 146 (1996). https://doi.org/https://doi.org/10.1103/PhysRev.146.543.

[32] R.J. Nemanich, S.A. Solin, R.M. Martin, Light scattering study of boron nitride microcrystals, Phys. Rev. B. 23 (1981). https://doi.org/https://doi.org/10.1103/PhysRevB.23.6348.

[33] R.F. Deacon, J.F. Goodman, Lubrication by lamellar solids, (1957). https://doi.org/https://doi.org/10.1098/rspa.1958.0013.

[34] F.P. Bowden, J.E. Young, Friction of diamond, graphite and carbon and the influence of surface films, R. Soc. 208 (1951) 444–455.

[35] Y. Kimura, T. Wakabayashi, K. Okada, T. Wada, H. Nishikawa, Boron nitride as a lubricant additive, Wear. 232 (1999) 199–206. https://doi.org/10.1016/S0043-1648(99)00146-5.

[36] N. Talib, E.A. Rahim, Performance of modified jatropha oil in combination with hexagonal boron nitride particles as a bio-based lubricant for green machining, Tribol. Int. 118 (2018) 89–104. https://doi.org/10.1016/j.triboint.2017.09.016.

[37] Y. Hwang, C. Lee, Y. Choi, S. Cheong, D. Kim, K. Lee, J. Lee, S.H. Kim, Effect of the size and morphology of particles dispersed in nano-oil on friction performance between rotating discs, J. Mech. Sci. Technol. 25 (2011) 2853–2857. https://doi.org/10.1007/s12206-011-0724-1.

[38] H.D. Huang, J.P. Tu, L.P. Gan, C.Z. Li, An investigation on tribological properties of graphite nanosheets as oil additive, Wear. 261 (2006) 140–144. https://doi.org/10.1016/j.wear.2005.09.010.

[39] C.J. Reeves, P.L. Menezes, M.R. Lovell, T.C. Jen, The size effect of boron nitride particles on the tribological performance of biolubricants for energy conservation and sustainability, Tribol. Lett. 51 (2013) 437–452. https://doi.org/10.1007/s11249-013-0182-2.

[40] A. Bahari, R. Lewis, T. Slatter, Friction and wear response of vegetable oils and their blends with mineral engine oil in a reciprocating sliding contact at severe contact conditions, Proc. Inst. Mech. Eng. Part J J. Eng. Tribol. 232 (2018) 244–258. https://doi.org/10.1177/1350650117712344.