Tribol Lett (2016) 64:41
DOI 10.1007/s11249-016-0778-4

ORIGINAL PAPER

Effect of 2D Boron Nitride Nanoplate Additive on Tribological Properties of Natural Oils

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Received: 22 August 2016 / Accepted: 18 October 2016 / Published online: 28 October 2016

Abstract Green tribology is a novel area of engineering that focuses on reducing friction, wear and the release of toxins to the environment caused by synthetic lubricants. The present study investigates the possibilities of utilizing natural, biodegradable olive and almond oils as a lubricant in place of synthetic oils. Boron nitride nanoplatelets (BNNP) are used as an additive (with concentrations of 0.1, 0.25 and 0.5 vol%) to olive and almond oils to enhance their tribological performance. BNNP have been selected as an additive because it is composed of a two-dimensional (2D) layered structure with weak van der Waals bonds between layers. Weak interlayer forces in BNNP enable easy shearing along the basal plane to promote lubrication. Wear experiments were also conducted using synthetic motor oil as a lubricant for a comparison with natural oils. As BNNP were added to olive and almond oil, the coefficient of friction (COF) decreased up to 84 %. The synthetic motor lubricant shows higher COF (0.189) in comparison with almond oil with BNNP (COF = 0.100) and olive oil with BNNP (COF = 0.028) at 20 N loads. Furthermore, coefficient of wear (k) of natural oils decreased up to 25 % on adding BNNP. The addition of BNNP resulted in a tribofilm formation, thereby enhancing the lubrication behavior of natural oils. However, a discontinuous layer of polymerized mixture of BNNP in almond oil was observed and this resulted in increased COF compared to olive oil with BNNP.

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Keywords Green tribology · 2D boron nitride nanoplatelet · Olive oil · Almond oil · Friction · Wear

1 Introduction

Synthetic lubricants predominate the lubricating market as a variety of chemistry compositions can be selected/created to optimize tribological systems in a wide variety of applications. Although such compositions are readily available, these types of lubricants result in significant amount of pollution [1]. This is why in recent years there has been a necessity to explore the usability of natural oils as lubricating agents. So far, several studies have proved that natural, biodegradable oils can be a viable alternative. Rapeseed oil and high-oleic sunflower-based natural oils are examples of predominantly used lubricants in the forestry, the petroleum and the mining industries among others [2–5]. The use of natural lubricants prevents excessive release of toxins into the environment. Further, it was discovered that besides castor and rapeseed oil, which have been established in the industry, certain commercially available natural oils are more suitable as lubricants than mineral oils [6, 7]. Natural oils have the advantage of providing good lubrication due to the presence of triglycerides [8]. The triglyceride is formed from a chain of three fatty acids and a glycerol backbone. These molecules are dipolar in nature, which causes a high interaction with metallic surfaces. In addition, their strong intermolecular interactions are resistant to a variation of temperature providing a more stable viscosity [8]. However, triglycerides can also be detrimental as the unsaturated double bonds in the fatty acid chains cause a faster oxidation rate. This, in turn, results in increasing the amount of lubricant needed per minute and the cost of operation [8].

In order for natural oils to be considered as lubricants, their physical properties need to match or supersede the ones desired in currently used mineral lubricants. The pour point has to be below 0 °C, and the flash point has to be above 150 °C [6]. Acid value (mg KOH/1 g), which measures the amount of free fatty acids in oils, must be minimal [6]. Iodine number, which measures the percentage of fatty acids with repeated single-bonded carbons in the triglyceride molecule, must be under 95 [6]. Lastly, it is preferable to have a high percentage of monounsaturated fatty acids and a low percentage of polyunsaturated fatty acids as the amount of polyunsaturated fatty acids dictates the oxidation and polymerization rates [6]. Based on these criteria, olive and almond oil are preferred over other natural oils. The chemical and thermal properties of olive and almond oils are summarized in Table 1 [6]. Although natural oils without additives have proved to provide better lubrication when compared to mineral oils and synthetic esters, mineral oils often include additives that enhance their lubricating properties. These properties include viscosity, viscosity index, pour point and resistance to oxidation [9]. To match the lubricating properties of mineral oils with additives while maintaining the added environmental benefits of natural oils, additives must be investigated.

This study is focused on using two-dimensional hexagonal boron nitride nanoplatelets (2D-BNNP) as an additive to olive and almond oils. Boron nitride nanoplatelets are a non-toxic additive that promotes shearing through its layered structure. This layered structure is composed of strong covalent bonds between molecules (B–N) and weak van der Waals forces between layers. This structure allows the platelets to easily shear at the contact interfaces, providing enhanced lubricity. BNNP exhibit good mechanical strength ($\sigma_y = \sim 250$ MPa), high thermal stability (up to ~1000 °C), and it is chemically inert and has high oxidation resistance [10–12].

There are several studies that prove the effectiveness of hexagonal boron nitride (h-BN) as an additive to lubricants [10–14]. For example, h-BN as an additive to paraffinic mineral oil was tested to examine what effects would h-BN have on tribological properties. The test resulted in approximately 30 % decrease in the coefficient of friction (COF) and approximately 70 % decrease in wear rate [13]. Similarly, concentrations varying from 0 to 10 % by volume of h-BN powders dispersed in engine oil (SAE-10 W) were used to lubricate AISI 4140 steel substrates in order to examine changes in friction and wear. The results indicated about 14.4 % improvement in COF and 65 % decrease in the wear rate [14]. Recently, alkyl-chain-grafted hexagonal BNNP (h-BNNP-ODTES) were created as an oil-dispersible additive to synthetic polyol ester in order to address poor dispersibility of h-BN and gain further insight into the effects on the lubrication mechanism. Tests proved that when 0.004 mg/mL of h-BNNP-ODTES was added to polyol ester, the COF resulted in 0.105 comparing to pure polyol ester where the COF resulted in 0.125. Wear depth also reduced 12.9 µm for polyol ester to 5.2 µm for polyol ester with 0.004 mg/mL of h-BNNP-ODTES [10].

Based on these literature results, BNNP are chosen as an additive to olive and almond oils in varying concentrations and its efficacy as lubricant additive is investigated. Variance in contact angle, coefficient of friction and wear rate was measured as a function of BNNP concentration. Tribological properties were also compared to traditional motor oil to determine whether these natural oils can be a viable alternative over those currently used in industries.

2 Experimental Procedures

2.1 Materials

Two natural oils were used for testing: cold pressed, unrefined pure olive oil and expeller pressed, unrefined pure almond oil (Organic Infusions, Camarillo, CA, USA). For comparison, SAE-10 W-40 motor oil (XCEL Lubricants, Tampa, FL, USA) was also tested without any additive. The additive used was hexagonal 2D-BNNP (pH Matter LLC, Columbus, OH, USA) as shown in Fig. 1a. The as-received BNNP have a flake-like morphology of particle size varying from 100 nm to 3 µm along with a thickness range of 40–65 nm. Further, an X-ray diffraction (XRD) study was carried out on the as-received BNNP. The XRD result confirmed the hexagonal structure of BNNP along with traces of B_4C as impurity (Fig. 1b). The measured lattice parameters for the hexagonal BNNP were ‘a’ = 2.506 Å and ‘c’ = 6.728 Å. Three different

Table 1 Lubricant criteria specifications for almond and olive oil [6]

Properties	Almond oil	Olive oil
Flash point (°C)	328	318
Pour point (°C)	−29	−3
Acid value (mg KOH/1 g)	0.3	1.1
Iodine number (g/1 g)	96	89
Monounsaturated fatty acid % versus polyunsaturated fatty acid %	65 versus 21	76 versus 7

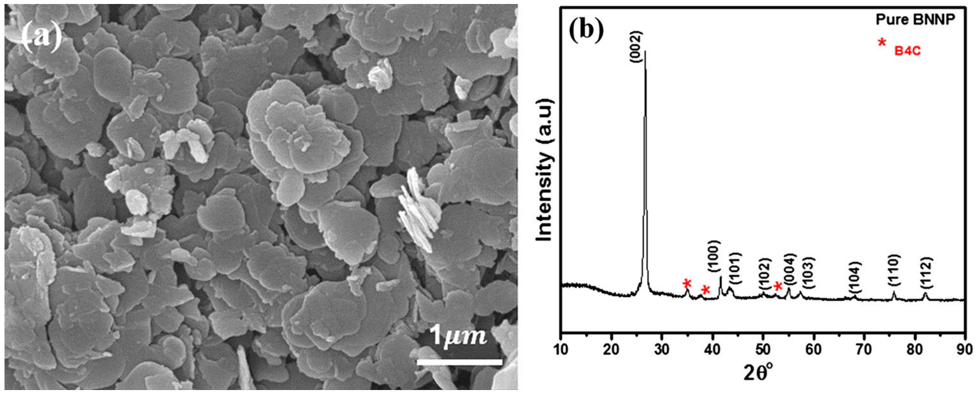


Fig. 1 **a** SEM micrograph of 2D boron nitride nanoplatelets and **b** X-ray diffraction pattern of pure BNNP

concentrations of BNNP were added to both natural oils: 0.1, 0.25 and 0.5 vol%. The BNNP were dispersed using a planetary centrifugal mixer (Thinky mixer, Laguna Hills, CA, USA). A homogenous lubricant was obtained by mixing 30 g of natural oil (with calculated amount of BNNP) for 4 min at a speed of 2000 RPM. Figure 2 shows the final mixtures for olive oil and almond oil with varying BNNP concentration. The substrate material was selected as 1020 carbon steel. Carbon steel is extensively used for engineering components (gears, ball and roller bearings, pumps and compressors, etc.) and finds in tribological applications. This is due to the fact that carbon steel is one of the most used steels in conditions that require wear resistance as they exhibit mild corrosion and oxidation rates [15].

2.2 Wetting Studies

Pure natural oils and the mixtures of BNNP with olive and almond oil were investigated for wettability properties using an optical tensiometer (KYOWA Contact Angle Meter, model no: DM-CE1, Niiza City, Japan). The contact angle of the lubricant mixture against a carbon steel substrate was measured for 30 s. The contact angle quantifies the wettability of a solid surface by a liquid via the Young equation (Eq. 1). A given system of solid, liquid and vapor at a given temperature and pressure has a unique equilibrium contact angle.

$$\gamma_{SG} - \gamma_{SL} - \gamma_{LG} \cos \theta_C = 0. \quad (1)$$

The equilibrium contact angle reflects the relative strength of the liquid, solid and vapor molecular interaction.

2.3 Tribological Tests

Tribological tests were conducted using a ball-on-disk tribometer (NANOVEA, Irvine, CA, USA). AISI 1020 carbon steel samples were subjected to 10 and 20 N normal loads for 10 min. The counter surface was an Al_2O_3 ball (3 mm diameter) moving at a linear speed of 0.016 m/s. The mixture of BNNP with natural oil was again centrifuged for 2 min at 2000 RPM right before application to ensure that the BNNP dispersed evenly through the oil. The flow of lubricant was dropped onto the substrate as a continuous flow, away from the contact surface at an approximate rate of 1.5 mL/min. Wear depth was measured using an optical profilometer (NANOVEA, Irvine, CA, USA). Wear volume was computed using Eq. 2. To supplement these calculations, coefficient of wear (k) was also calculated. The wear tracks were furthered analyzed to understand the wear mechanism using a scanning electron

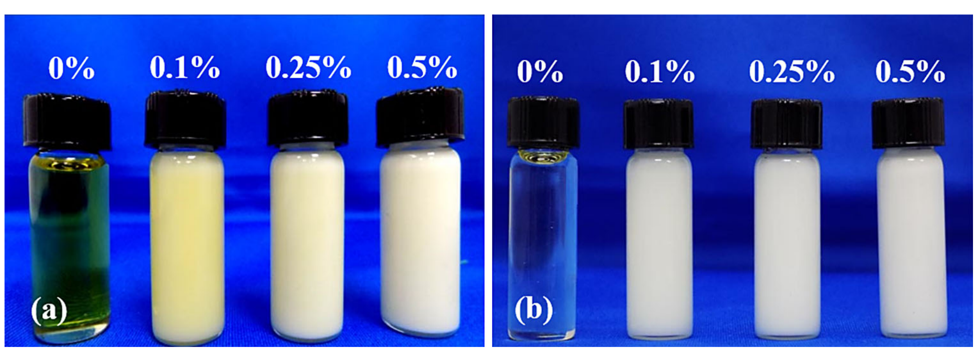


Fig. 2 Various concentrations of BNNP dispersed in **a** olive oil and **b** almond oil

microscope (SEM) (JEOL JSM-6330F, Peabody, CA, USA).

3 Results and Discussion

3.1 Wetting Studies

Wetting studies show that pure olive oil has a contact angle of 17°, whereas pure almond oil has a contact angle of 27° (Fig. 3). This shows that there is 45 % difference in wettability between oils. If the liquid molecules gain higher energies than the potential energy barrier for adhesion, slip occurs at the interface, predicting that almond oil will have a higher COF than olive oil.

Wetting studies show contact angles ranged from 14° to 16° for varying concentration of BNNP added to olive oil (Fig. 3). Hence, there is no significant difference between contact angles for varying concentrations of BNNP. Moreover, contact angle of pure olive oil (17°) is also similar suggesting only a slight improvement in wettability on BNNP addition. Contact angles ranged from 12° to 13° as volume concentration of BNNP was increasingly added to almond oil (Fig. 3). Differences are observed for olive oil; it is noticeable that the addition of BNNP (independent of concentration) drastically affects the contact angle. There is 55 % reduction in contact angle when 0.5 vol% BNNP almond oil is compared to pure almond oil. No significant effect in contact angle is seen within almond oil with varying concentration of BNNP.

Based on the wetting studies and the conclusions made above, it could be predicted that olive oil with BNNP may result in a higher COF than almond oil. However, there are other parameters that affect this mechanism, which will be explained later.

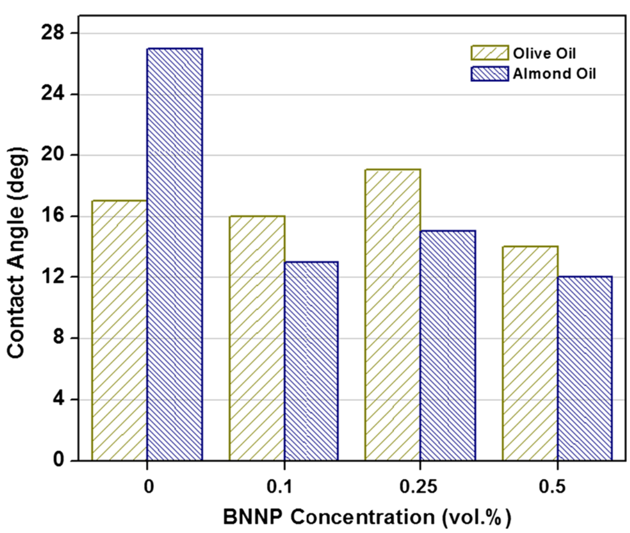


Fig. 3 Contact angle for various mixtures of olive oil and almond oil

3.2 Tribological Tests

Figure 4 shows COF for olive and almond oils with varying BNNP concentration at 10 and 20 N normal loads. When tests were conducted with olive oil as a lubricant, COF resulted in 0.087 and 0.176 for 10 and 20 N loads, respectively. When almond oil was used as a lubricant, COF resulted in 0.168 and 0.187 for 10 and 20 N loads, respectively. These results show that without any BNNP there is up to a 48 % decrease in COF when almond oil is compared to olive oil. The COF for motor oil resulted in 0.210 and 0.189 for 10 and 20 N loads, respectively. Both natural oils showed prominent lubrication properties when compared to the synthetic oil as shown in Fig. 4 COF decreased up to 59 %.

COF values ranged from 0.032 to 0.083 (10 N) and 0.028 to 0.115 (20 N) when olive oil was used as a lubricant with BNNP as an additive. When almond oil with BNNP as an additive was used as a lubricant, the COF values were higher and ranged from 0.068 to 0.142 (10 N) and 0.10 to 0.160 (20 N) (Fig. 4). COF had up to a 72 % decrease from almond oil to olive oil with BNNP for both loads.

The decrease in COF on BNNP addition is attributed to the layered molecular structure of BNNP. When the alumina ball and the carbon steel substrate rub against each other, the van der Walls forces break creating a tribofilm. Due to the sliding mechanism, a part of the tribofilm is deposited onto the counter surface allowing for shearing to occur between tribofilm and transfer film (Fig. 5).

Although COF decreased as BNNP concentration increased for both cases, there is a larger drop of COF for

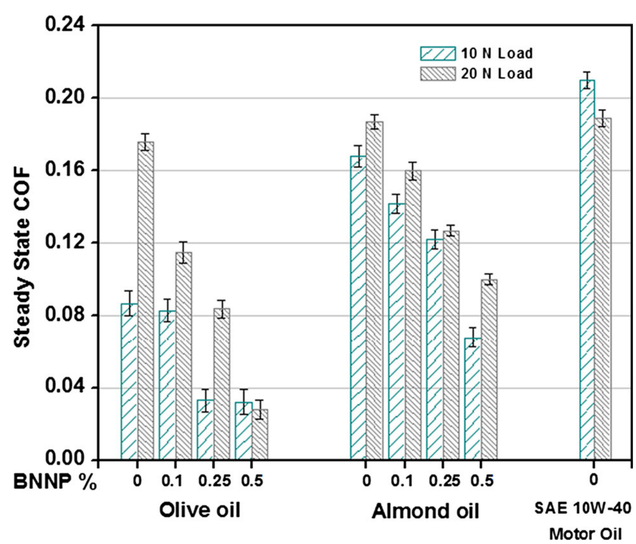


Fig. 4 Measured COF of olive oil and almond oil for various concentrations of BNNP at 10 and 20 N Load

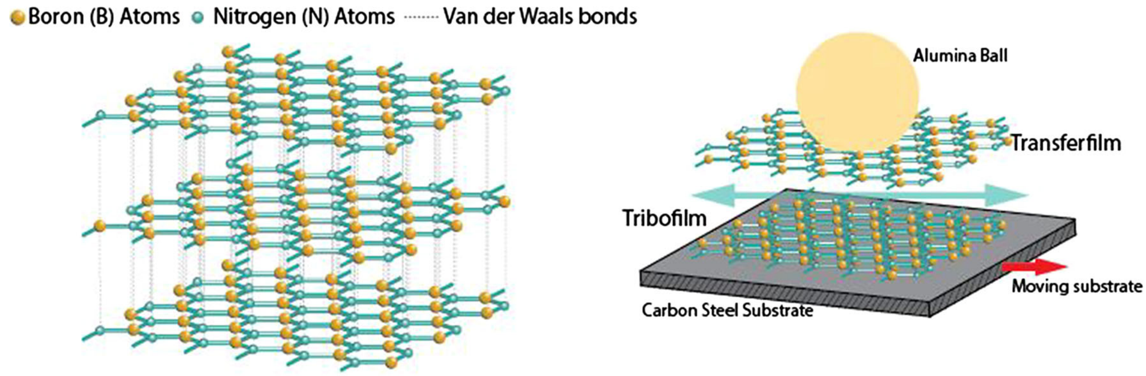


Fig. 5 Schematic of tribofilm formation as shearing mechanism of BNNP occurs

almond oil than for olive oil when testing with a 10 N normal load (Fig. 4). In the case of olive oil, the reduction in COF can be attributed to interplatelet sliding of BNNP, providing an additional lubrication layer between the sample and counter face, whereas the decreases in COF for almond oil with BNNP can be attributed to the same sliding mechanism, the reduction in contact angle and the subsequent increase in wetting between the lubricant and the sample surface. As the normal load increases to 20 N, this disparity between the relative decreases in COF is reduced. The added pressure on the lubricant can reduce the influence of the added wetting behavior, and the dominant mechanism of increased lubrication becomes sliding BNNP.

Overall, olive oil shows prominent lubrication when compared to almond oil. Such behavior can be elucidated by the higher oxidation of almond oil due to their higher percentage of polyunsaturated fatty acids. Referring to Table 1, the monounsaturated-to-polyunsaturated fatty acid ratio for olive oil is 76:7 and for almond oil is 65:21 [6]. Unsaturated fatty acids are classified into two categories: polyunsaturated fatty acids and monounsaturated fatty acids. Monounsaturated fatty acids have the presence of only one double bond, whereas polyunsaturated fatty acids have two or more double bonds. The presence of multiple double bonds makes the liquid more susceptible to oxidation making almond oil less preferred for lubrication as compared to olive oil.

The wear volume from each test was calculated using the area (A) of the wear track profiles taken from optical profilometer scan and the radius (R) of track with the following equation:

$$\text{Volume loss} = 2\pi \times A_{\text{profiles}} \times R_{\text{track}} \tag{2}$$

where volume loss is in mm^3.

An example of the wear track profiles is shown in Fig. 6.

Coefficient of wear was calculated using Archard's equation,

$$k = \frac{Q}{WL} \tag{3}$$

where k is the coefficient of wear (m^3/Nm), Q is the volume of material removed (m^3), W is the normal load (N) and L is the sliding distance (mm).

This equation assumes that wear rate is independent of the apparent area of contact. Changes in k denote changes in surface conditions and are a factor in determining the intensity of wear that is occurring in the system. Mild wear is said to be denoted when k is in the range of 10^{-8} m^3/N-m. Severe wear is said to occur when k is in the range of 10^{-2} m^3/N-m [16].

In this study, wear volume and wear rate were calculated for the olive oil samples. However, these same calculations were not performed for samples lubricated with almond oil as it was observed that even after thoroughly washing the samples, a polymerized layer of oil, caused by frictional heating, was still present on the surface of the substrate. A polymerization reaction involves the cross-linking of carbon–carbon double bonds within fatty acids. The more the carbon–carbon double bonds that are involved, the quicker the polymerization occurs and the stronger the polymer layer becomes. As mentioned previously, almond oil has a high percentage of polyunsaturated fatty acids plus the one double bond from each monounsaturated fatty acid. These double bonds contribute to the creation of this thin polymer layer and compromise wear volume analysis.

Using Eq. 3, wear rate (k) was calculated. The results for olive oil-based lubricants are shown in Fig. 7. It can be observed that when lubricating with olive oil, mild wear rate occurs. In addition, it can be seen that the rate in which volume is being removed decreases as BNNP concentration increases with a maximum decrease of 25 % for 0.25 vol%. However, there is an exception for 0.5 vol% of BNNP as wear rate increased from 1.40×10^{-7} (at 0.25 vol%) to 1.75×10^{-7} m^3/Nm (at 0.5 vol%) when tested under 10 N load and from 2.91×10^{-7} (at 0.25 vol%) to 3.14×10^{-7} m^3/Nm (at 0.5 vol%) when tested under 20 N Load.

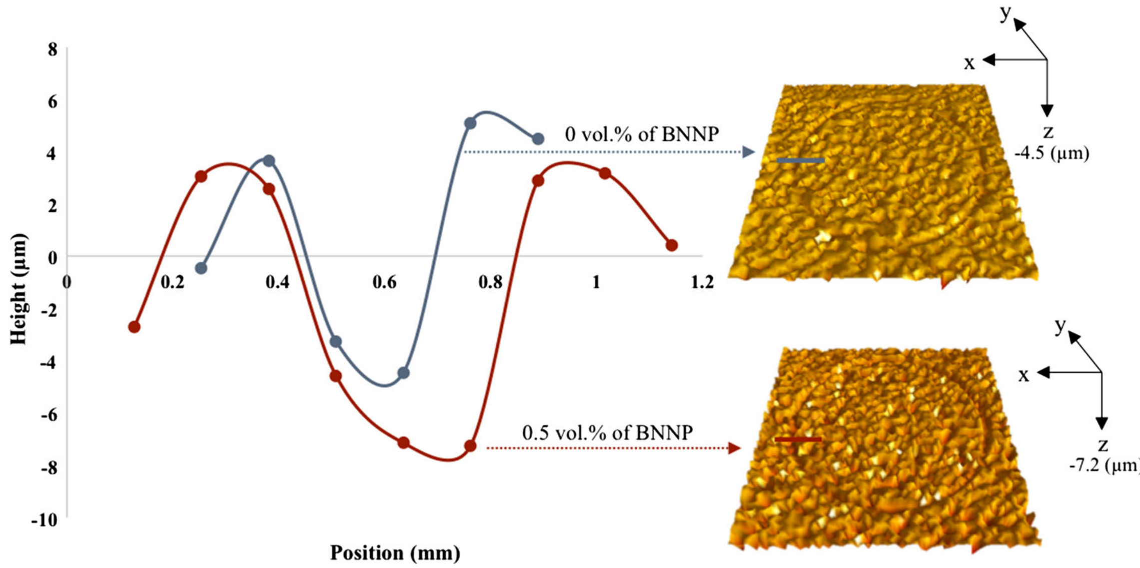


Fig. 6 Wear track profile of olive oil with 0 vol% BNNP and 0.5 vol% BNNP under a 20 N Load

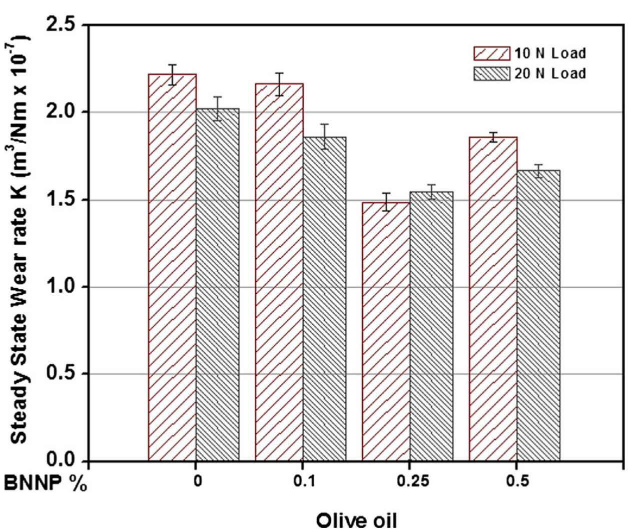
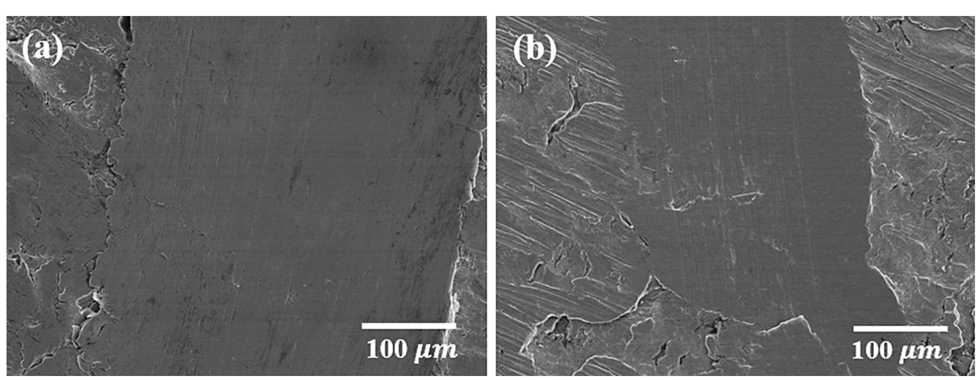


Fig. 7 Wear rate calculated for olive oil with various concentrations of BNNP

To understand the wear mechanism, the wear surfaces were examined using SEM. The wear track for pure olive oil at 20 N load is shown in Fig. 8a, and it displays fine scratches along the sliding direction. The average width of the wear track is 350 μm. In a few places of the wear track, delamination and pit formation were observed (not shown here) resulting in higher wear rate. Therefore, the dominant wear mechanism for pure olive oil is abrasive wear. Further, with the addition of 0.5 vol% BNNP in pure olive oil at 20 N load narrower (250 μm) track surface can be observed (Fig. 8b). The narrow wear track with 0.5 vol% BNNP addition is attributed to the tribofilm formation. The layered structure of 2D-BNNP under shearing action results in the formation of transfer film and tribofilm as shown in schematic Fig. 5b. Further, this effect resulted in decreased wear rate and mass loss as compared to pure olive oil. It is possible that BNNP aligned along the sliding direction and reduced the COF [17, 18]. Therefore, the

Fig. 8 Wear track of steel substrate lubricated with olive oil under SEM **a** for pure olive oil and **b** for 0.5 vol% BNNP



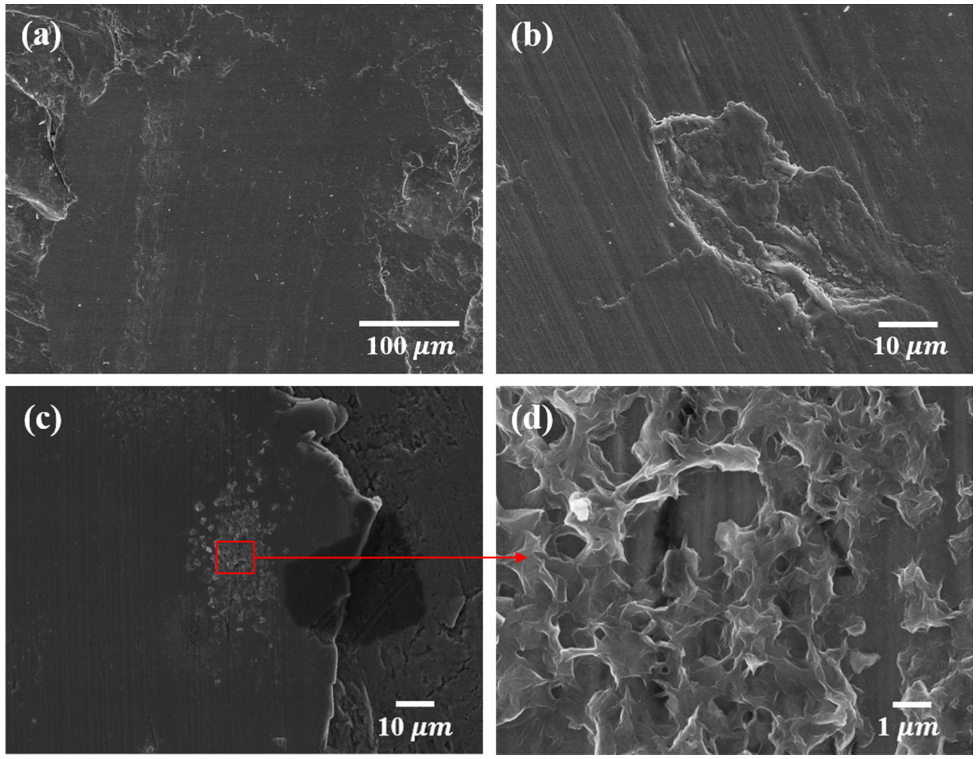


Fig. 9 Wear track of substrate lubricated with almond oil under SEM **a** low magnification, **b** high magnification, ×600, **c** almond oil with 0.5 vol% of BNNP low magnification and **d** almond oil with 0.5 vol% of BNNP high magnification

lubrication mechanism with the addition of BNNP in olive oil is the mending effect [18].

The SEM images in Fig. 9 show the wear track of the substrate at 20 N load lubricated with almond oil with 0.5 vol% BNNP and without BNNP. The wear track of pure almond oil displays grooves along the sliding direction and plastic deformation of the substrate (Fig. 9a, b). In addition, there was fracture and fine wear debris observed along the wear track of pure almond oil which would have caused higher COF. Therefore, the possible wear mechanism for pure almond oil is abrasive wear. Similar to olive oil, the addition of BNNP resulted in lowering the COF. However, the 0.5 vol% of BNNP in almond oil shows agglomerated BNNP as a layer of polymerized mixture at different locations of the wear track as shown in Fig. 9c, d. This layer of polymerized mixture with BNNP is not a continuous layer along the wear track and is formed due to a higher percentage of polyunsaturated fatty acids in almond oil. Hence, there is an increase in the rate of polymerization and this further limits the mobility of BNNP along the wear track. This formation of polymer layer further explains why COF for almond oil is higher than olive oil for all the conditions.

4 Conclusion

- Coefficient of friction (COF) drastically decreases with increasing addition of BNNP to olive and almond oil
- As a lubricant, olive oil exhibits lower COF than almond oil due to lower oxidation rate of olive oil. Almond oil tends to polymerize with agglomerated BNNP resulting in higher COF.
- Both natural oils showed lower COF as compared with synthetic SAE-10 W-40 motor oil.
- Wear rate (k) showed to be mild when the substrate was lubricated with both natural oils.

It can be concluded that BNNP improve green tribological properties of natural oils such as olive and almond oil. These enhanced properties make them potential lubricants for industrial machinery with the added benefit of limited environmental impact.

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