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Effect of Nanodiamonds on Friction Reduction Performance in Presence of Organic and Inorganic Friction Modifiers

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Abstract: The strive to reduce harmful emissions from transport has resulted in an increased emphasis on minimising friction in lubricated contacting components to improve the energy efficiency of automotive engines. In this sense, it is of particular interest to investigate whether a synergistic tribological performance could be achieved by combining two or more friction modifier additives with nanoparticles. This study conducts a comprehensive investigation into the tribological characteristics of lubricant formulations enriched with nanodiamonds (NDs), combined with organic (Glycerol Monooleate, GMO) and inorganic (molybdenum dithiocarbamate, MoDTC) friction modifiers and a low-concentration anti-wear additive (Zinc dialkyl dithio-phosphate, ZDDP). The interaction between NDs and MoDTC has been evaluated using reciprocal sliding tests at two different temperatures. The outcomes of the tribological experiments revealed that the interaction of NDs and MoDTC can enhance the friction and wear performance of steel pairs. However, this enhanced performance is shown to highly depend on other additives present in the lubricant mixture. Analysis of wear scars using High-Resolution Transmission Electron Microscopy (HRTEM), Atomic Force Microscopy (AFM) and Raman spectroscopy reveals that when NDs are fully entrapped into the formed tribofilm that contains the MoDTC-derived MoS_2 layer, the lowest friction coefficient can be achieved.

Keywords: nanodiamonds; tribofilm; friction; wear; synergy

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1. Introduction

Lubricating oil plays a dynamic role in the functionality of machines and devices by forming a thin layer between the moving components of the machine elements. The unique characteristics of lubricating oils enable them to reduce friction, generate a protecting film against wear, aid heat dissipation and corrosion resistance, etc. One important way to reduce the energy consumption and emissions from internal combustion engines is by using environmentally friendly lubricants with improved fuel efficiency. One effective way to develop efficient lubricants that fulfil the environmental legislation, as well as accomplishing the required functions of lubricants, is by incorporating a number of additives, which include anti-wear additives and friction modifiers [1–4].

Zinc dialkyl dithiophosphate (ZDDP) is a well-known and widely used anti-wear additive with anti-corrosion and antioxidant characteristics, which has the ability to produce phosphate-based sacrificial tribofilms that protect the surfaces in contact under boundary lubrication conditions [5,6]. On the other hand, to reduce friction in the boundary lubrication regime, different friction modifiers have been widely used [7]. Among several types of friction modifiers, four major classes are currently used to reduce friction. They are oil-soluble organo-molybdenum, functionalised polymers, organic friction modifiers and nanoparticles that can disperse or dissolve in base oils [8,9]. Molybdenum dialkyl dithiocarbamate (MoDTC) is one of the most extensively used organo-molybdenum friction modifiers. Its ability to reduce friction is primarily due to the formation of MoS_2 on the wear scar [10], reducing the coefficient of friction (COF) to around 0.05 [10,11]. However, MoDTC is shown to develop antagonistic interactions with other additives, impacting its ability to reduce friction [1].

Moreover, the problem with ZDDP and MoDTC is that they contain metal, sulphur and phosphorus. These elements are shown to contaminate the exhaust gas recirculation system, detrimentally affecting its performance in reducing harmful environmental contaminants [12]. Therefore, it is highly important to develop an efficient lubricant formulation with a reduced concentration of harmful lubricant additives [3,13].

Another prominent type of friction modifier is organic friction modifiers (OFMs). These are molecules of amphiphilic surfactant, which contain a hydrocarbon tail and a polar head group. The polar head group usually adsorbs or chemically reacts on metallic or ceramic surfaces to develop dense monolayers that effectively reduce friction [1,14]. Glycerol Monooleate (GMO) is an effective organic friction modifier, widely used in the lubrication industry due to its ability to form a low-friction tribofilm between contacting surfaces. The use of GMO lines up with the growing need for the use of alternative solutions for sustainable lubrication systems. This makes GMO the key component for the development of fully biodegradable, greener lubrication technology [14]. Researchers have shown that GMO hydrolyses and, within the contacting surfaces, forms carboxylic acid [15]. GMO has shown synergistic [16] and antagonistic [17] effects with different additives present in the lubricant formulations. Cyriac et al. [18] has shown an improved frictional performance for lubricants containing mineral oil, ZDDP and GMO. Another study showed that a combination of MoDTC, GMO and ZDDP exhibits a synergistic effect in reducing friction of about 30–50%, when utilising this mixture with PAO oil and in palm trimethylolpropane ester [19].

Similarly, nanoparticles are another group of friction modifiers that have gained popularity due to their distinctive tribological properties [20]. Various types of nanoparticles with distinct characteristics are currently in use with the aim to minimise friction and wear [21]. Several studies have investigated the impact of incorporating different nanoparticles into various base oils to assess the wear and friction performance. Potential nanomaterials that could be used as lubricant additives are graphene, graphene oxide, carbon nanotubes, metal oxides, molybdenum disulfides, nanodiamonds, etc. [22]. Among different additives, nanodiamonds (NDs) have shown improved frictional and wear properties and a higher load-carrying capacity [23,24]. Also, NDs have shown excellent compatibility as a lubricant additive due to their chemical and thermal stability and superior mechanical and tribological properties [25]. The presence of NDs in oil can not only form robust tribofilms but also increase interface bonding between tribofilms and the substrate surface, which can significantly reduce both friction and wear under fretting contact [26]. Nanodiamonds are also effective in lowering friction and wear in water-based lubrication [27]. However, it was reported that NDs' efficiency depends on the optimum concentration, as higher concentrations may, by agglomeration, prevent the rolling movement needed to bring NDs into action [28]. Considering that the lubricants contain other additives, it is important for the tribological performance of NDs in conjunction with other additives to be investigated. A recent study has demonstrated that a multi-additive system containing GMO, ZDDP and NDs tends to enhance the lubricating performance by forming a thicker ND-enriched tribofilm [29]. A few studies have explored the effect of NDs with conventional additives like tricresyl phosphate (TCP) and ZDDP [22,30], but the compatibility and optimisation of NDs in lubricant formulation with other additives still remains limited, especially with MoDTC, which is widely used in many commercial Fully Formulated (FF) oils as a friction modifier [31]. MoDTC can potentially reduce friction further when added with nanoparticles [32]. However, not all the nanoparticles showed a synergistic effect with MoDTC, depending on a number of physio-chemical factors, including size, shape, additive interaction, contact stress and pairs, etc. While NDs showed a positive impact on the performance of low-concentration ZDDP lubricants [29], not much is known about whether a similar synergy can be achieved with MoDTC for friction reduction.

The aim of the current study is to explore the potential of developing low SAPS (Sulphated Ash, Phosphorous, and Sulphur) lubricant formulations by exploiting synergistic interactions between conventional friction modifiers, anti-wear additives and nanodiamonds (NDs). To achieve this goal, a multi-additive lubricant system has been formulated by incorporating NDs, MoDTC and GMO with ZDDP in PAO oil, and their friction and wear behaviour have been analysed in a pin-on-plate tribometer. While previous studies have demonstrated the effect of commonly used additives mainly in a single-additive system with a more straightforward formulation, this study investigates the synergistic interaction of nanodiamonds (NDs) with both organic (GMO) and inorganic (MoDTC) friction modifiers in a multi-additive system. This study focuses on the additive formulation and evaluates its impact on friction reduction, wear performance and the mechanism of tribofilm formation. Furthermore, this study assesses the possible application of NDs as an alternative solution to minimise the concentration of traditional additives, which could lead to potentially reducing the environmental impact associated with compounds containing sulphur and phosphorus elements. White light interferometry (WLI), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), High-Resolution Transmission Electron Microscopy HRTEM and Raman spectroscopy were used to investigate the properties of the tribofilms formed and their correlation with friction and wear performance.

2. Material and Methods

2.1. Lubricant and Specimen Preparation

A synthetic PAO oil (Synfluid PAO 6 cSt) was used as a base oil to formulate the lubricants. Molybdenum dithiocarbamate (MoDTC) as an inorganic friction modifier, Glycerol Monooleate (GMO) as an organic friction modifier and Zinc dialkyl dithiophosphate (ZDDP) as an anti-wear additive were provided by TOTAL Energies (Lyon, France). Carboxylated NDs were procured from Sigma Aldrich, Gillingham, UK. The nominal diameter of NDs used was 5 nm [29]. When purchased, ND particles were diluted in PAO oil with a concentration of 0.1 wt%. The purchased ND solution was then dispersed in the PAO base oil to give a final ND concentration of 0.05 wt%. Previous research has shown that NDs with a diameter of 5–10 nm effectively reduced friction at an ultra-low concentration of 0.01 wt% by the nano-bearing effect. Increased concentrations impact the friction reduction capability by aggregation and create abrasion [27]. Hence, to detect the optimum concentration of NDs, preliminary tribological tests were performed on a range of concentrations (0.01 wt%, 0.05 wt%, 0.1 wt% and 0.3 wt%). Our results indicated that 0.05 wt% provided the best tribological performance within the multi-additive system. This concentration is also consistent with findings from similar studies in the literature, which have shown that optimal ND concentrations tend to fall within this range for effective tribological improvement [29]. Next, the other additives were added in a specific weight percentage as shown in Table 1 and stirred for 1 h at 500 rpm using magnetic stirring to prepare homogeneous nanolubricant samples. The shortforms for the oil and additives are P for PAO oil, G for GMO, Z for ZDDP, N for nanodiamonds and Mo for MoDTC.

Table 1. Lubricant combinations tested.

No.	Lubricant ID	PAO Oil (P) wt%	GMO (G) wt%	ZDDP (Z) wt%	Nanodiamonds (N) wt%	MoDTC (Mo) wt%
1	PMo	99	0	0	0	1
2	PMoG	98	1	0	0	1
3	PMoZ	98.8	0	0.2	0	1
4	PMoGZ	97.8	1	0.2	0	1
5	PMoN	98.95	0	0	0.05	1
6	PMoGN	97.95	1	0	0.05	1
7	PMoZN	98.75	0	0.2	0.05	1
8	PMoGZN	97.75	1	0.2	0.05	1

Before the tribological experiments, the size and shape of the NDs needed to be verified. But as the carboxylated NDs were already dispersed in an oil medium, customised dried carboxylated ND particles were purchased to characterise and verify the shape and size of ND particles using a Transmission Electron Microscope. The FEI Titan3 Themis 300 Scanning Transmission Electron Microscopy (STEM) (Hillsboro, OR, USA), fitted out with Gatan Quantum ER energy filter TEM, was used to analyse the particle-size distribution.

ND particles have been analysed and presented in reference [29]. The particle-size distribution of the dried NDs, their shape and size were analysed and are presented in Figure 1. Figure 1a,b show that NDs are spherical in shape, and a slight agglomeration has been observed from the HRTEM analysis. The reason for this agglomeration could be surface attraction forces between the ND particles [33]. The particle size of the NDs was measured using DLS after mixing them with PAO. However, when mixed with MoDTC, the DLS measurements encountered challenges due to a colour change, which interfered with the analysis. Therefore, DLS measurements of NDs with PAO have been reported here in Figure 1d,e.

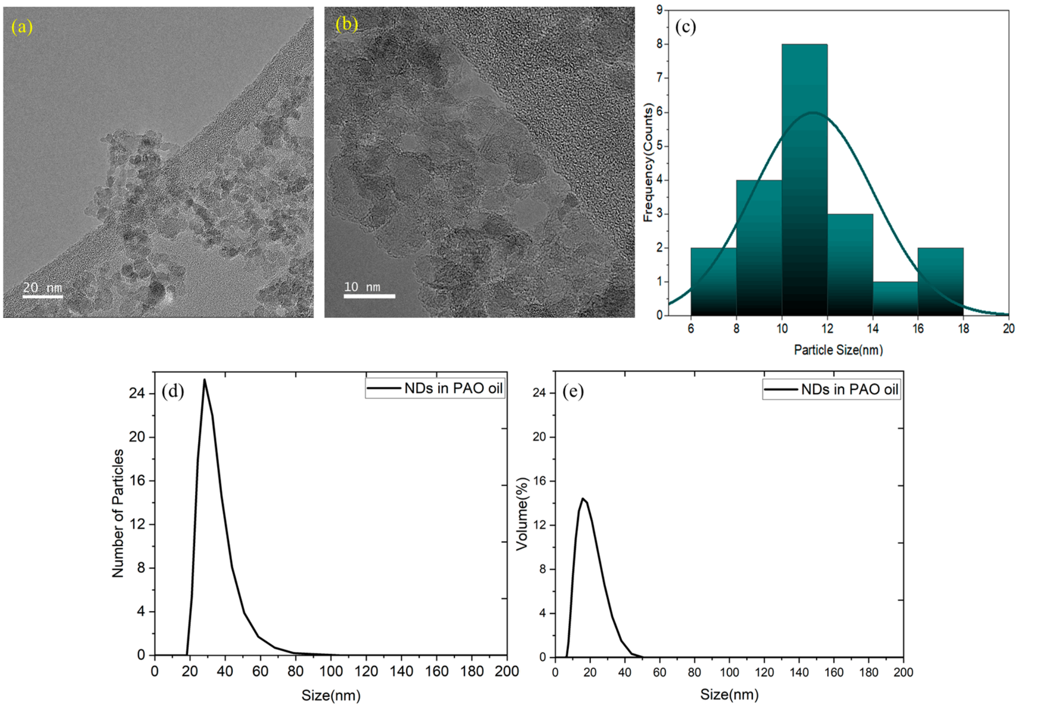

Figure 1. (**a**,**b**) HRTEM image of dried NDs, (**c**) particle-size distribution of NDs in vacuum environment, (**d**,**e**) particle distribution in oil environment.

A difference was observed between the dry measurements using TEM and the DLS measurements, attributed to the differing environments in the two methods. The DLS results indicated that the majority of particles remained within the range of 10–40 nm, likely due to slight aggregation caused by weak intermolecular forces (van der Waals forces). However, Figure 1c reveals that the size of the NDs varied between 6 and 18 nm. To achieve the best frictional performance of NDs, the range should be lower than 50 nm, and these NDs are within this range [4].

The pins and plates used in this work were made of the steel EN31, with a radius of 10 (mm) and dimensions of 7 * 7 * 3 (mm). The measured roughness for the pin and plate surfaces was 401 ± 1.2 (nm) and 57.8 ± 1.02 (nm), respectively. The hardness of the pins was 59.2 ± 0.6 (HRC), and for plates, it was 64.8 ± 0.12 (HRC). Also, the elastic modulus for pins and plates was within the range of 190–210 GPa.

2.2. Tribological Tests

In order to evaluate the efficiency of newly formulated lubricants, pin-on-plate tribological tests were conducted using a Cameron Plint TE 77 reciprocating tribometer (Kingsclere, UK). Figure 2 displays the schematic illustration of the experimental rig. A normal load is applied on the contacting surface by the cantilever, and a force transducer is used to measure the frictional force, which afterwards is used to calculate the friction coefficient. The friction tests were conducted at a constant pressure of 1 GPa and at two temperatures, 50 °C and 80 °C. These temperatures were selected to mimic the normal operating conditions of automotive systems, where components frequently encounter a range of moderate to elevated temperatures. Testing at 50 °C and 80 °C enabled the evaluation of the lubricant's performance under boundary lubrication conditions across a temperature range and to study the mechanism of tribofilm formation, which is essential for understanding these lubricants' ability to reduce wear and friction.

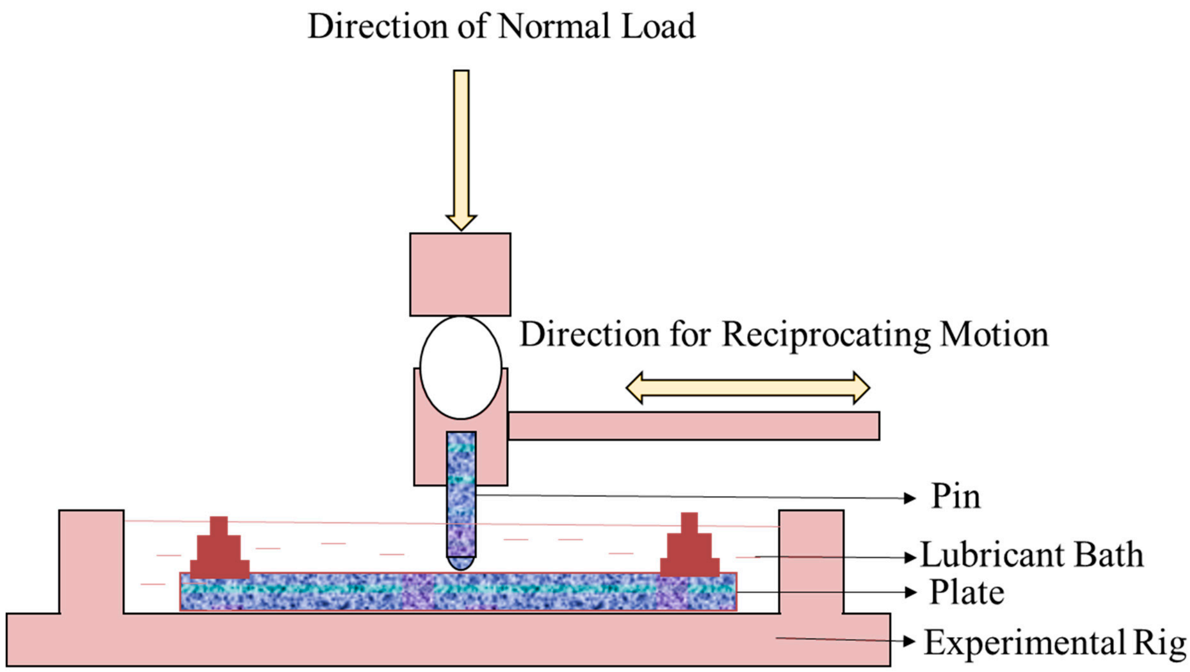

Figure 2. Schematic illustration of Cameron Plint TE 77, pin on-plate reciprocating tribological experiment set-up.

The stroke length was 5 mm, with a frequency of 20 Hz, and the sliding speed was consistently held at 0.2 m/s. The duration of each test was 120 min. To ensure the reproducibility and reliability of the results, all experiments were conducted three times.

The friction and wear data presented in this study are averaged over three repeats, with error bars representing the standard deviation. The establishment of the boundary lubrication regime was confirmed by referring to the Hamrock–Dowson lubricant film thickness equation and initial surface roughness [29,34].

To prepare the samples for the tribological experiment, plates and pins were cleaned in an ultrasonic bath for ten minutes. Heptane was used as a solvent to clean the plates and pins before and after the test to remove any wear debris or remaining oil fragments from the tested surfaces.

2.3. Wear and Tribofilm Characterisation

Optical white light interferometry (WLI) was employed to measure the width of the wear scar and volume loss of the plates. Some of the wear scar depths were very shallow, and in some cases, no measurable wear was detected by the white light interferometer. As a result, the width of the wear scar on the plate samples has been measured and reported here. The measurements were carried out after using the EDTA solution on the wear track to remove the tribofilm for an understanding of the surface wear mechanism. The pin wear volume was analysed and measured by WLI as well [29].

For tribofilm analysis, the wear tracks of the plate surfaces were initially analysed using a high-performance cold field emission (CFE) Scanning Electron Microscope (Hitachi SU8230, Tokyo, Japan) before and after EDTA solution was applied to remove the tribofilm on the wear track to see the tribofilm morphology [35].

To investigate the tribofilm structure, cross-sections were prepared with a high-resolution monochromated Focused Ion Beam (FIB, Helois G4 CX Dual Beam, Hillsborough, OR, USA). Then, the cross-sections were analysed with an FEI Titan3 Themis 300 Scanning Transmission Electron Microscope (STEM). This STEM is fitted with a Gatan Quantum ER energy filter, Energy-Dispersive X-ray (EDX) and High-Angle Annular Dark-Field Scanning (HAADF).

A Dimension Icon Bruker AFM (Billerica, MA, USA), was employed to image the tribofilms' surface morphology using the tapping mode. A 125 μm long cantilever silicon probe with a 10 μm tip diameter was used to scan the surface with a lever force constant of 40 N/m and a resonant frequency of about 300 kHz. All AFM images were obtained with a scan rate of 1 Hz over different selected areas in dimensions of 5 μm × 5 μm.

Raman spectroscopy (inVia Renishaw, New Mills, UK) was used to detect the trace of the NDs in the tribofilm. The accumulation time was set to 20 with a laser excitation source of a 785 nm wavelength, while the exposure time was set to 5 s.

3. Results

3.1. Tribological Performance

Figure 3 illustrates the changes in frictional coefficient value for various combinations of lubricant formulations tested at 50 °C and 80 °C. Figure 3a indicates variations at 50 °C in the coefficient of friction (COF) for lubricant combinations without NDs. The COF obtained by the lubricant containing MoDTC and GMO (PMoG) was found to be the highest (~0.07), compared to the others. The lubricant containing MoDTC and ZDDP (PMoZ) provided a reduced COF, which can be attributed to the interaction between the two additives and the generation of molybdenum sulphides, as reported in earlier studies [10,36]. Previous research has shown that lubricants containing both MoDTC and ZDDP are more effective at reducing friction than those containing only MoDTC additive in base oil [20,37]. Interestingly, the lubricant with MoDTC, GMO and ZDDP (PMoGZ) showed a fluctuating COF throughout the experiments but reached the lowest COF (~0.06) at the final stage. The reason could be the formation of an additive-derived tribofilm due to tribochemical interaction between additives and contacting surfaces [19].

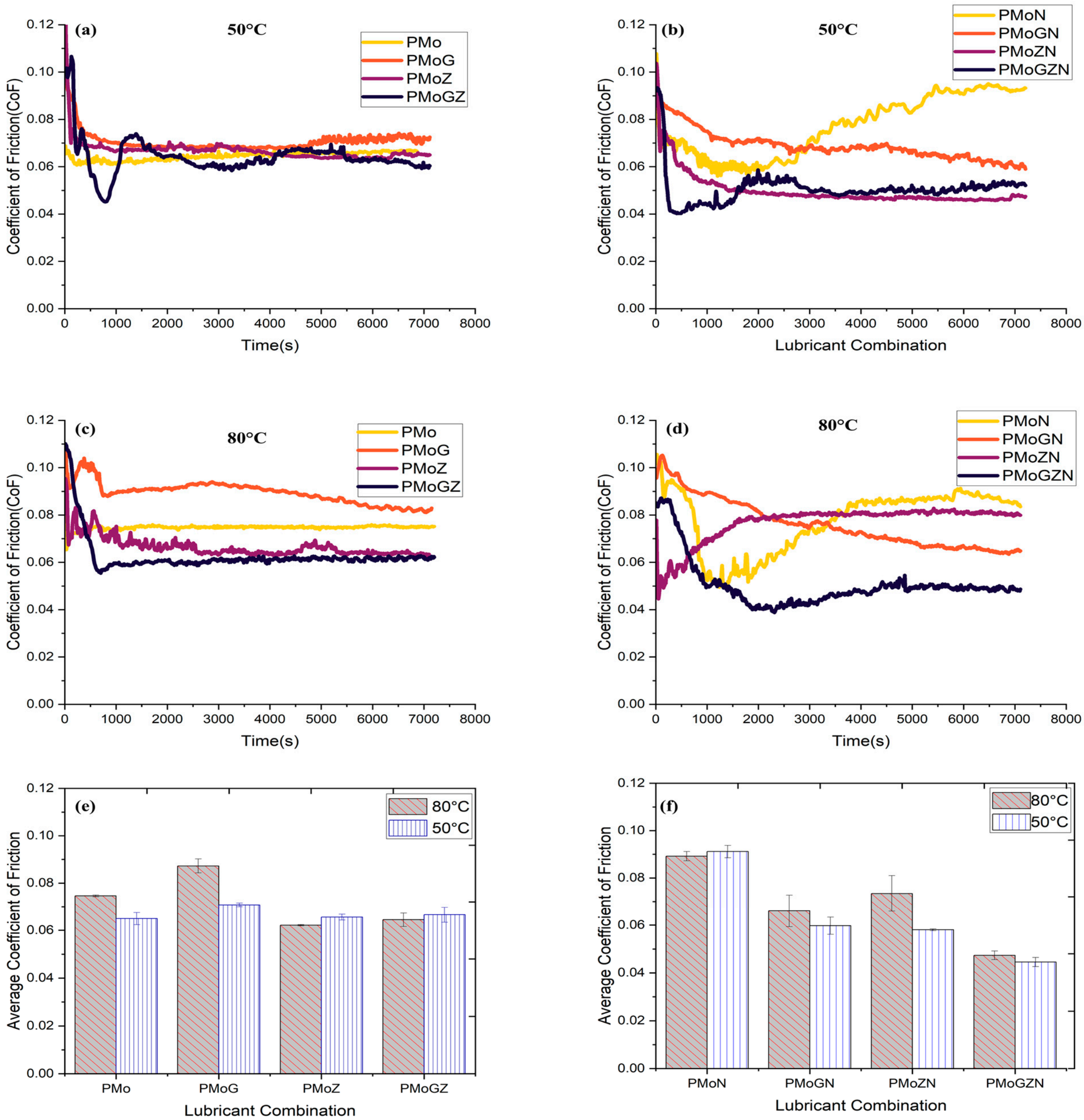

Figure 3. Changes in coefficient of friction at 50 °C for lubricant formulations (**a**) without NDs, (**b**) with NDs. Changes in coefficient of friction at 80 °C for lubricant formulations (**c**) without NDs, (**d**) with NDs. Average coefficient of friction for last 30 min of tribotests for (**e**) lubricants without NDs at 50 °C and 80 °C, (**f**) lubricants with NDs at 50 °C and 80 °C.

Figure 3b shows the frictional performance of lubricant combinations containing NDs at 50 °C. For lubricant with MoDTC and NDs (PMoN), the friction was lower initially but over time, the COF increased, reaching a value of ~0.10 at the end of the test. The lubricant with MoDTC, GMO and NDs (PMoGN) showed a COF of ~0.06, lower than the COF obtained from lubricant with MoDTC and GMO (PMoG). The calculated COF value (average) for lubricant with MoDTC, GMO, ZDDP and NDs (PMoGZN) was around 0.052, whereas the lowest COF was exhibited by lubricant with MoDTC, ZDDP and NDs (PMoZN), approximately 0.048. It was found that the incorporation of NDs with different lubricant formulations showed variations in friction reduction performance depending on the characteristics of individual additives. Thus, aside from the MoDTC and ND combination (PMoN), lubricants containing NDs exhibited a reduced COF compared to lubricants without NDs.

Figure 3c shows the variation in frictional performance for lubricant combinations without NDs at 80 °C. Similarly, the highest COF at this elevated temperature was also observed by lubricant containing MoDTC and GMO (PMoG), ~0.09, which is even higher than the 50 °C temperature test (~0.07). The lubricant with MoDTC (PMo) showed a friction coefficient of around 0.07, whereas the lubricant with MoDTC and ZDDP (PMoZ) showed a lower COF (~0.06), notably similar to the COF of lubricant containing MoDTC, GMO and ZDDP (PMoGZ) (~0.06). Previous studies have demonstrated that lubricants containing MoDTC and ZDDP exhibit a synergistic effect, resulting in the formation of a MoS_2 tribofilm that further reduces friction [8]. The COF of the PMoGZ lubricant combination remained relatively stable at the increased temperature. However, the observed friction performance exhibited greater stability compared to the lubricant tested at 50 °C.

Figure 3d shows the frictional performance of lubricant combinations containing NDs at 80 °C. The lubricant PMoN generated the highest COF, similar to the COF at 50 °C. The lubricant combination with MoDTC, GMO and NDs (PMoGN) showed a decreased coefficient of friction of approximately 0.06, equivalent to the COF at 50 °C without NDs. However, the lubricant with MoDTC, ZDDP and NDs (PMoZN) showed a higher COF of approximately 0.08 at this temperature. The reason for this higher COF could be the formation of a ZDDP tribofilm at elevated temperatures [10]. At higher temperatures, the PMoGZN lubricant showed the lowest COF, approximately 0.045.

The average coefficient of friction values for lubricants with and without NDs, tested at 50 °C and 80 °C, are shown in Figure 3e,f. The average coefficient of friction was determined by averaging the COF values of the three repeated tests recorded during the final 30 min of the test. The error bars represent the results of the three repeated tests. The coefficient of friction (COF) showed minimal variations with the temperatures. However, there was a significant difference in the COF between the lubricants with and without NDs for both temperature ranges. PMoGZN at both temperatures showed a lower COF than any other lubricant combination. The stability of the frictional curves is depicted in Figure 3b,d. The decrease in the coefficient of friction can be attributed to the synergistic impact of the lubricant combination containing the additives. From the findings presented in Figure 3, it can be concluded that the combination of PMoGZN lubricant showed the lowest coefficient of friction at 80 °C. The lubricants with the inclusion of NDs showed a visible decrease in the value of the coefficient of friction, which was not evident for most of the lubricant combinations. Although the addition of NDs in the PMoN lubricant increased the COF, PMoGZN showed a lower COF at both temperatures, indicating a potential synergy among the additives present in the formulation. The frictional performance and tribofilm formation mechanism will be discussed in Section 4.

3.2. Wear Surface Analysis

Following two hours of tribological tests, the wear surface was analysed by white light interferometry (WLI) to determine the wear volume loss of the plates and pins. However, it was observed that some of the wear scar depths were very shallow, and white light interferometer could not detect any quantifiable wear in certain positions. Hence, the wear volume loss of the pin surfaces is presented here. Figure 4 shows pin wear scar images from white light interferometry generated at 80 °C for lubricant combinations with MoDTC, GMO and ZDDP without NDs (a) and with NDs (b).

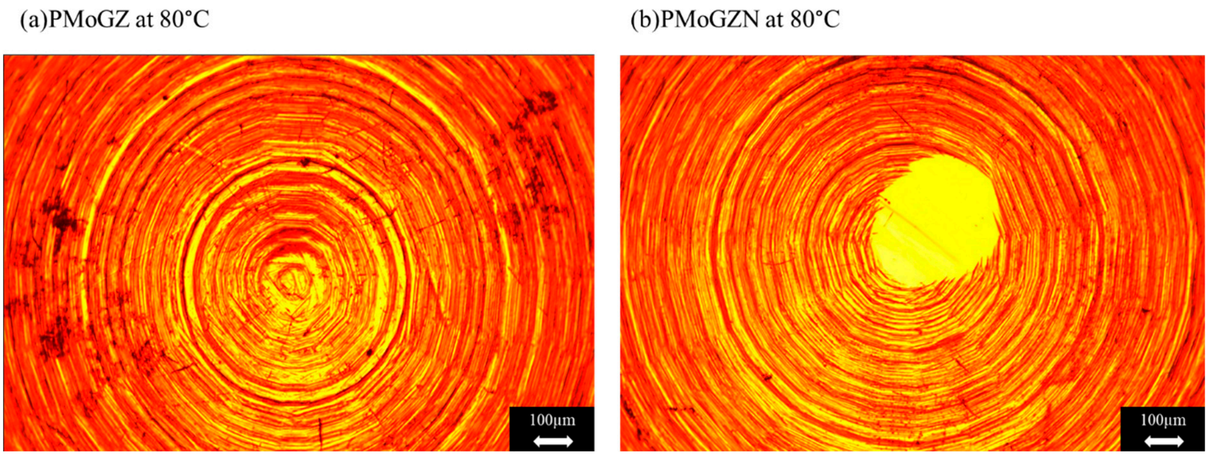

Figure 4. Wear analysis for lubricants with PAO, MoDTC, GMO, ZDDP (**a**) without NDs and (**b**) with NDs at 80 °C.

Shallow wear could be visible from the pin wear surfaces, and the abrasive polishing effect of NDs is visible from the optical image of the pin surface, which is absent for the lubricant without NDs. The pin volume loss was calculated using wear scar measurements obtained by white light interferometer and is presented in Figure 5. The error bars represent the results of the three repeated tests.

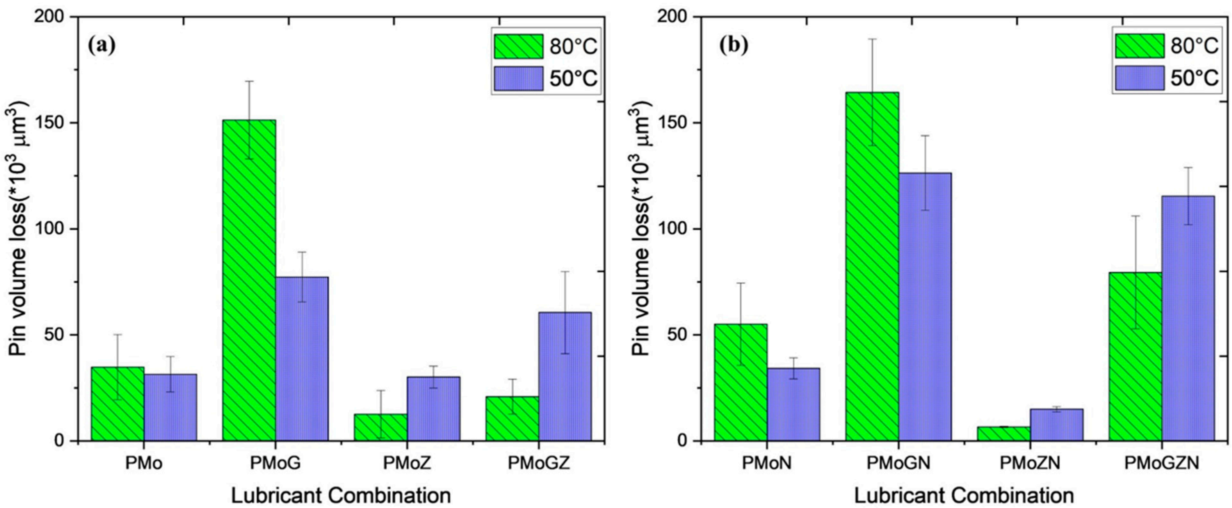

Figure 5. Pin volume loss for lubricants (**a**) without NDs and (**b**) with NDs at 50 °C and 80 °C.

From Figure 5a, it can be observed that for lubricant containing MoDTC (PMo), the wear volume loss of the pin increased with higher temperatures, as MoDTC is only a friction modifier and it does not have significant anti-wear properties. Without the presence of any other anti-wear additive in the lubricant combination, the MoDTC did not reduce wear at both tested temperatures [37]. Interestingly, lubricant with MoDTC and GMO (PMoG) showed a high wear volume loss at 80 °C, which was not observed for other lubricant combinations without NDs. PMoZ lubricant that contained MoDTC and ZDDP showed the lowest wear volume loss, which could be due to the presence of the anti-wear additive ZDDP, which created a protective layer that further reduced wear [16]. Lubricant combinations with MoDTC, ZDDP and GMO (PMoGZ) also showed a lower wear volume loss at higher temperatures, which could be due to the formation of a protective phosphate-rich tribofilm [10]. From Figure 5b, the incorporation of NDs into the lubrication system resulted in an enhanced wear volume loss (except for the PMoZN lubricant) when compared to the other lubrications operating without NDs. A negative effect was observed for the PMoN lubricant combination when tested at 80 °C. There are several factors that may contribute to the observed phenomenon, including the delayed formation of a tribofilm and the generation of additional abrasive particles. These factors, rather than reducing wear, appear to intensify wear at 80 °C [38]. For lubricant combination PMoZN, the wear volume loss for the pin surfaces was reduced significantly at 80 °C, which was not observed for any other combination. The observed phenomenon can be ascribed to the influence of surface modification caused by NDs and the combined reaction of additives present in the lubricant mixture. A noteworthy observation in this context is that the incorporation of NDs did not consistently reduce wear, even at a temperature of 50 °C. At 80 °C, it was observed that the lubricants containing NDs did not demonstrate a substantial decrease in wear, with the exception of the lubricant containing ZDDP. Previous studies have demonstrated that the combination of MoDTC and ZDDP resulted in a reduction in wear [6,10,29]. Nevertheless, it can be expected that the wear reduction mechanism will also be affected by the higher hardness of NDs [39]. Also, the presence of GMO molecules and NDs could have interrupted the formation of phosphate and MoS_2 films. The effect on the tribofilm properties will be shown in Section 3.4. Figure 4b illustrates abrasive wear, likely attributable to the presence of nanodiamonds with superior hardness, potentially resulting from inadequate dispersion, which caused surface scratching or damage [40]. GMOs or NDs may enhance surface protection in certain instances; however, when combined with MoDTC and ZDDP, they are likely to disrupt the formation of the phosphate chain, which constitutes the protective layer created by ZDDP and MoDTC [41]. Hence, to understand the tribochemical changes due to the incorporation of NDs and to understand the corresponding synergistic effect, further chemical and morphological analyses have been conducted for the PMoGZ and PMoGZN samples.

3.3. Changes in Surface Morphology

The formation of tribofilms inside the wear track for different lubricant combinations is assessed by comparing surface morphological changes using SEM (Figure 6) and AFM (Figure 7). Figure 6a,b show the SEM images of plate worn surfaces for the PMoGZ and PMoGZN nanolubricants tested at 80 °C. From the SEM images, the difference between the two wear surfaces is prominently visible. The surface morphology of the PMoGZ lubricated plate surface (a) showed a patchily structured tribofilm. These tribofilms have similarities with the traditional ZDDP tribofilm that also showed patchy, pad-like structures [29]. In contrast, the morphology of the PMoGZN lubricated plate surface (b) did not show the patchily structured tribofilm; rather, a visually polished surface could be observed. This morphology showed a similarity with the tribofilm that contained NDs [29].

Figure 7 shows the 3D surface morphology of the plate surfaces for lubricants (a) PMoG, (b) PMoGN, (c) PMoZ, (d) PMoZN, (e) PMoGZ and (f) PMoGZN after 2 h of tribological tests at 80 °C. The lubricants (a) PMoG, (c) PMoGZ did not show any significant difference in surface morphology. But the lubricants with nanodiamonds show smoother surface with abrasive impact of NDs which can be visually observed from Figure 7 b and d. For (e) the PMoGZ plate surface, pad-like structures were observed as expected from a ZDDP-rich tribofilm [7]; however, these structures were not homogeneously distributed. On the other hand, for the (f) PMoGZN wear scar, small spherical structures were visible, which are likely to be NDs, as suggested by the TEM analysis of Figure 1a,b. To further investigate the presence of NDs on the wear scar, an HRHEM analysis was conducted.

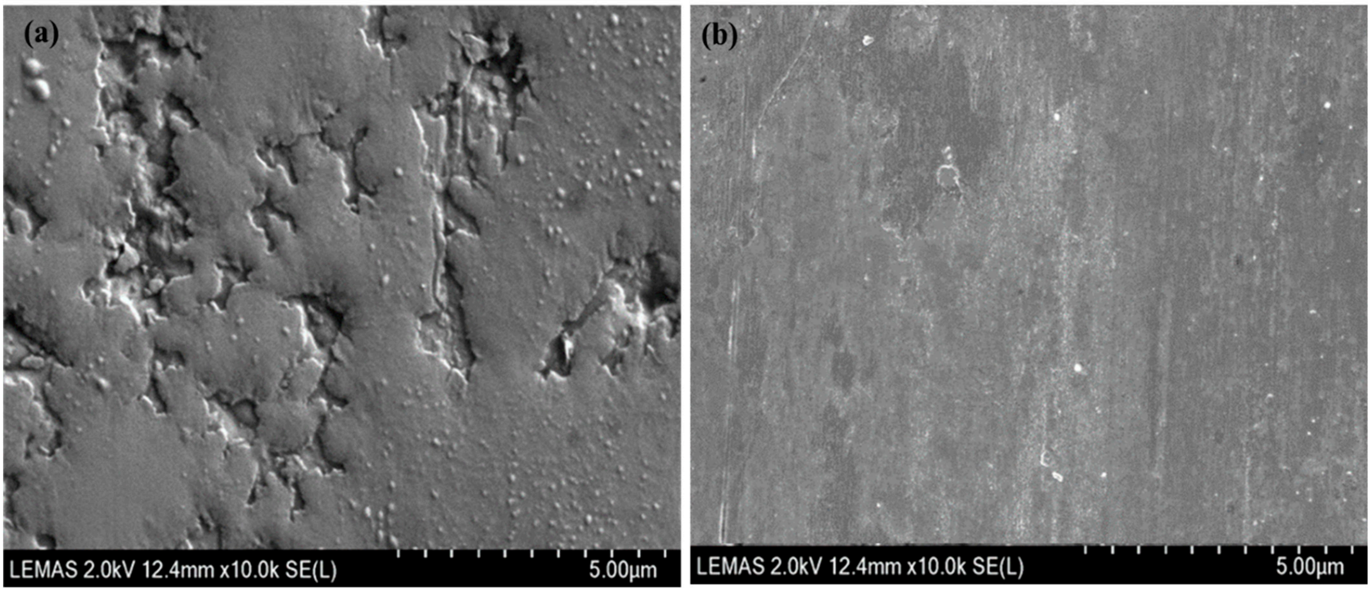

Figure 6. Surface morphological analysis of (**a**) PMoGZ and (**b**) PMoGZN tribofilm formed at 80 °C by SEM.

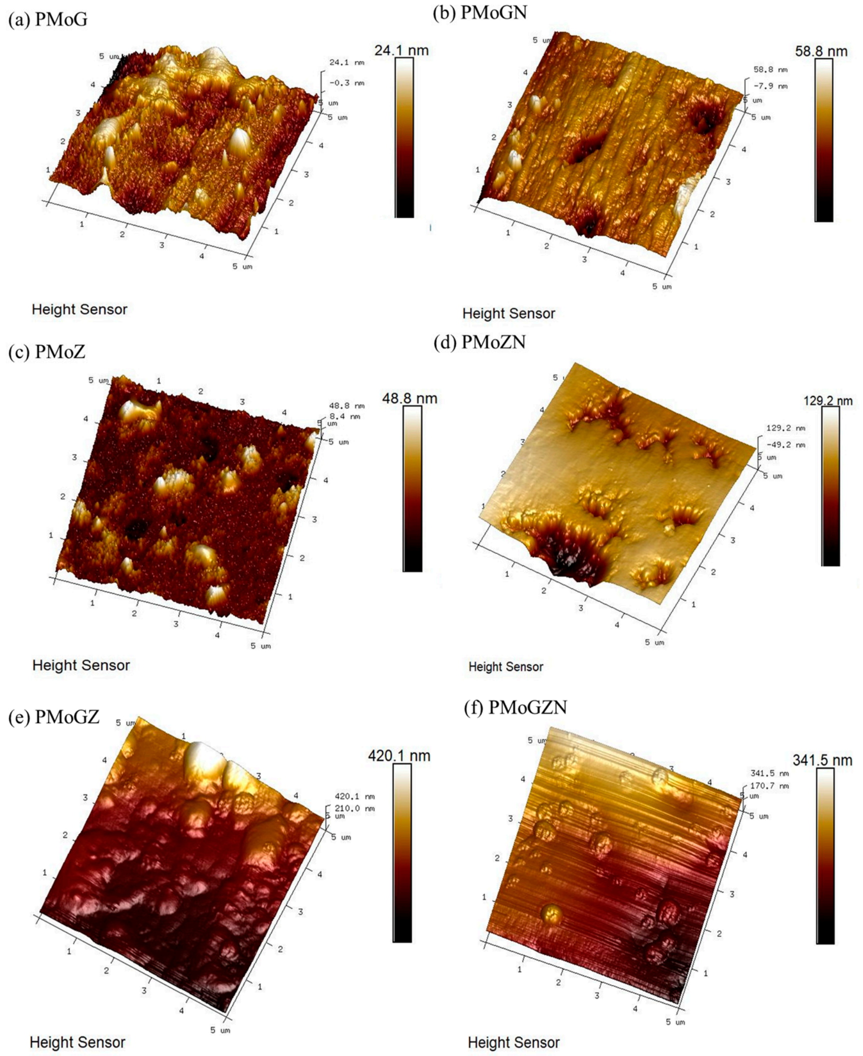

Figure 7. AFM topographical analysis of tribofilm formed on disc surfaces after tribological tests at 80 °C. (**a**) PMoG, (**b**) PMoGN, (**c**) PMoZ, (**d**) PMoZN, (**e**) PMoGZ and (**f**) PMoGZN.

3.4. Characterisation of Tribofilm

Figure 8 shows High-Resolution Transmission Electron Microscopy (HRTEM) images illustrating the structure and elemental variation of the tribofilm for the PMoGZN lubricant formed at an 80 °C temperature. Subfigure (a) represents the cross-sectional view of the tribofilm formed, while subfigure (b) represents the HAADF tribofilm formed by the lubricant combination.

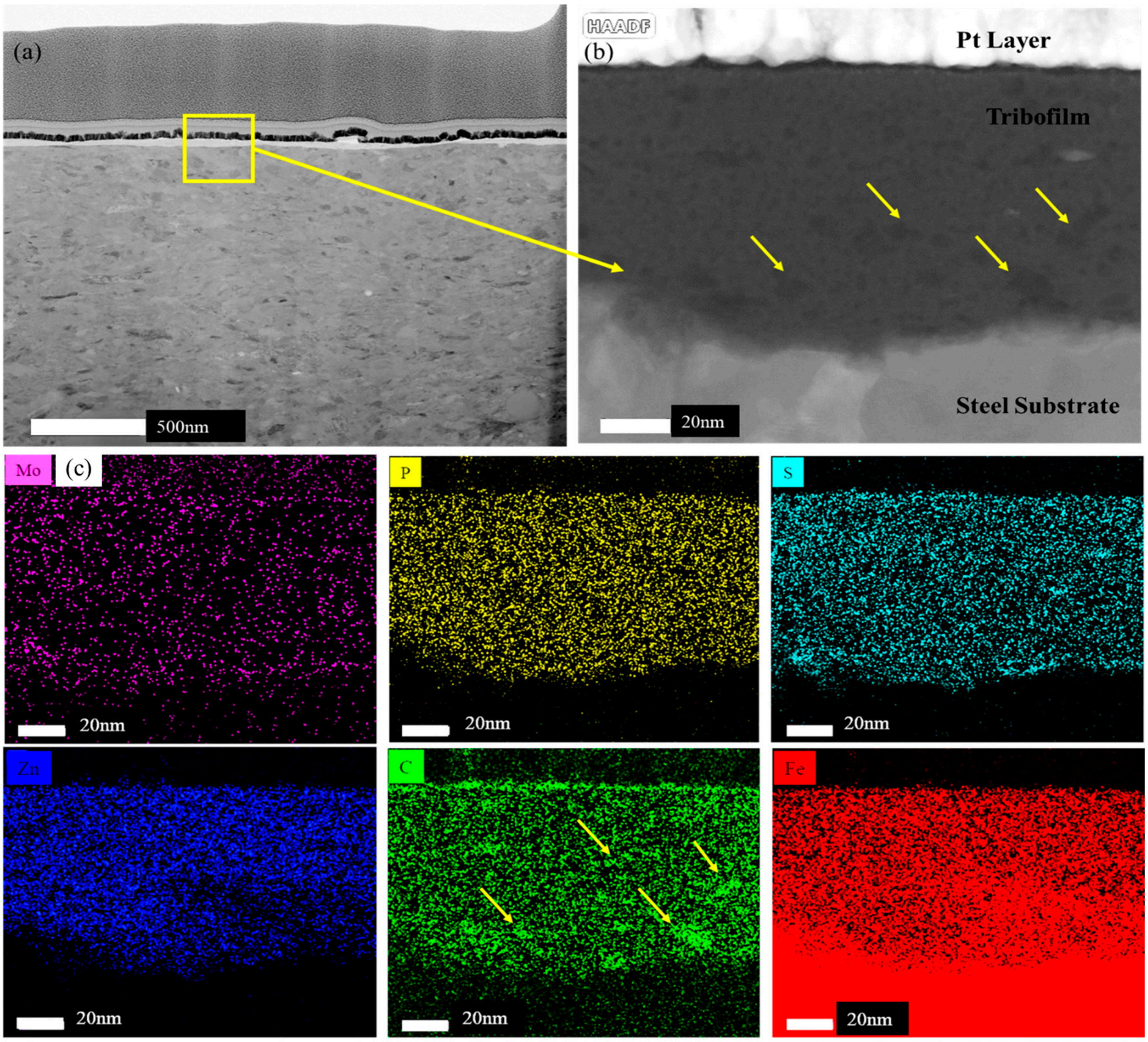

Figure 8. HRTEM images of tribofilm formed on steel surface, showing (**a**) cross-section of tribofilm for PMoGZN lubricant, (**b**) HAADF image for cross-section of tribofilm, (**c**) EDS measurement from mapped tribofilm for PMoGZN at 80 °C. The arrows are pointing out the possible clusters of NDs.

Figure 8a,b show the FIB cross-section of the PMoGZN tribofilm. Here, it is visible that the upper layer is the deposited Pt layer, and the middle layer is the formed tribofilm. The bottom part of the cross-section is the steel substrate. The cross-sectional view of the tribofilm validates the presence of a tribofilm for a lubricant combination containing MoDTC, GMO, ZDDP and NDs (PMoGZN). From the HRTEM, it is observed that a tribofilm approximately 40 nm thick has been formed. With the elemental analysis, it can be seen that this tribofilm is rich in Mo, Zn, C, S and P elements. From the EDS and HAADF analysis, clustered C elements are visible (Figure 8c). Also, the AFM surface topography (Figure 7b) confirmed the presence of small particles on the wear surface. The reduction in friction could be caused by the formation of Mo sulphides and also due to the mechanical interlocking of NDs inside the tribofilm [29]. These results are in line with previous studies that showed the mechanical interlocking of NDs and the polishing effect of NDs reduced friction and improved tribological properties [29,42].

For the lubricant combination PMoGZN, the tribofilm is quite homogeneous. EDS analysis proved that the tribofilm is rich in Mo, S, P, Zn and C elements. The chemical analysis confirmed the higher intensity of Mo element present in the tribofilm.

The authors' previous work [29] has shown that the inclusion of NDs in the lubricant containing GMO and ZDDP can significantly change the tribofilm thickness due to the presence of NDs inside the tribofilm. In the current study, as MoDTC is used, the mechanism of tribofilm formation and friction-wear reduction varied depending on the tribochemical reaction among the additives present in the lubricant combination. The presence of Mo-rich elements on the rubbing surface is evident by the EDS analysis, as shown in Figure 8. The mechanical interlocking is clearly visible for the lubricant without MoDTC, as shown in Figure 9a compared to Figure 9b. This is because of the additional transfer layer from MoDTC molecule sheets onto the asperity of the contacting surfaces and the formation of MoS_2 by tribochemical interaction as the sliding continues [42].

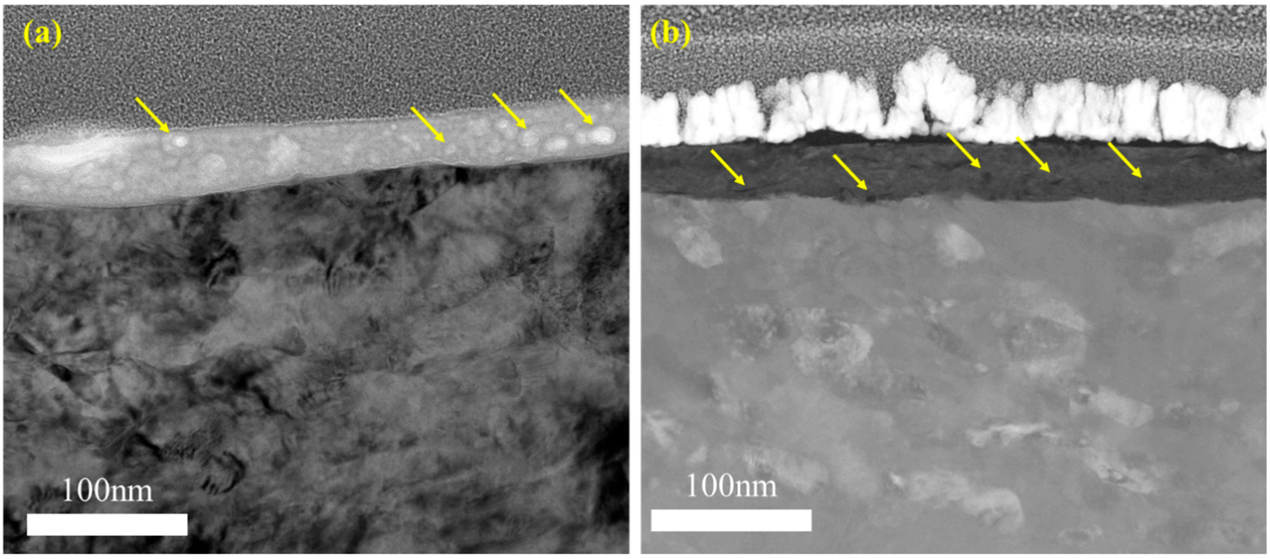

Figure 9. HRTEM images of tribofilm formed on steel surface, for (**a**) PGZN lubricant, (**b**) PMoGZN lubricant. Arrows indicate possible location of NDs embedded inside tribofilm.

Figure 10 shows raman spectra from the wear track of the PMoGZN lubricated plate surface have been acquired to identify the peaks on the wear surface. The analysed sample (PMoGZN) showed MoS_2 peaks at 380 cm^{-1} ($E^1{}_{2g}$ peak) and 410 cm^{-1} (A_{1g} peak) generated at higher temperatures from MoDTC decomposition [43]. However, peaks are also detected at 1326 cm^{-1} (asymmetric peak) and 1582 cm^{-1} (G band), and high-frequency lines at about 2910 cm^{-1} in the wear scar that could be due to NDs embedded in the tribofilm, as reported earlier [44].

The findings of the Raman measurement can be validated by AFM and HRTEM images (Figures 7 and 8), which also proved the NDs' embedment in the form of nanospherical elements on the wear scar, as well as inside the tribofilm. These embedded NDs in the tribofilm thus reduced the friction coefficient substantially due to their mechanical interlocking, including a polishing effect [29].

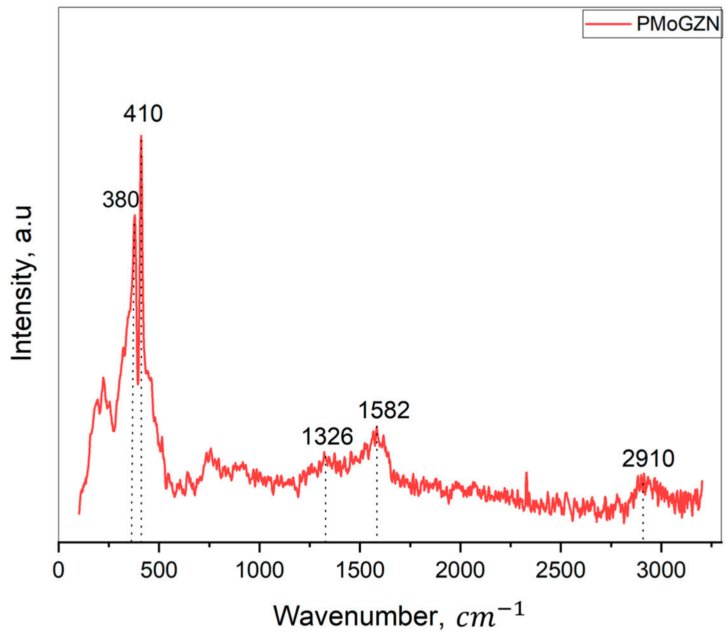

Figure 10. Raman elemental analysis of tribofilm PMoGZN formed at 80 °C.

4. Discussion

With the aim of understanding the impact of nanodiamonds (NDs) alongside other friction-modifying and anti-wear additives such as MoDTC, GMO and ZDDP in base oil, this study presents an in-depth analysis of the friction and wear effects for different combination of additives in lubricant formulations. The details of the outcomes are discussed below.

1. Friction Performance and Variability

Friction tests showed (Figure 3) that the addition of NDs had several positive and negative effects depending on the formulation and testing conditions. At 50 °C, the formulations with MoDTC, GMO and NDs provided a reduction in COF, proving the synergy of NDs with those additives included in the formulated oils, including PMoGN and PMoGZN. The PMoGZN formulation, containing MoDTC, GMO, ZDDP and NDs, had the lowest COF, and it is reasonable to assume that under boundary lubrication, a combination of NDs with these additives would reduce friction more effectively due to the formation of a more robust tribofilm on the contacting surfaces. In cases where there was synergy—the PMoN formulation, MoDTC + NDs—the friction first decreased and later increased as time progressed, leading to a higher final COF compared with other formulations. This may be due to several factors, such as the following:

- Abrasive Nature of Nanodiamonds: Due to the hardness of NDs, they could act as abrasive particles in the case of the inappropriate integration of NDs into the tribofilm [45]. A poor dispersion or embedding of the NDs results in increasing surface roughness and, hence, increased friction [46]. The abrasive properties of the NDs can also disrupt the protective films developed by other additives, especially because of interference with MoDTC's ability to form a uniform MoS_2 tribofilm [47];
- Tribofilm Formation Delayed or Incomplete: The efficiency of NDs depends on being incorporated into a stable tribofilm. In formulations like PMoN, friction rose with time, which suggests that tribofilm formation was either delayed or incomplete. Without a stable tribofilm, NDs could have acted abrasively and increased friction due to the inappropriate formation of the protective layers [48];

- Interactions with other Additives: The interaction between NDs and other additives can be inconsistent. In some formulations, such as PMoGZN, the NDs acted synergistically to reduce friction; in other formulations, such as PMoN, they might interfere with the chemical reactions to produce a low-friction tribofilm. In the cases of some of the formulations studied here, a lack of synergy between MoDTC and NDs could have resulted in increased friction by preventing the stable MoS_2 layer from being formed [41].

2. Temperature-Dependent Effects

Temperature also played a role in friction performance. At 80 °C, some formulations with NDs showed improved performance compared to 50 °C due to increased tribochemical reactions. For example, PMoGZN showed the lowest COF constantly (~0.045) at 80 °C, probably due to the more effective formation of a MoS_2-rich tribofilm at a higher temperature [49]. The higher thermal energy at 80 °C accelerates tribochemical reactions between MoDTC, ZDDP, GMO and NDs. The high temperature can accelerate the thermal decomposition of MoDTC into MoS_2, a lamellar-structured solid lubricant, which lowers shear stress. At the same time, ZDDP generates a phosphate-based tribofilm that stabilises the MoS_2 layer into a strong protective barrier [49]. GMO is a bio-friction modifier that adsorbs on the surface and, through the formation of a low-shear boundary film, further reduces friction in synergy with the MoS_2 and ZDDP layers [2]. At higher temperatures, GMO transforms into carboxylates and chemically stabilises the tribofilm [50]. Concurrently, the NDs could support the tribofilm mechanically by embedding into it, interlocking mechanically and smoothing surface asperities—both wear and friction would be reduced consequently [39]. Due to the higher temperature, a combination of such additives gives quicker tribochemical reactions and a faster tribofilm build-up, which explains the higher friction reduction and expected better wear protection. On the other hand, at a lower temperature of 50 °C, NDs became inconsistent with some formulations, which resulted in an increase in friction. This would point out that the ND interaction with the other additives is temperature-dependent; at higher temperatures, the facilitation of NDs embedding their particles into the tribofilm may occur, while at lower temperatures, the NDs could remain as abrasive particles on the surface and increase friction.

3. Wear performance

The wear results showed (Figure 5) more scatter, with NDs showing positive and negative effects. In lubricant formulations such as PMoN, the addition of NDs increased wear at 80 °C. Indeed, NDs are abrasive in their nature; thus, if these are not properly embedded within the tribofilm, they may behave like hard particles [4]. Their own hardness can cause surface scratches, as shown in Figure 6b, and wear if their integration with other additives is not adequate or they are present as free particles in the lubricant. By contrast, the addition of NDs can intensify the wear if not fully embedded, especially under higher localised loads for pin surfaces, as observed in the PMoZ and PMoGZ formulations. Again, the addition of NDs resulted in a radical wear reduction in the PMoZN formulation; their abrasive nature was repressed due to the anti-wear additive, ZDDP, which allowed the formation of a protective tribofilm in which the NDs could be successfully embedded, creating an extremely robust tribolayer that reduced both friction and wear [51]. This enhanced interaction was synergistic between NDs and ZDDP, helping to form a thicker and more protective tribofilm that provided better wear resistance. The wear mechanism for pins and plates is different due to their geometry, which creates different thermo-mechanical stress distributions at the contact. The pin often bears the primary load, owing to its continuous contact with the plate surface throughout the sliding process, leading to higher localised stress and a more severe tribological interaction. However, the plate surface has a larger contact area and, during the sliding process, does not consistently engage with the pin surface at the exact location, resulting in a reduced tribological interaction and, hence, lower wear than the pin surface [29]. Again, incorporating NDs in lubricants can intensify the wear if the particles are not fully embedded. These NDs may act as abrasive particles that increase wear, especially under higher localised loads for pin surfaces, as observed in the PMoZ and PMoGZ formulations. On the other hand, as the plate surface endures lower stress and possesses a larger contact area, it facilitates the better dispersion and mechanical embedding of NDs into the tribofilm. This further improves the polishing effect and causes better surface uniformity, as observed from the tribofilm analysis of PMoGZN.

4. Tribofilm Formation and Mechanical Interlocking

The formation of tribofilms from lubricant formulations such as PMoGZN was checked with SEM, AFM and TEM analyses, showing the embedment of NDs inside the tribofilm. The smoothest surface topography mechanically achieved with these formulations evidences that NDs gave rise to a polishing effect, which is responsible for surface roughness and friction reduction. The explanation for this effect lies in the spherical shape of the NDs, which would allow it to fill surface asperities, and thus form a resistant tribofilm [4,30]. The term "mechanical interlocking" describes the embedding of NDs into the tribofilm, where they serve as reinforcing agents to enhance tribofilm stability [29]. If integrated properly, such NDs prevent wear by maintaining the integrity of the tribofilm under load and reduce friction. However, in non-embedded situations, NDs behave like abrasive particles, roughening the surface, which resulted in higher friction and wear of some of these formulations [40].

Consequently, the movement of nanoparticles is predominantly governed by the overall behaviour of the oil in bulk. At elevated temperatures, it is hypothesised that the contacting surfaces may undergo oxidation in the presence of base oil, until nanoparticles can be entrained into the contact. Again, GMO decomposed into carboxylic acid and formed a protective layer around the carboxylate functionalised NDs [29]. Conversely, in the case of oil containing ZDDP, it is expected that a ZDDP film will form on the contacting surfaces. The presence of a layer, such as an oxide or ZDDP film, facilitates the retaining of NDs, as they are able to embed onto this matrix [42]. Here, ZDDP is an influencing element for generating a robust tribofilm due to its ability to form phosphate-rich protective layers. These tribofilms significantly reduce wear by developing a sacrificial layer visible for the PMoZ and PMoGZ formulations. However, GMO also plays a critical role by forming a low-shear boundary layer that further enhances the tribological performance when combined with MoDTC, ZDDP and NDs. The anti-wear tribofilm of ZDDP and the friction-reducing properties of GMO resulted in a synergistic effect that is dominant in the PMoGZ system. The synergistic effect with nanoparticles preferentially occurred in the PMoGZ system, as NDs were better integrated into the tribofilm. The ZDDP-derived phosphate layer provided a stable matrix for the ND embedment, as seen in the HRTEM analysis, which improved the tribological performance. While incorporating NDs also improved the PMoG system, the absence of ZDDP might have reduced the robustness of tribofilm, limiting the synergy.

Further, the friction reduction performance was facilitated by the formation of MoS_2 by the tribochemical reaction of MoDTC [52]. The inclusion of NDs and GMO did not interrupt friction reduction; rather, a synergistic effect was found between MoDTC and NDs that further improved the tribological performance of the newly developed nanolubricant PMoGZN. Figure 11 explains the possible mechanism of friction reduction and tribofilm formation for the PMoGZN lubricant at 80 °C.

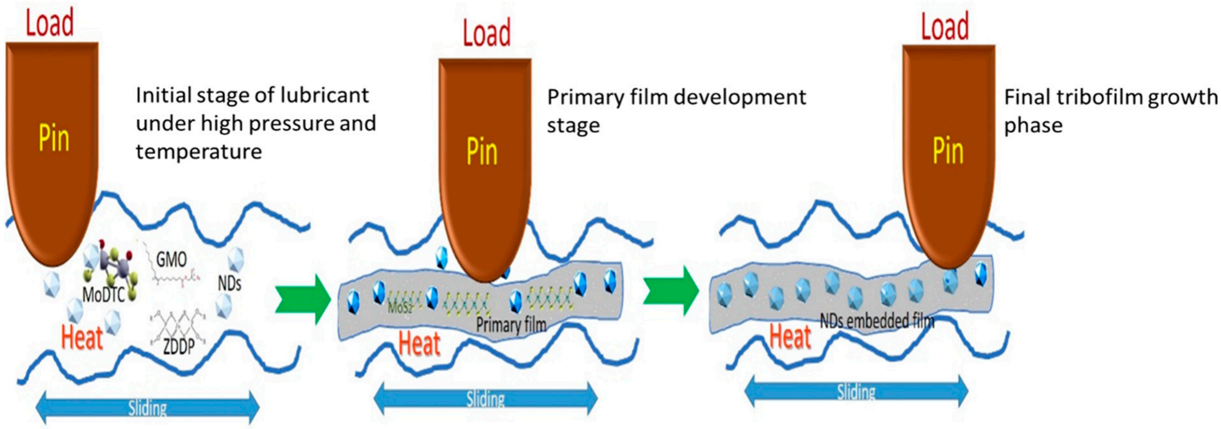

Figure 11. Friction reduction and tribofim formation mechanism for PMoGZN lubricant at 80 °C.

5. Conclusions

With the aim of understanding the impact of nanodiamonds (NDs) with other friction-modifying and anti-wear additives such as MoDTC, GMO and ZDDP in base oil, this study presents an in-depth analysis of the friction and wear behaviours of steel–steel contact pairs in formulated lubricants having different combination of additives. The role of nanodiamonds (NDs) as an effective additive in the lubricant depends on their successful incorporation into the tribofilm and chemical interaction with other additives present in the lubricant formulation. The proper embedment of NDs within the tribofilm enhances its properties, leading to reduced friction and wear. In addition, this incorporation prevents the abrasive nature of free NDs, allowing the tribofilm to act as a protective layer that stabilises mechanical interactions at the sliding surfaces.

Our key conclusions are as follows:

- The addition of NDs with widely used lubricant additives like MoDTC and ZDDP has the potential to reduce the coefficient of friction. Especially, the formulation PMoGZN, which includes MoDTC, GMO, ZDDP and NDs, at both 50 °C and 80 °C exhibited the lowest coefficient of friction, demonstrating the synergy among the additives present in the formulation. However, some exceptional cases were also visible; the PMoN formulation, which includes MoDTC and NDs, showed an antagonistic impact on friction reduction. The reason could be due to incomplete tribofilm formation and the abrasive nature of NDs when they were not integrated properly into the formed film;
- The wear results also showed mixed characteristics. NDs, if not fully embedded inside the tribofilm, could perform as abrasive particles, increasing the wear, as observed in the PMoN and PMoGN formulations. Nevertheless, the appropriate embedment of NDs can form protective tribofilm that will result in reduced wear;
- A robust thick tribofilm was formed for the observed PMoGZN lubricant formulation. The newly developed tribofilm has shown mechanical stability due to the presence of NDs. This thicker tribofilm, and the embedment of NDs inside the tribofilm, could be the reason for lower friction due to smoother sliding between the surfaces.

This study intensively explored the role of nanodiamonds when incorporated with other widely used additives. This is particularly important to understand while formulating new lubricant combinations. Nanodiamonds can potentially reduce the usage of S- and P-containing additives; however their performance depends on the additive matrix that would incorporate the particles. By understanding the mechanism of NDs in the tribofilm, lubricant can be formulated to simultaneously improve the friction and wear properties of the contact pairs and minimise the impact of widely used traditional lubricant additives on the environment. These findings pave the way for further research in lubrication science and technology to create high-performance lubricants having lower environmental impacts.

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