Tribological compatibility analysis of conventional lubricant additives with palm trimethylolpropane ester (TMP) and tetrahedral amorphous diamond-like carbon coating (ta-C)

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Abstract
Modern industrial applications involve rigorous operating conditions due to which lubricant either slips out of the contact or its thin layer resides between the interacting surfaces. Deposition of diamond-like carbon coatings and using lubricants capable of physically adsorbing on the interacting surfaces can significantly improve tribological performance. In this study, tribological compatibility of glycerol mono-oleate, molybdenum dithiocarbamate and zinc dialkyl-dithiophosphate with palm trimethylolpropane ester and tetrahedral amorphous diamond-like carbon coating has been investigated using universal wear testing machine. For comparison, additive-free and formulated versions of polyalphaolefin were used. Moreover, spectroscopic techniques were used to investigate mechanisms responsible for a particular tribological behavior. Among base oils, trimethylolpropane ester proved to be more effective in enhancing friction performance and mitigating wear of contacts when one of the interacting surfaces was ferrous-based. Self-mated tetrahedral amorphous diamond-like carbon coating surfaces resulted in lowest values of friction and wear coefficient of balls.

Keywords
Antiwear additives, friction modifiers, tribology, DLC coating, bio-lubricants

Introduction
A considerable amount of improvement in tribological performance of mechanical components operating under boundary-lubrication regime can be achieved by depositing hard coatings such as diamond-like carbon (DLC) coatings. These coatings possess a unique combination of properties with the help of which they can minimize the friction induced energy and material losses even under starved lubrication conditions.¹ The lubricity of DLC coatings can be further enhanced by using lubricants which can physically adsorb on the interacting surfaces due to their polar components and unsaturated structure such as vegetable oils.²,³ Although, vegetable oils have tribological characteristics (lubricity, flash point, viscosity index, and evaporative losses) comparable to conventional base oils but they also have some deficiencies.⁴–⁷ Some of the undesirable properties of vegetable oils include oxidation instability, inferior low-temperature characteristics, and thermal instability. These shortcomings arise due to the presence of carbon–carbon double bonds in their structure which react with atmospheric oxygen and cause degradation.⁸ In order to decrease the inherent unsaturation and improve the low temperature

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properties of vegetable oils, several chemical modification techniques were used by researchers which include esterification/transesterification,9 estolide formation,10 epoxidation,11 and partial hydrogenation of carbon double bond.12

Since, lubricant additives are manufactured to interact synergistically with conventional base oils and optimized to enhance tribological performance of metallic surfaces, therefore, a lot of experimental studies were carried out by researchers to investigate tribological compatibility of vegetable oils with additives in combination with various types of DLC coatings. Kalin and Vižintin3 studied tribological characteristics of hydrogenated amorphous DLC coating (a-C:H) and tungsten-doped DLC coating (W-DLC) using sunflower and paraffinic mineral oil formulated with zinc dialkyldithiophosphate (ZDDP) and amine phosphate additives. They reported enhanced tribological performance of above-mentioned DLC coatings with sunflower-based lubricants due to their unsaturated and polar nature. They also observed significant improvement in wear resistance of DLC coatings when conventional additives were used as a result of tribochemical interactions. In a similar study, Kalin et al.13 observed 30–50% reduction in wear of a-C:H/a-C:H contacts when amine phosphate and dialkyldithiophosphate ester were used as additives in sunflower oil. They also reported improved tribological performance of symmetrical a-C:H contacts when formulated sunflower oils were used instead of mineral oils irrespective of their formulation. In another experimental study, Kržan et al.14 reported enhanced wear resistance of W-DLC-coated interacting surfaces with rapeseed oil compared to polyalphaolefin (PAO). They also observed that W-DLC/W-DLC contacts resulted in lower values of friction coefficients compared to steel/steel contacts but this enhanced friction performance is not because of the additives but actually due to the inherent lubricity of W-DLC coating. In most of those studies, rapeseed and sunflower oils, formulated with conventional additives, were used as bio-lubricants. Although, few of the researchers also considered palm oil in combination with DLC coatings but without conventional additives. Al Mahmud et al.15 studied tribological characteristics of additive-free sunflower, palm, and coconut oils in combination with tetrahedral amorphous diamond-like carbon coating (ta-C)/steel contacts and found that lowest values of friction and wear coefficients can be achieved with sunflower oil as a result of graphitization and carbon transfer layer. To address this research gap, there is need to investigate tribological characteristics of formulated palm oil-based lubricants with DLC coatings.

Therefore, the main focus of the research presented in this paper is to investigate the tribological compatibility of most widely used lubricant additives (glycerol mono-oleate (GMO), molybdenum dithiocarbamate (MoDTC), ZDDP) with palm trimethylolpropane ester (TMP) and tetrahedral amorphous DLC coating (ta-C). For reference, PAO was used as conventional base oil, with and without additives. Mechanisms responsible for a particular tribological behavior were investigated by analyzing the interacting surfaces using material characterization techniques which include scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS), and Raman spectroscopy.

Materials and methods

Synthesis of TMP

Thermo-oxidative stability and low temperature characteristics of palm oil were improved by chemically modifying it using transesterification process. Palm oil was first converted into its methyl ester and then reacted with trimethylolpropane. Chemical equation of the reaction is shown in Figure 1. Trimethylolpropane [2-ethyl-2-(hydroxymethyl)-1,3-propanediol] was selected because of its low melting point compared to other polyols. During the transesterification process, ester (–COOR–) group from palm methyl ester was replaced by hydroxyl (–OH–) group of trimethylolpropane. Transesterification reaction was conducted in 500 ml three-necked reactor equipped with a reflux condenser, a thermometer, and a sampling port. The condenser was coupled to a vacuum line with a relief valve, an accumulator, and a vacuum trap. During the synthesis, the reactor was immersed in a temperature-controlled silicone oil bath.

![Figure 1. Chemical equation for synthesis of trimethylolpropane ester.](image)
and the solution was agitated with a magnetic stirrer. A 200 ml volume of palm methyl ester and a known amount of trimethylolpropane were placed in the reactor and the mixture was heated to the operating temperature before a catalyst was added. Vacuum was gradually applied after catalyst addition to avoid the spillover of reaction materials. Trimethylolpropane triesters were obtained at a palm methyl ester to trimethylolpropane molar ratio of 10:1. This ratio helped maintain the reaction temperature by providing a heat reservoir and driving forward reaction. Sodium methoxide was used as the catalyst because it minimizes saponification of esters. Samples were taken at predetermined time intervals for the gas chromatographic analysis of product yield. After the reaction was completed, the catalyst was separated from the product mixture by vacuum filtration whereas distillation was conducted to remove unreacted methyl esters from the final product.

**Formulation of lubricants**

In this study, TMP and PAO were used as base oils. Most widely used friction modifiers and antiwear additives which include GMO, MoDTC, and ZDDP were formulated with above mentioned base oils to further enhance their tribological performance. Other lubricant additives (detergents, dispersants, antioxidants, etc.) were not considered while formulating lubricants so that effectiveness of tribologically relevant additives can be analyzed in isolation. Lubricant additives were acquired from Adeka, Japan whereas PAO was purchased from Ineos, USA. Each formulated lubricant was prepared in a batch of 500 g by mixing 5 g of each additive in 495 g of base oil. A precision weighing balance with a least count of 0.1 mg was used for accurate weight measurements. Initially, a beaker containing base oil was heated to 80 °C using electric hot plate and then additives were added to it. The solution was then magnetically stirred at 300 r/min till the time additives fully dissolved in the base oil to get a homogenous mixture. Although homogeneous single phase was obtained for TMP-based lubricants irrespective of their composition but some sedimentation was observed when MoDTC was mixed in PAO. It is mentioned in the literature that lubricant additives are polar in nature and readily soluble in polar unsaturated vegetable oils. Organic metal salts or metal complex compounds have organic moieties to increase solubility in the lubricating oil. For example, MoDTC has dialkyldithiocarbamoyl groups, and ZDDP has dialkyldithiophosphoryl groups. Polar nature of TMP improve solubility to keep the additive components in solution. Sulfur and phosphorus are extreme pressure and antiwear active elements, and have good oil solubility. Formation of sediments in case of PAO + MoDTC can be attributed to the nonpolar nature of PAO, which makes the solubility of MoDTC difficult. However, sedimentation was not observed when GMO and ZDDP were mixed in PAO.

In order to remix the sediments and maintain equal concentration of additives in each test, formulated lubricants were preheated at 60 °C using hotplate and thoroughly mixed using magnetic stirrer before using them in tribotesting. Formulation details and physicochemical properties of the lubricants considered in this research are shown in Tables 1 and 2, respectively.

**Tribological experiments**

Reciprocatory sliding tests were conducted using universal wear testing machine with ball-on-plate geometric configuration (Figure 2). AISI 52100 steel plates with length, width, and thickness of 100, 30, and 5 mm, respectively, were used as flat surfaces whereas AISI 52100 steel balls with a diameter of 15 mm were used as counterbodies. Average surface roughness ($R_a$) and hardness values of interacting surfaces were 0.05–0.07 μm and 60–66 HRC, respectively. In order to evaluate the tribological compatibility of conventional additives with TMP and ta-C coating, friction, and wear coefficients of symmetrical ta-C contacts obtained with additive-free and formulated versions of TMP were compared with those of PAO-based lubricants A linear variable differential transformer (LVDT) sensor was used to determine the frictional force between the interacting surfaces. In order to calculate coefficient of friction, frictional force was divided by normal applied load. Wear coefficient of ball was calculated by measuring the wear scar diameter (WSD) using SEM and converting it into wear volume by using Microsoft® Excel®-based mathematical equation for spherical segments. In order to calculate wear volume of plate, Surftest SJ-210 mechanical stylus profilometer was deployed to

<table>
<thead>
<tr>
<th>Lubricants</th>
<th>Formulation details</th>
<th>TMP (wt.%)</th>
<th>PAO (wt.%)</th>
<th>GMO (wt.%)</th>
<th>MoDTC (wt.%)</th>
<th>ZDDP (wt.%)</th>
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</thead>
<tbody>
<tr>
<td>TMP</td>
<td>100</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PAO</td>
<td>100</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>TMP + GMO</td>
<td>99</td>
<td>1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PAO + GMO</td>
<td>99</td>
<td>1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>TMP + MoDTC</td>
<td>99</td>
<td>—</td>
<td>1</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>PAO + MoDTC</td>
<td>99</td>
<td>—</td>
<td>1</td>
<td>—</td>
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<tr>
<td>TMP + ZDDP</td>
<td>99</td>
<td>—</td>
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<td>1</td>
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</table>

Table 1. Formulation details of additive-free and formulated lubricants.

TMP: trimethylolpropane ester; PAO: polyalphaolefin; GMO: glycerol mono-oleate; MoDTC: molybdenum dithiocarbamate; ZDDP: zinc dialkyldithiophosphate.
obtain the depth profile of wear track using area under the curve method and then multiplying it by the stroke length, that is, 10 mm. Wear volume was then divided with applied load and total sliding distance to get coefficient of wear. In addition to that, tribological performance parameters of ta-C/ta-C contacts were also compared with those of steel/steel contacts. Moreover, influence of steel counterbody on triboochemical interactions between conventional additives and ta-C coating was investigated by using uncoated-steel balls on ta-C-coated plates. Each tribotest was conducted for 2 h with an applied load of 10 N which is equivalent to 700 MPa of Hertzian contact pressure. Other test parameters such as temperature, stroke length, and linear speed were kept at 90 °C, 10 mm, and 0.04 m/s, respectively. Before each test, plates and balls were cleaned with acetone in ultrasonic bath whereas surfaces were washed with cyclohexane and kept in desiccator before carrying out surface analysis. Each test was conducted twice to see repeatability and reproducibility of results and to calculate standard deviations.

### Deposition of ta-C coating

In this study, ta-C was selected for evaluation because it is the form of DLC coatings without any foreign elements (hydrogen, metals, and nonmetals) in its structure. Deposition of ta-C coating on substrates was done in Oerlikon Balzers, Singapore using hybrid magnetron sputtering technique, which is a combination of filtered cathodic vacuum arc (FCVA) and magnetron sputtering. The above-mentioned coating is commercially available with the name of Balinit Hard Carbon. During the deposition process, preheated and cleaned substrates were placed on a turntable and loaded into the vacuum chamber of physical vapor deposition (PVD) sputtering machine.

<table>
<thead>
<tr>
<th>Lubricants</th>
<th>Kinematic viscosity at 100 °C (cSt)</th>
<th>Viscosity index</th>
<th>Density (g/cm³)</th>
<th>Pour point (°C)</th>
<th>Flash point (°C)</th>
<th>TAN (mgKOH/g)</th>
<th>TBN (mgKOH/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMP</td>
<td>9.33</td>
<td>194.50</td>
<td>0.92</td>
<td>−10¹⁹</td>
<td>270¹⁹</td>
<td>0.44¹⁹</td>
<td>0.37¹⁹</td>
</tr>
<tr>
<td>PAO</td>
<td>9.85</td>
<td>135.40</td>
<td>0.84</td>
<td>−54⁺</td>
<td>271⁺</td>
<td>0.01⁺</td>
<td>0.34⁺</td>
</tr>
<tr>
<td>TMP + GMO</td>
<td>9.42</td>
<td>193.00</td>
<td>0.92</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PAO + GMO</td>
<td>9.99</td>
<td>135.70</td>
<td>0.84</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>TMP + MoDTC</td>
<td>9.70</td>
<td>193.50</td>
<td>0.92</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PAO + MoDTC</td>
<td>9.93</td>
<td>135.90</td>
<td>0.84</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>TMP + ZDDP</td>
<td>9.39</td>
<td>192.20</td>
<td>0.92</td>
<td>—</td>
<td>—</td>
<td>—</td>
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</tr>
<tr>
<td>PAO + ZDDP</td>
<td>9.98</td>
<td>134.70</td>
<td>0.84</td>
<td>—</td>
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</tr>
</tbody>
</table>

*TMP: trimethylolpropane ester; PAO: polyalphaolefin; GMO: glycerol mono-oleate; MoDTC: molybdenum dithiocarbamate; ZDDP: zinc dialkyldithio-phosphate; TAN: Total Acid Number; TBN: Total Base Number.

*Provided by INEOS Oligomers (DURASYN™ 170).
Substrates were bombarded with argon ions by a process known as ion etching to remove the contaminants from the surfaces. A high negative potential was applied to the coating material and a stream of positively charged argon ions was then accelerated toward the carbon source. In order to keep the thickness of the coating uniform, substrates were rotated at constant speeds at several axes during the deposition process. In this way, a compact and thin layer of ta-C coating was deposited on the substrate surface. Some of the important properties of ta-C coating are listed in Table 3.

**Characterization of worn surfaces**

In order to investigate the mechanisms responsible for a particular tribological behavior, balls and plates were analyzed using various surface characterization techniques. The wear tracks on balls and wear mechanisms were analyzed using Phenom Pro X SEM. The chemical composition of elements deposited on balls as a result of tribochemical interaction with additives was investigated using EDS system integrated with SEM. In order to study the formation of tribochemical compounds and quantify the structural transformation of ta-C-coated plates from diamond to graphite phase, Renishaw inVia Raman spectroscopy was used.

### Results and discussion

#### Tribological results

The effectiveness of lubricants in facilitating the sliding and mitigating the wearing out of interacting surfaces can be quantified by comparing their friction and wear coefficients. Average friction coefficients of ta-C/ta-C, ta-C/steel, and steel/steel contacts under lubricated conditions are presented in Figure 3 whereas wear coefficients of balls and plates are shown in Figures 4 and 5, respectively.

**ta-C/ta-C contacts.** Self-mated ta-C contacts demonstrated better friction performance when additive-free PAO was used as lubricant resulting in 12% lower friction coefficient value compared to TMP (Figure 3). If we compare average friction coefficient values of steel/steel, ta-C/steel, and ta-C/ta-C contacts in combination with base oils, it can be seen that symmetrical ta-C contacts demonstrated significantly less friction compared to others (Figure 3). A possible justification for superior friction characteristics of ta-C/ta-C contacts can be the inherent self-lubrication characteristics of ta-C coating.20 No significant change in the friction characteristics of ta-C/ta-C contacts was observed when formulated lubricants were

#### Table 3. Properties of ta-C coating.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition technique</td>
<td>FCVA combined with magnetron sputtering</td>
</tr>
<tr>
<td>Thickness</td>
<td>2–3 μm</td>
</tr>
<tr>
<td>Average surface roughness</td>
<td>0.05–0.07 μm</td>
</tr>
<tr>
<td>Hardness</td>
<td>40–50 GPa</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>650–700 GPa</td>
</tr>
<tr>
<td>Maximum service temperature</td>
<td>500°C</td>
</tr>
<tr>
<td>Atomic concentration of hydrogen</td>
<td>&lt;1.0 wt.%</td>
</tr>
<tr>
<td>Color</td>
<td>Black rainbow</td>
</tr>
</tbody>
</table>

FCVA: filtered cathodic vacuum arc; ta-c: tetrahedral amorphous diamond-like carbon.

![Figure 3. Average friction coefficient values of ta-C/ta-C, ta-C/steel, and steel/steel contacts with (a) polyalphaolefin and (b) trimethylolpropane ester-based lubricants. ta-C: tetrahedral amorphous diamond-like carbon.](image-url)
used instead of base oils irrespective of lubricant formulation. Inability of conventional lubricant additives in further reducing the friction coefficients of ta-C/ta-C contacts was also reported by other researchers.\textsuperscript{18} The only exception to this finding was MoDTC which resulted in reduced friction coefficients when mixed with PAO and TMP separately. This shows that MoDTC can tribochemically interact with ta-C coating even in the absence of ferrous counterbody. An improved friction performance of ta-C/ta-C contacts was also observed by Vengudusamy et al. when they use MoDTC as an additive in API Group III base oil.\textsuperscript{21}

Among base oils, PAO outperformed TMP in providing surface protection and resulted in values of wear coefficient of balls and plates which were almost one-half compared to TMP (Figures 4 and 5). It is mentioned in the literature that ta-C coatings are chemically inert in nature and possess low surface energies.\textsuperscript{22} Therefore, polar molecules of TMP were not able to adsorb on ta-C-coated interacting surfaces and unable to provide sufficient wear protection. Among the additives, ZDDP was able to perform its primary role and resulted in lowest values of wear coefficient of balls irrespective of base oil type. A significant difference in wear coefficients of balls and plates was observed irrespective of lubricant formulation. This variance implies that balls and plates wear out at different rates under same test conditions. In general, additives were not able to play an effective role in providing surface protection to ta-C-coated plates. They either deteriorated the wear characteristics of their additive-free versions or maintained wear coefficients of plates at the same level. The only exception to this finding was GMO which played its role to appreciable extent in moderating wearing rates of plates.

ta-C/steel contacts. Contrary to friction results of self-mated ta-C contacts, ta-C/steel contacts resulted in lower values of friction coefficients when additive-free TMP was used as lubricant (Figure 3). As mentioned earlier, this enhanced friction performance of TMP can be attributed to its polar structure due to which its molecules attached on the metallic surfaces such as steel and facilitates sliding of the interacting surfaces whereas PAO is not capable of doing so because of its neutral chemical structure.\textsuperscript{23} Additives were able to further enhance the friction characteristics of ta-C/steel contacts irrespective of their type and base oil used (Figure 3). GMO-containing lubricants were proved to be most effective in reducing the frictional force and offered lowest value of friction coefficients when mixed with PAO and TMP separately. Kano et al.\textsuperscript{24} also observed similar improvement in friction performance of ta-C/steel contacts when PAO + GMO was used instead of additive-free PAO. This friction reducing behavior of GMO can be attributed to its hydroxyl functional group which attaches itself to the metallic surfaces and helps in effectively lubricating the contact.\textsuperscript{25} A possible justification for lowest value of friction coefficient achieved with TMP + GMO among the formulated lubricants can be polar nature of both base oil and additive due to which lubricant never slips out of the sliding surfaces and prevents lubricant starvation condition throughout the course of sliding. Although, MoDTC was also able to reduce friction levels compared to additive-free base oils but not to an extent of GMO. Lubricants containing ZDDP as an additive were not able to make any significant difference in friction behavior of ta-C/steel contacts.

Similar to friction results, additive-free TMP offered better wear resistance to ta-C-coated balls and plates compared to PAO (Figures 4 and 5).
This improved wear protection of ta-C/steel contact in the presence of TMP can be attributed to adsorption of its molecules on the contact area and mitigation of asperity-breakages due to direct contacts. Formulation of base oils with additives resulted in improved wear performance of ta-C/steel contacts irrespective of lubricant formulation. Optimum wear-resistance to ta-C/steel contact was provided by ZDDP-containing lubricants. This behavior can be attributed to the formation of ZDDP-derived tribofilms, as a result of tribochemical interaction, which strongly adhered and stayed on the contact during the complete course of sliding and provided maximum wear protection. Similar type of tribofilm, rich in sulfur and phosphorus was also observed by other researchers when ta-C/steel contact was lubricated with PAO+ZDDP.26

Steel/steel contacts. In case of steel/steel contacts, TMP-based lubricants displayed lower levels of friction compared to PAO-based lubricants irrespective of their formulation (Figure 3). Additive-free TMP facilitates sliding between interacting surfaces and resulted in 15% less value of average friction coefficient compared to pure PAO due to its superior lubricity and polar structure. In case of formulated lubricants, only MoDTC-containing variants were able to give lower values of average friction coefficient compared to their base oils.

Like ta-C/ta-C contacts, PAO was proved to be more effective in mitigating the wearing of interacting steel surfaces compared to TMP in its additive-free state (Figure 3). Inferior wear behavior of TMP in combination with interacting steel surfaces can be attributed to slippage of TMP from the contact and its inability to form surface-protective film during the course of sliding, resulting in direct asperity contacts.

Another justification can be customized synthesis of PAO by the manufacturer, keeping in mind that it will interact with ferrous surfaces, due to which it performed better than TMP. ZDDP played its primary role of antiwear additive and provided the optimum wear protection to interacting steel surfaces compared to other additives when mixed with TMP (Figures 4 and 5). Contrary to that, GMO outperformed ZDDP in further enhancing the wear performance of PAO and resulted in lowest wear coefficients values of both ball and plate.

When additive-free base oils were used in combination with steel/steel, ta-C/ta-C, and ta-C/steel contacts, TMP resulted in better friction performance compared to PAO. This behavior can be attributed to higher concentration of unsaturated molecules and polar components (fatty acids) in the structure of TMP which makes it more interactive with the sliding surfaces compared to saturated and nonpolar PAO. Nonpolar molecules of PAO only performed weak chemical interactions with the sliding surfaces and did not have significant effect on boundary regime mechanisms.27 Polar molecules of TMP such as carboxyl group of fatty acids formed a monomolecular layer and attached on the chemically reactive steel surfaces as a result of physisorption.23 This thin layer of lubricant separated the contacting surfaces and prevented metal-to-metal contact.28

TMP base oil resulted in higher values of wear coefficients compared to additive-free PAO irrespective of contact type. A possible justification for high wear coefficient values in the presence of TMP can be formation of organic acids due to the thermal decomposition of esters, which chemically attacked the interacting surfaces and formed soft oxide layer.29 This oxide layer possessed low shear strength due to which it facilitated the sliding between the
interacting surfaces and resulted in low friction coefficients. However, it can be easily removed from the contact, due to its weak adhesion, by the scraping action of the counterbody and reformed by further chemical reaction resulting in accelerated wearing.\textsuperscript{17,30} In an experimental investigation, Kalin and Vizi\’ntin\textsuperscript{3} also observed excessive wearing of interacting surfaces in W-DLC/steel contact compared to W-DLC/W-DLC contact, when additive-free sunflower was used as lubricant.

Most of the lubricant additives are polar in nature and are attracted to the metal surfaces. Since, TMP molecules are more polar than PAO, therefore experience stronger interactions with polar additives, as well as the metal surfaces.\textsuperscript{31} Polar end groups of additives either physically adsorbed onto the metal surfaces and/or chemically reacted with the surfaces to form monolayers or viscous thick films, while the hydrocarbon chains extended into the base oil.\textsuperscript{32} Difference in tribological performance was observed when same additives were used in TMP and PAO. When additives were used in nonpolar PAO, tribofilms were developed more rapidly and thicker than those derived from the TMP-based lubricants. High affinity of the TMP molecules for the metal surface limits the access of the additive molecules to the surface and their ability to attach and react with it to form a protective reaction layer.\textsuperscript{33}

**Raman spectroscopy**

DLC coatings comprised of a chemical structure in which carbon atoms are bonded with each other in sp\textsuperscript{3}, sp\textsuperscript{2} and/or sp\textsuperscript{1} configuration.\textsuperscript{34} Transformation of sp\textsuperscript{3} bonded carbon atoms into sp\textsuperscript{2} ones occurs when the interacting surfaces undergo extreme operating conditions and this phenomenon is known as graphitization.\textsuperscript{35} Graphitization involves structural transformation of bonded carbon atoms from diamond to graphite phase and plays a vital role in determining the tribological characteristics of DLC coatings. Graphitization usually results in decreased friction and facilitates sliding because of low shear strength possessed by graphitic layer compared to diamond.\textsuperscript{36} Contrary to that, graphitization has detrimental effects on wear resistance of DLC coatings.\textsuperscript{20} The extent of graphitization can be realized from an increase in the intensity ratio (I\textsubscript{D}/I\textsubscript{G}) indicated by the maximum disordered D-peak (I\textsubscript{D}) intensity and the maximum graphite G-peak (I\textsubscript{G}) intensity in the Raman spectra.\textsuperscript{37} Intensity of D-peaks (I\textsubscript{D}) and G-peaks (I\textsubscript{G}) are usually measured at 1380 and 1560 cm\textsuperscript{-1} wavelengths, respectively.\textsuperscript{38} In order to determine I\textsubscript{D}/I\textsubscript{G} ratio, Renishaw WiRE (Windows-based Raman Environment)\textsuperscript{4} software was used. It analyzed the Raman spectra by a peak pick function to determine the peaks automatically. It also controls the acquisition of Raman data and provides with dedicated data processing and analysis options.

First of all, spectral data were removed by doing background subtraction and performing baseline correction using polynomial function which resulted in flat spectrum with just the Raman information. After that, curve-fitting was performed using Gaussian/Lorentzian peak-fitting method.

In this study, Raman spectroscopy was carried out on ta-C-coated plates to identify whether improved friction performance of ta-C/ta-C contacts is due to inherent low-friction characteristics and self-lubrication ability of ta-C coating or it is the result of graphitization and/or tribochemical interaction of ta-C-coated surfaces with the additives. In order to quantify the extent of graphitization, broad Raman spectra of ta-C-coated plates after 2 h of sliding against ta-C-coated balls were acquired from 800 to 2600 cm\textsuperscript{-1} wavelength before and after 2 h of sliding. Renishaw inVia Raman microscope with 514 nm diode laser in combination with 50\times magnification and maximum output power of 300 mW was used in this research work. Other related parameters such as resolution, spectra accumulation and collection time were kept at 2400 lines/nm, 2 and 60 s, respectively. For each surface, three Raman spectra were obtained to achieve a good statistical representation so that the inaccuracies resulting from peak fitting can be minimized. The laser power was kept at 10\% to concentrate only on ta-C coating and minimize the influence of substrate material while obtaining Raman spectra. The higher the laser power, the deeper it goes to the coating surface. When laser power of 50\% was used just for trial, it resulted in laser induced carbon coating damage both inside and outside of the wear scars. Laser power of 10\% was found to represent only the coating/triobfilm and not the steel substrate underneath, so this laser power was used for all measurements.

Raman spectra of ta-C-coated plates before and after tribotesting are shown in Figures 6 and 7.
respectively. In Figure 7, it can be seen that Raman spectrum of ta-C-coated plate after 2 h of sliding against ta-C-coated balls in the presence of TMP is different from rest of the spectra. This difference shows that ta-C coating was completely delaminated from the plate during sliding tests and Raman spectra shown in Figure 7(b) is actually of steel surface. A similar Raman spectra was also observed by Al Mahmud et al. after delamination of a-C:H coating from the substrate. Complete delamination of
ta-C coating in the presence of TMP was also confirmed by highest wear coefficient of plate among TMP-based lubricants (Figure 5(b)). Delamination of ta-C coating can be attributed to either inability of TMP to provide proper lubrication or removal of soft graphitic layer due to graphitization. Since, ta-C/ta-C contacts demonstrated one of the lowest values of friction coefficients when TMP was used as lubricant, therefore, it can be assumed that removal of coating was due to high extent of graphitization (Figure 3). It is mentioned in the literature that graphitization adversely affects the structural integrity of DLC coatings due to which they become soft and more vulnerable to excessive wearing. Delamination of ta-C coating was also observed when TMP + ZDDP was used as lubricant in Raman spectra similar to that of TMP (Figure 7). An increase in I_D/I_G ratio was seen when PAO was used as lubricant resulting in occurrence of graphitization phenomenon but no signs of coating delamination were observed in Raman spectra. As a result, PAO resulted in low friction coefficient value compared to TMP. Similar graphitization of ta-C-coating was also observed by Tasdemir et al. when additive-free PAO was used. When formulated lubricants were used, a significant decrease in I_D/I_G ratio and suppression in graphitization was seen irrespective of lubricant formulation. It is widely accepted that additives have the ability of suppress the graphitization of DLC coating by passivating their dangling carbon bonds resulting in improved wear resistance.

Raman spectroscopy was also carried out on ta-C-coated plates after 2 hours of sliding against ta-C-coated balls to obtain narrow scans (100–1300 cm⁻¹ wavelength). The purpose of obtaining narrow scans (Figure 8) was to identify the compounds formed on the contact area as a result of tribochemical interactions between additives and interacting surfaces. Raman spectroscopy was employed by many researchers for identifying MoS₂ and MoO₃. In most of the Raman spectroscopic studies related to MoS₂, four Raman active modes have been discussed which are E₁g (286 cm⁻¹), E₂g (383 cm⁻¹), A₁g (408 cm⁻¹), and E₂g (32 cm⁻¹). Since, Rayleigh filter has a cut off wavelength of 100 cm⁻¹, therefore, only three first order Raman active modes can be identified.

In case of PAO + MoDTC, a broad peak of MoS₂, centered at 383 cm⁻¹, was observed due to phase vibrations of S-Mo-S layers (Figure 8(a)). Formation of MoS₂ resulted in lowest friction coefficient value of ta-C/ta-C contacts among all the lubricants (Figure 3). Out of four active Raman peaks associated with MoS₂, none of them were seen when TMP + MoDTC was used as lubricant. This shows that either MoS₂ was not formed or undesirably oxidized to MoO₃ after interacting with atmospheric oxygen during sliding. During tribotesting, friction of ta-C/ta-C contact started to decrease after 5 min of sliding in the presence of PAO + MoDTC and then stabilized at 0.04 after 15 min. No such reduction in friction was observed with TMP + MoDTC and steady-state friction coefficient was achieved after few minutes of sliding. From this observation, it can be assumed that MoS₂ was not formed when MoDTC was used as an additive in TMP. MoO₃ peaks were observed at 820 cm⁻¹ in both MoDTC-containing lubricants in addition to iron oxides peaks which were observed at 800 cm⁻¹ irrespective of lubricant formulation. Peaks at 800 cm⁻¹ wavelengths can also be related to the formation of zinc oxide (ZnO). In addition to that, Raman shifts at 694 cm⁻¹, associated with the formation of Fe₂O₃, were also observed when MoDTC was used as additive in TMP. TEMP + ZDDP showed a small peak at 964 cm⁻¹ which can be related to the formation of zinc phosphate [Zn₃(PO₄)₂]. As a result of tribochemical interaction of ZDDP with interacting
surfaces, significant reduction in wear coefficient of ball was observed when TMP + ZDDP was used as lubricant instead of additive-free TMP. From all these observation, it can be concluded that tribological improvements seen in symmetrical ta-C contacts, when formulated lubricants were used instead of additive-free base oils, were primarily due to inherent self-lubrication characteristics and tribochemical interaction of ta-C coating with additives resulting in formation of tribologically beneficial tribofilm and not because of surface graphitization.

Surface characterization using SEM/EDS

SEM was used to measure WSDs and analyze topography of ta-C-coated (ta-C/ta-C contacts) and uncoated-steel balls (ta-C/steel contacts). Steel/steel contacts were not considered for SEM/EDS analysis as a lot of information is already available in the literature. SEM was operated at an electron acceleration voltage of 10 keV while obtaining micrographs and performing EDS analysis so that it captures data only from the coating and electron beam do not penetrate till the substrate material.

In Figure 9, SEM micrographs of ta-C-coated balls after 2 h of sliding against ta-C-coated plates are shown whereas EDS results are summarized in Table 4. When TMP was used as lubricant, ta-C/ta-C contact was not able to sustain 2 h of sliding and resulted in complete delamination of coating (Figure 9(b)). Three distinct regions were observed in the micrograph of TMP. At the left, steel surface (dark grey region) with scratch lines in the direction of sliding can be clearly seen whereas unaltered ta-C-coated surface (light grey region) is evident at the right side. At the middle, bright region representing unaltered steel surface is clearly visible. When GMO was mixed with TMP, wear resistance of ta-C/ta-C contact was substantially increased resulting in unaltered and clean surface after 2 hours of sliding.

![Figure 9. SEM micrographs of tetrahedral amorphous diamond-like carbon (ta-C)-coated balls after 2 h of sliding against ta-C-coated plates in polyalphaolefin and trimethylolpropane ester-based lubricants.](image)

**Table 4.** Atomic percentage of elements found on ta-C-coated balls in case of ta-C/ta-C contacts after 2 h of sliding.

<table>
<thead>
<tr>
<th>Lubricants</th>
<th>Fe</th>
<th>C</th>
<th>O</th>
<th>Cr</th>
<th>Zn</th>
<th>S</th>
<th>P</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAO</td>
<td>9.1</td>
<td>74.4</td>
<td>15.4</td>
<td>0.8</td>
<td>0</td>
<td>0.1</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>TMP</td>
<td>19.5</td>
<td>69.2</td>
<td>9.9</td>
<td>0.9</td>
<td>0</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>PAO + GMO</td>
<td>2.1</td>
<td>89.3</td>
<td>7.2</td>
<td>0.8</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>TMP + GMO</td>
<td>1.7</td>
<td>79.7</td>
<td>17.8</td>
<td>0.7</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PAO + MoDTC</td>
<td>1.6</td>
<td>85.4</td>
<td>8.8</td>
<td>0.8</td>
<td>0</td>
<td>1.4</td>
<td>0.1</td>
<td>1.9</td>
</tr>
<tr>
<td>TMP + MoDTC</td>
<td>6.3</td>
<td>76.2</td>
<td>13.9</td>
<td>0.8</td>
<td>0</td>
<td>1.2</td>
<td>0.1</td>
<td>1.5</td>
</tr>
<tr>
<td>PAO + ZDDP</td>
<td>1.8</td>
<td>73.1</td>
<td>20.8</td>
<td>0.6</td>
<td>2.5</td>
<td>0.5</td>
<td>0.7</td>
<td>0</td>
</tr>
<tr>
<td>TMP + ZDDP</td>
<td>1.3</td>
<td>77.4</td>
<td>15.3</td>
<td>1.1</td>
<td>2.6</td>
<td>0.5</td>
<td>1.8</td>
<td>0</td>
</tr>
</tbody>
</table>

TMP: trimethylolpropane ester; ta-C: tetrahedral amorphous diamond-like carbon; PAO: polyalphaolefin; GMO: glycerol mono-oleate; MoDTC: molybdenum disiocarbamate; ZDDP: zinc dialkylthiodiphtosphate.
This decrease in wear coefficient of ball compared to that of additive-free TMP can be attributed to the transfer of coating material from ta-C-coated plate and adsorption of hydroxyl group from GMO resulting in increased oxygen content (Table 4). Although, improvement in wear performance of ta-C/ta-C contact was also observed when PAO + G was used as lubricant but no signs of tribochemical interaction or transfer layer can be seen in micrograph. Among ta-C/ta-C contacts, lowest friction coefficient values were observed when MoDTC-containing lubricants were used (Figure 3). This can be attributed to the formation of white-colored MoDTC-derived tribofilm, composed of molybdenum, oxygen, and sulfur, on ta-C-coated balls irrespective of the base oil. MoDTC tribochemically decomposes into MoS2 and MoO3 during sliding.21 MoDTC is primarily a friction modifier and its effectiveness in mitigating friction between interacting surfaces depends on ratio of MoS2 and MoO3 formed as a result of its tribochemical decomposition. Higher concentration of MoS2 results in reduced friction whereas no such behavior is attributed with MoO3. MoS2 consists of multiple layers which are bonded together with weak Van der waal forces resulting in low shear strength.41 Contrary to that, MoO3 has a sharp crystalline structure due to which it increases wear instead of reducing friction.47 Formation of MoS2 was also confirmed by Raman spectroscopy results (Figure 8). From this observation, it can be concluded that ta-C is capable of tribochemically interacting with conventional additives, especially MoDTC, even in the absence of ferrous counterbody. Although, MoDTC is primarily a friction modifier and plenty of cracks/crevices were observed in the micrograph of TMP + MoDTC due to brittle fracture (Figure 9(d)) but still significant reduction in wear coefficients was observed (Figures 4 and 5). As compared to PAO + MoDTC, higher concentration of oxygen and lower concentration of sulfur and molybdenum were observed in EDS result of TMP + MoDTC which shows that MoO3 was formed in higher ratio in comparison to MoS2 as a result of tribochemical decomposition of MoDTC. Similar to MoDTC-containing lubricants, ZDDP was also able to interact with structurally ta-C contacts and resulted in lowest values of wear coefficient of balls (Figure 4). On the contrary, presence of ZDDP accelerated the wearing out of ta-C-coated plates (Figure 5). It is well-known that there is a threshold temperature below which additives cannot perform their intended temperature.48 This disagreement in wear behavior of sliding surfaces under same test conditions can be attributed to relatively high temperature of ball compared to plate during sliding, resulting in formation of strongly adhered and stable ZDDP-derived tribofilm. Although concentration of zinc and sulfur remained same for both PAO + ZDDP and TMP + ZDDP but phosphorus was present in higher concentration on ta-C-coated ball when latter was used as lubricant. Raman spectroscopy also confirmed the formation of ZDDP-derived tribo-compounds, majorly [Zn3(PO4)2], on ta-C-coated plate (Figure 8). As a result, lowest value of wear coefficient of ball was observed in the presence of ZDDP-containing TMP (Figure 4). Brittle fracture, resulting in cracks and crevices, was the predominant wear mechanism observed in the micrograph of TMP + ZDDP but polishing wear was also seen in addition to cracking of ta-C coating in the presence of PAO + ZDDP.

SEM micrographs of uncoated-steel balls obtained after 2 h of sliding against ta-C-coated plates are shown in Figure 10 whereas atomic percentage of elements present on the ball surface are presented in Table 5. A lot of surface deterioration was seen in the micrographs of PAO-based lubricants compared to those of TMP ones. As a result, ta-C/steel contacts resulted in high values of friction and wear coefficients when different variants of PAO were used. When additive-free PAO was used, abrasion was observed as main wear mechanism which resulted in the formation of scratch lines in the direction of sliding especially in the lower part of the micrograph accompanied with few pits and grooves (Figure 10(a)). Although, few scratch lines and pits were also observed with TMP but the major difference between two micrographs was the transfer of carbon material from ta-C-coated plate represented by black region in the middle. High percentage of carbon observed in EDS results (Table 5), low value of friction coefficient (Figure 3) and delamination of coating from the plate (Figure 7) confirmed the transfer of carbon material from ta-C-coated plate. Micrographs of GMO-containing lubricants showed excessive abrasive wear represented by deep grooves and concentrated scratch lines throughout the scan area especially when TMP + GMO was used (Figure 10(c) and (d)). In case of PAO + GMO, pitting was the other predominant wear mechanism in addition to abrasive wear. This excessive pitting can be attributed to adsorption of hydroxyl group from GMO, resulting in high content of oxygen in EDS analysis and lowest value of friction coefficients among ta-C/steel contacts. Those pits act as small reservoirs to maintain continuous supply of lubricant to the contact and prevent starvation conditions. Formation of white-colored MoDTC-derived tribofilm as a result of its tribochemical decomposition was observed in the micrograph of PAO + MoDTC especially at the middle and top regions. In addition to that, some of the coating material was also transferred to the steel ball from ta-C-coated plate and can be seen as black and grey-colored patches. Although, MoDTC-derived tribofilm was also observed in EDS results of TMP + MoDTC but it was mostly comprised of MoO3 as sulfur was present in low percentage compared to oxygen (Table 5). In case of ZDDP-based lubricants, additive-derived tribofilm composed of zinc, phosphorus, and sulfur was observed on steel
balls irrespective of base oil type (Table 5). When PAO + ZDDP was used as lubricant, ZDDP-derived tribofilm was seen in micrograph. In addition to abundant cracks, crevices and wear debris; scratch lines were also observed in the direction of sliding. Compared to PAO + ZDDP, relatively clean and unaltered ball surface was seen in the micrograph of TMP + ZDDP and no signs of brittle fracture or wear debris were detected. As a result, TMP + ZDDP resulted in improved tribological performance when used as lubricant in ta-C/steel contact.

Conclusions
In this study, tribological compatibility of conventional lubricant additives with TMP and ta-C coating has been investigated and comparison of vital tribological parameters was made with PAO-based lubricants. The following conclusions can be drawn from the experimental results:

- In additive-free state, TMP proved to be more effective in enhancing friction performance of contacts when one of the interacting surfaces was ferrous-based. This behavior can be attributed to unsaturated and polar structure of TMP due to which it adsorbs on the active sites of chemically reactive interacting surfaces. On the other hand, additive-free PAO outperformed TMP in mitigating wear of sliding surfaces in case of symmetrical contacts.
- Symmetrical ta-C contacts resulted in lowest values of friction and wear coefficient of balls irrespective of lubricant formulation whereas lowest wear coefficient values of plates were observed when uncoated-steel balls were used as counterbody against ta-C-coated plates.

Table 5. Atomic percentage of elements found on uncoated steel balls in case of ta-C/steel contacts after 2 h of sliding.

<table>
<thead>
<tr>
<th>Lubricants</th>
<th>Fe</th>
<th>C</th>
<th>O</th>
<th>Cr</th>
<th>Zn</th>
<th>S</th>
<th>P</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAO</td>
<td>69.1</td>
<td>14.2</td>
<td>15.5</td>
<td>1.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TMP</td>
<td>53.2</td>
<td>35.7</td>
<td>9.7</td>
<td>0.9</td>
<td>0.2</td>
<td>0</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>PAO + GMO</td>
<td>66.3</td>
<td>12.5</td>
<td>20.9</td>
<td>0.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TMP + GMO</td>
<td>60.9</td>
<td>15.1</td>
<td>22.9</td>
<td>0.8</td>
<td>0</td>
<td>0.2</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>PAO + MoDTC</td>
<td>67.5</td>
<td>24.8</td>
<td>4.2</td>
<td>1.2</td>
<td>0</td>
<td>1.2</td>
<td>0.3</td>
<td>0.8</td>
</tr>
<tr>
<td>TMP + MoDTC</td>
<td>70.9</td>
<td>12.7</td>
<td>13.9</td>
<td>0.8</td>
<td>0</td>
<td>0.5</td>
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<td>1.1</td>
</tr>
<tr>
<td>PAO + ZDDP</td>
<td>82.4</td>
<td>7.8</td>
<td>6.5</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.9</td>
<td>0</td>
</tr>
<tr>
<td>TMP + ZDDP</td>
<td>75.6</td>
<td>13.4</td>
<td>6.6</td>
<td>1.1</td>
<td>1.2</td>
<td>0.9</td>
<td>1.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

TMP: trimethylolpropane ester; ta-C: tetrahedral amorphous diamond-like carbon; PAO: polyalphaolefin; GMO: glycerol monoooleate; MoDTC: molybdenum dithiocarbamate; ZDDP: zinc dialkyldithiophosphate.

Figure 10. SEM micrographs of uncoated steel balls after 2 h of sliding against tetrahedral amorphous diamond-like carbon-coated plates in polyalphaolefin and trimethylolpropane ester-based lubricants.
• Tribological improvements seen in symmetrical ta-C contacts, when formulated lubricants were used instead of additive-free base oils, were primarily due to inherent self-lubrication characteristics and tribochemical interaction of ta-C coating with additives, resulting in the formation of additive-derived tribofilm and not because of surface graphitization.

• ZDDP performed its primary role and resulted in lowest values of wear coefficients of balls and plates when mixed with PAO and TMP separately. However, it resulted in deteriorated friction performance of all the contacts whereas GMO and MoDTC further enhance the friction performance characteristics in most of the cases irrespective of base oil type.

• Symmetrical ta-C contacts were able to sustain 2 h of tribotesting without significant coating delamination irrespective of lubrication formation. The only exceptions to this finding were TMP and TMP + ZDDP lubricants which resulted in delamination of coating from ta-C-coated interacting surfaces at the end of sliding tests.

Declaration of Conflicting Interests
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References


