

Article

Enhanced Tribological Behaviour of Hybrid MoS₂@Ti₃C₂ MXene as an Effective Anti-Friction Additive in Gasoline Engine Oil

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Abstract: Hybrid molybdenum disulfide (MoS₂)-MXene (Ti₃C₂) was added as an additive in SAE 5W-40-based engine oil in an attempt to reduce interfacial friction between contact surfaces. It was found that the coefficient of friction (COF) and wear scar diameter (WSD) were reduced by 13.9% and 23.8%, respectively, with the addition of 0.05 wt.% MoS₂-Ti₃C₂ compared to base engine oil due to the interlaminar shear susceptibility of MXene. However, we postulate that the high surface energy and presence of -OH, -O and -F functional groups on the surfaces limited the dispersibility and stability of MXene in base oil, while high activity of MoS₂ nanoparticles due to large surface area and vigorous Brownian motion prompted fast settling of nanoparticles due to gravitational force. As such, in the present study, hybrid MoS₂-Ti₃C₂ were amine-functionalized to attain stability in SAE 5W-40-based engine oil. Experimental findings indicate that amine-functionalized 0.05 wt.% MoS₂-Ti₃C₂ exhibited higher COF and WSD, i.e., 12.8% and 12.3%, respectively, compared to base oil added with 0.05 wt.% unfunctionalized MoS₂-Ti₃C₂. Similarly, Noack oil volatility was reduced by 24.6% compared to base oil, indicating reduced oil consumption rate, maximal fuel efficiency and enhanced engine performance for a longer duration.

Keywords: MXene; MoS₂; tribology; nanolubricant; superlubricity



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1. Introduction

In automotive engines, parasitic energy loss due to friction and wear of worn surfaces remains a major concern. According to studies, the overall power produced by the engine can be reduced by 17–19% due to frictional losses, whereas 33% of fuel energy in passenger automobiles is squandered to reduce frictional losses [1,2]. The high frictional losses result in higher engine wear, failures of steady running components, higher energy consumption and fuel energy loss [3]. As such, employing lubricants can effectively reduce friction and wear, fulfilling the low carbon emission and fuel economy requirements in car engines. Generally, lubrication can be categorized into four regimes—(i) boundary lubrication, (ii) elastohydrodynamic lubrication, (iii) hydrodynamic lubrication and (iv) mixed

lubrication. Engine and transmission systems in cars operate under all the aforementioned lubrication regimes.

Recent studies have reported that adding nanomaterials as lubricant additive can potentially improve tribological behaviour, such as the wear and friction properties of commercial lubricants. This is because, besides affecting the physiochemical properties of engine oil, nanoparticles could minimize possibilities of asperities direct contact (i.e., valleys between asperities of frictional surfaces filled) to form a tribo-boundary film on worn surfaces to enhance tribological behaviour of an engine, i.e., via boundary lubrication conditions [4]. For instance, in a study by Ali et al., coefficient of friction (COF) of SAE 5W-30 oil was reduced by 50% and 45% with the addition of TiO_2 and Al_2O_3 nanoparticles, respectively [5]. In other studies, Li et al., reported that the addition of 0.1 wt.% of $\text{ZrO}_2\text{-SiO}_2$ nanoparticles reduced COF of base oil by 16.24% [6], while Ali et al., [1] reported that the addition of graphene improved anti-friction and antiwear properties by 29% and 22%, respectively.

Today, the family of 2D materials has been augmented by MXene made of 2-dimensional transition metal carbides, nitrides or carbon-nitrides with a general formula $\text{M}_{n+1}\text{X}_n\text{T}_x$ where M represents the transition metal ($n = 1, 2$ or 3), X denotes C and/or N while T_x represents the termination group (e.g., OH, -O or -F) [7–10]. MXene is produced from the MAX phases, where A layers (i.e., group IIIA or IVA element) of M_{n+1}X_n are removed by selective etching. In addition to energetic and catalytic applications, the lamellar Ti_3C_2 , as the most representative member of the MXene family, are particularly interesting for tribological purposes owing to its graphite-like structure with low shear strength and self-lubricating properties [11,12]; all of which were verified by density functional calculation and molecular dynamic simulations [13]. In a study by Liu et al., it was reported that the addition of 0.8 wt.% Ti_3C_2 reduced the COF of PAO8 oil by 9.6% [14]. In another study by Gao et al., it was reported that $\text{Ti}_3\text{C}_2\text{T}_x$ -based nano additives reduced the wear volume of base oil by 87% with a high load carrying capacity (i.e., 500 N) [15]. Despite the tremendous potential of MXene, studies on tribological behaviour of Ti_3C_2 , particularly as an additive (or hybrid additive) in gasoline engine oil, remain limited.

In view of these limitations, the present study aims to investigate the tribological behaviour of hybrid molybdenum disulfide (MoS_2)- Ti_3C_2 as an additive in SAE 5W-40-based engine oil. The hexagonal crystal structured MoS_2 is a very stable compound made of Mo atoms sandwiched between double layers of sulphur atoms and linked via van der Waals forces [16–18]. MoS_2 exhibits low COF owing to the ease of its basal plane shearing, particularly under vacuum conditions. Studies have reported that (MoS_2) is capable of imparting excellent lubrication at high contact stress by the mechanism of settling a solid lubricant layer on the contact surfaces [19]. As such, the present study aims to investigate the effect of hybrid $\text{MoS}_2\text{-Ti}_3\text{C}_2$ additive on the coefficient of friction, wear scar diameter, viscosity index, oxidative induction time (OIT) and Noack volatility of SAE 5W-40-based engine oil. To explore the stability of nanoparticle dispersion in base oil (i.e., sufficient repulsive interaction to counter agglomeration) and the subsequent increase in tribological behaviour, the effect of amine functionalization of $\text{MoS}_2\text{-Ti}_3\text{C}_2$ was also studied in detail.

2. Materials and Method

2.1. Materials

All chemicals used in this experiment were analytical grade and used as received. Ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) purchased from Fisher Chemicals (Chicago, IL, USA), titanium aluminium carbide (Ti_3AlC_2) purchased from Xiamen TOB New Energy Technology (Xiamen, China), thiourea ($\text{SC}(\text{NH}_2)_2$) purchased from R&M Chemicals (Dundee, UK), octadecylamine ($\text{C}_{18}\text{H}_{37}\text{NH}_2$), ethanol ($\text{C}_2\text{H}_5\text{OH}$), lithium fluoride (LiF), hydrochloric acid (HCl) and ethanol purchased from Sigma-Aldrich, St. Louis, MO, USA were used for $\text{MoS}_2\text{-Ti}_3\text{C}_2$ hybrid nanoparticle synthesis. The lubricant oil used was gasoline engine oil, SAE5W40.

2.2. Synthesis of MXene (Ti_3C_2)

The microwave-hydrothermal synthesis method was used to synthesize Ti_3C_2 since it is advantageous compared to conventional etching or delamination process due to remarkably reduced synthesis time, energy requirement and high quality of MXene that can be produced in bulk quantities. The procedure has been described in detail in our previous study [20,21]. A total of 1.6 g of LiF was dissolved in 10 mL of 9M HCl by stirring for 15 min at room temperature. Later, 1 g of Ti_3AlC_2 was slowly added to the mixture and left to stir at room temperature for another 30 min. The mixture was later sonicated for 30 min and transferred into the advanced microwave synthesis platform (Milestone, flexiWAVE, Bergamo, Italy). The mixture was heated for 30 min at 40 °C and left to cool naturally at room temperature once the synthesis was completed. The synthesized sample was centrifuged and washed with distilled water and ethanol to attain pH of >5.0, then sonicated in Argon (Ar) atmosphere for an hour and later centrifuged to separate the precipitate from the supernatant where finally, the supernatant will be freeze-dried to extract Ti_3C_2 powder.

2.3. Preparation of MoS_2 - Ti_3C_2 Hybrid Nanoparticle

The hybrid MoS_2 - Ti_3C_2 nanoparticles were also synthesized by advanced microwave synthesis method. A total of 3.70758 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and 6.8508 g thiourea were slowly added in 105 mL of deionized water and continuously stirred for 30 min to obtain a homogeneous solution. Later, 1 g of Ti_3C_2 powder was dissolved in the mixture by sonicating for 30 min. The mixture was then transferred into the advanced microwave synthesis platform (Milestone, flexiWAVE, Italy) and heated for 15 min at 200 °C. Upon completion of synthesis, the reaction mixture was left to cool naturally to room temperature and later centrifuged and washed with distilled water and ethanol and finally freeze-dried to obtain MoS_2 - Ti_3C_2 particles.

2.4. Synthesis of Amine-Functionalized MoS_2 - Ti_3C_2 Hybrid Nanoparticle

Amine-functionalized MoS_2 - Ti_3C_2 hybrid nanoparticles were synthesized by adding 1 g of MoS_2 - Ti_3C_2 in 100 mL of DI water and stirred continuously for 30 min. Later, 2 g of octadecylamine was added to 100 mL ethanol and stirred until all solutes were completely dissolved. Both these solutions were slowly mixed and heated at 40 °C under constant stirring for 24 h. The as-formed amine-functionalized MoS_2 - Ti_3C_2 hybrid nanoparticles were washed with DI water to remove unreacted octadecylamine and freeze-dried to obtain the functionalized MoS_2 - Ti_3C_2 hybrid nanoparticle.

2.5. Characterizations

The morphology of MoS_2 , Ti_3C_2 and hybrid MoS_2 - Ti_3C_2 particles was obtained using FEI Quanta 400F, Fremont, CA, USA, at 20 kV. XRD analysis was performed using a PANalytical X-ray Diffractometer using copper material to generate X-rays with wavelength (K alpha) of 1.54 Å and filtered through Ni using an operational voltage of 45 kV and current of 27 mA. The samples were scanned from 20 to 80 degrees at a step size of 1 degree/min and divergence slit of 0.9570 degrees. Raman spectroscopy analysis was performed using a stellar-Pro ML150 laser coupled to an optical microscope (Leica DM 2500 M) with Renishaw He-Ne laser with 633 nm wavelength as excitation source while zeta potential measurements to evaluate the stability of lubricants were determined using Zetasizer Nano (Malvern, Worcestershire, UK).

The Ducom four-ball tribotester TR-30L was used to analyze the tribological behaviour of nanolubricants, such as coefficient of friction (COF) and wear scar diameter (WSD). Before performing each tribological experiment, the steel balls were washed in ethanol and dried to avoid contamination. The hardness, density and diameter of the steel balls were 1 HRC, 7.79 g/cm³ and 12.7 mm, respectively. The test was conducted according to ASTM 4172-94, where the rotational speed, applied load, time, and temperature were 12,000 rpm,

392.5 N, 3600 s and 75 °C, respectively. The coefficient of friction was calculated using Equation (1)

$$\mu = 2.22707 \frac{\tau}{\rho} \quad (1)$$

where μ represents the coefficient of friction, τ represents the average frictional torque in kg-cm, and ρ is the load exerted while performing the test. The viscosity index was calculated according to ASTM D2270 based on kinematic viscosity at 40 °C and 100 °C. Kinematic viscosity in the present study was calculated according to Equation (2).

$$v = \frac{\mu}{\rho} \quad (2)$$

where v , μ and ρ represent kinematic viscosity, dynamic viscosity and density, respectively. Densities of the lubricant were determined using Anton Paar (DMA 4500 M) at 40 °C and 100 °C. Oxidation induction time (OIT) were determined using TA Instrument's High Pressure Differential Scanning Calorimeter (HP-DSC) 25P with ultrahigh purity (UHP) grade oxygen gas in an airtight sample chamber with flow rate of 50 mL/min, pressure of 500 psi and isothermal temperature of 200 °C with ramping rate of 10 °C/min. Approximately 3.2 mg of oil samples equilibrated at 50 °C were used for the testing. The relationship between kinetic rate constant and temperature in kinetic expressions, which governs OIT measurements, was based on the Arrhenius equation. Sample volatility was determined according to ASTM D6375 using Noack analysis. Approximately 40 mg of samples were heated to 249 °C at 65 °C/min with a continuous air purge at 150 mL/min using the NETZSCH TGA (TG 209 F3 Tarsus). The samples were held isothermally at 249 °C for 15 min, and percentage mass loss was determined at Noack reference time ($t = 11.7$ min), as specified by analyzing a Noack reference oil (RL-N).

3. Results and Discussion

3.1. Morphology and Characterization

The structure and composition of bulk MAX phase precursor, MXene sheets and the synthesized hybrid $\text{MoS}_2\text{-Ti}_3\text{C}_2$ were characterized by SEM and EDX, as shown in Figure 1. From Figure 1A, the microstructure of bulk MAX phase precursor Ti_3AlC_2 shows solid and stacked multilayer nanosheets, while Figure 1B shows the SEM image of Ti_3AlC_2 after etching and exfoliation with HCl-LiF via microwave-assisted hydrothermal synthesis. The MXene sheets in Figure 1B showed crumpled structures with thinner and few layered structures, indicating the successful formation of thin layers of 2D MXene nanosheets by excluding Al element from packed MAX layers during the etching and exfoliation process. Additionally, it can be seen in Figure 1C,D that the hybrid $\text{MoS}_2\text{-Ti}_3\text{C}_2$ was properly formed where MoS_2 and a densely aligned enclosed surface of Ti_3C_2 MXene. The MoS_2 nanoparticles were uniformly distributed, well faceted, densely grown, semi-vertically and interleaving lamellar nanosheets with rough edges, which ascertains the nanosheet morphology of MoS_2 . The edge-oriented structure of MoS_2 is highly desirable to expose more active sites to enhance tribological behaviour [22]. The EDX spectrum and elemental mapping are shown in Figure 1E,F, ascertaining the existence of sulphur, molybdenum and titanium and the successful formation of hybrid $\text{MoS}_2\text{-Ti}_3\text{C}_2$ via microwave-assisted hydrothermal synthesis method.

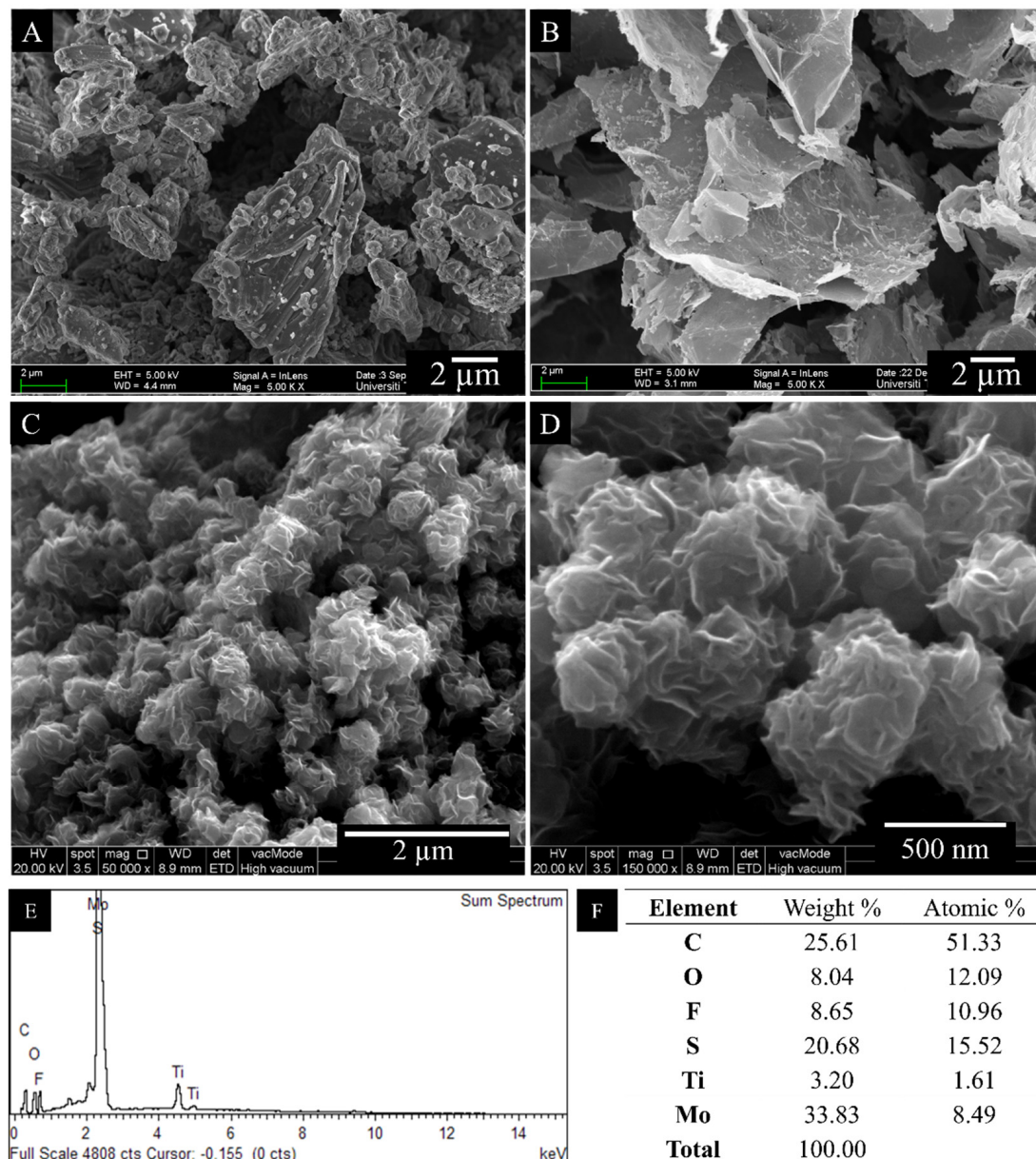


Figure 1. SEM images of (A) Ti_3AlC_2 MAX phase (B) Ti_3C_2 MXene (C,D) Low and high magnification images of hybrid MoS_2 - Ti_3C_2 (E,F) EDX spectra of hybrid MoS_2 - Ti_3C_2 .

Figure 2 shows the XRD spectrum of MoS_2 , Ti_3C_2 and MoS_2 - Ti_3C_2 composites, which is used to characterize the phase and crystal structure of the samples. From the XRD spectrum (Figure 2A), the diffraction peaks located at 14.1, 33 and 59.1 degrees can be attributed to the (002), (100) and (110) peaks of pure hexagonal MoS_2 in accordance with JCPDS 371492 [21,23]. The diffraction pattern of Ti_3C_2 MXene shows peaks at 9, 19.4, 27 and 61 degrees which correspond to (002), (006), (008) and (110) crystal planes, respectively. Previous studies have reported the (002) peak shift of Ti_3C_2 Tx composites when deposited with MoS_2 (i.e., downshifted from 8.96 to 7.33 degrees after deposition with MoS_2) [24]. This was attributed to the interlayer spacing of both MoS_2 and Ti_3C_2 MXene, which was expanded simultaneously by the formation of MoS_2 - Ti_3C_2 composite due to ion intercalation and integrated 2D layer stackings [24,25]. However, in the present study, the peak shift was minimal (i.e., from 9 to 8.6 degrees), indicating that MoS_2 did not significantly impact the interlayer distance of MoS_2 and Ti_3C_2 MXene.

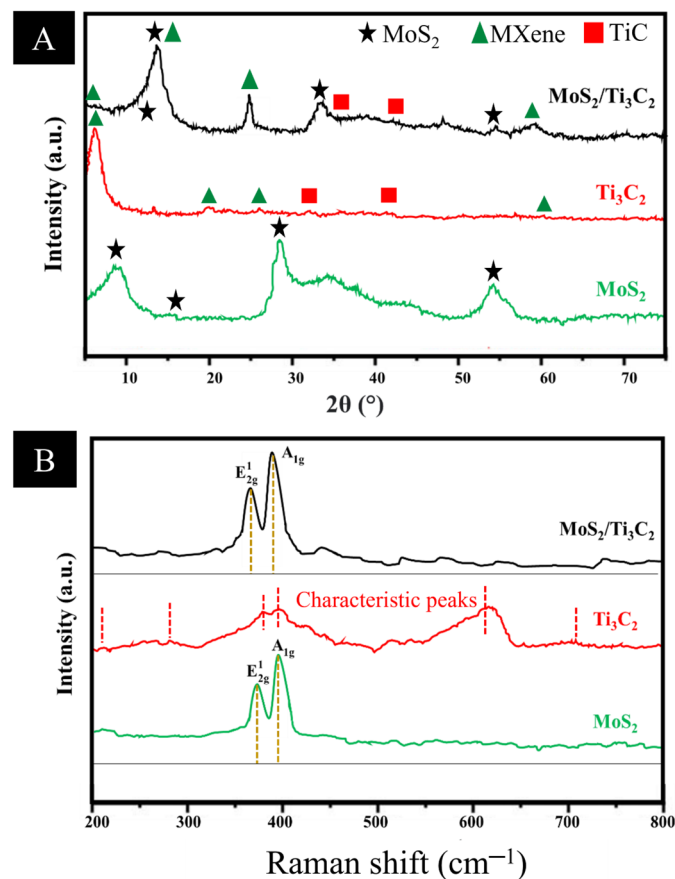


Figure 2. (A) XRD spectrum and (B) Raman analysis of MoS₂, Ti₃C₂ and MoS₂-Ti₃C₂.

Figure 2B shows the Raman spectrum of MoS₂, Ti₃C₂ and MoS₂-Ti₃C₂ composites. The MoS₂ samples have shown characteristics at 377 cm⁻¹ and 403 cm⁻¹, corresponding to E_{2g} and A_{1g} vibration peaks, respectively. The A_{1g} vibration mode is favoured for edge-terminated structures owing to polarization dependence [25]. The relative intensity of A_{1g} to E_{2g} can be used to describe the MoS₂ planes where in the present study, the A_{1g}/E_{2g} ratio was approximately 1.7 indicating an edge-enriched MoS₂ structure. On the other hand, characteristic peaks of Ti₃C₂ were observed, such as at 208 cm⁻¹ and 719 cm⁻¹, which correspond to the A_{1g} symmetry out-of-plane vibrations of Ti and C atoms, while the peak at 272 cm⁻¹ and broad peak at 622 cm⁻¹ corresponds to the Eg group vibrations including the in plane shear modes of Ti, C and surface functional group atoms [26,27]. Notably, Ti₃C₂ related peak (e.g., 622 cm⁻¹) diminished in the MoS₂-Ti₃C₂ due to the high surface coverage of MoS₂ and the intrinsically weak signal nature of Ti₃C₂ [25]. Nevertheless, the co-existence of peaks of MoS₂ and Ti₃C₂ in the MoS₂-Ti₃C₂ ascertains the successful preparation of the composite.

3.2. Tribological Behaviour

Figure 3 shows the coefficient of friction (COF), average wear scar diameter as well as SEM images of the wear surfaces of MoS₂-Ti₃C₂-based nanolubricant. From Figure 3A,B, it can be seen that COF of the base oil was 0.108. The addition of MoS₂-Ti₃C₂ gradually reduced the COF of nanolubricant by 13.9% when 0.05 wt.% MoS₂-Ti₃C₂ was added. Sliding off the nanosheets at the asperities and deformed surfaces of individual nanosheets produces a protective layer (i.e., tribofilm) which effectively reduces COF while providing an excellent ability to withstand shear failure [28,29]. The hybrid MoS₂-Ti₃C₂ also covers the plateau region between rough asperities, which assists in forming robust tribofilm on the steel surface. The formed tribofilm effectively prevents the occurrence of tribo-oxidation, which in turn reduces the COF.

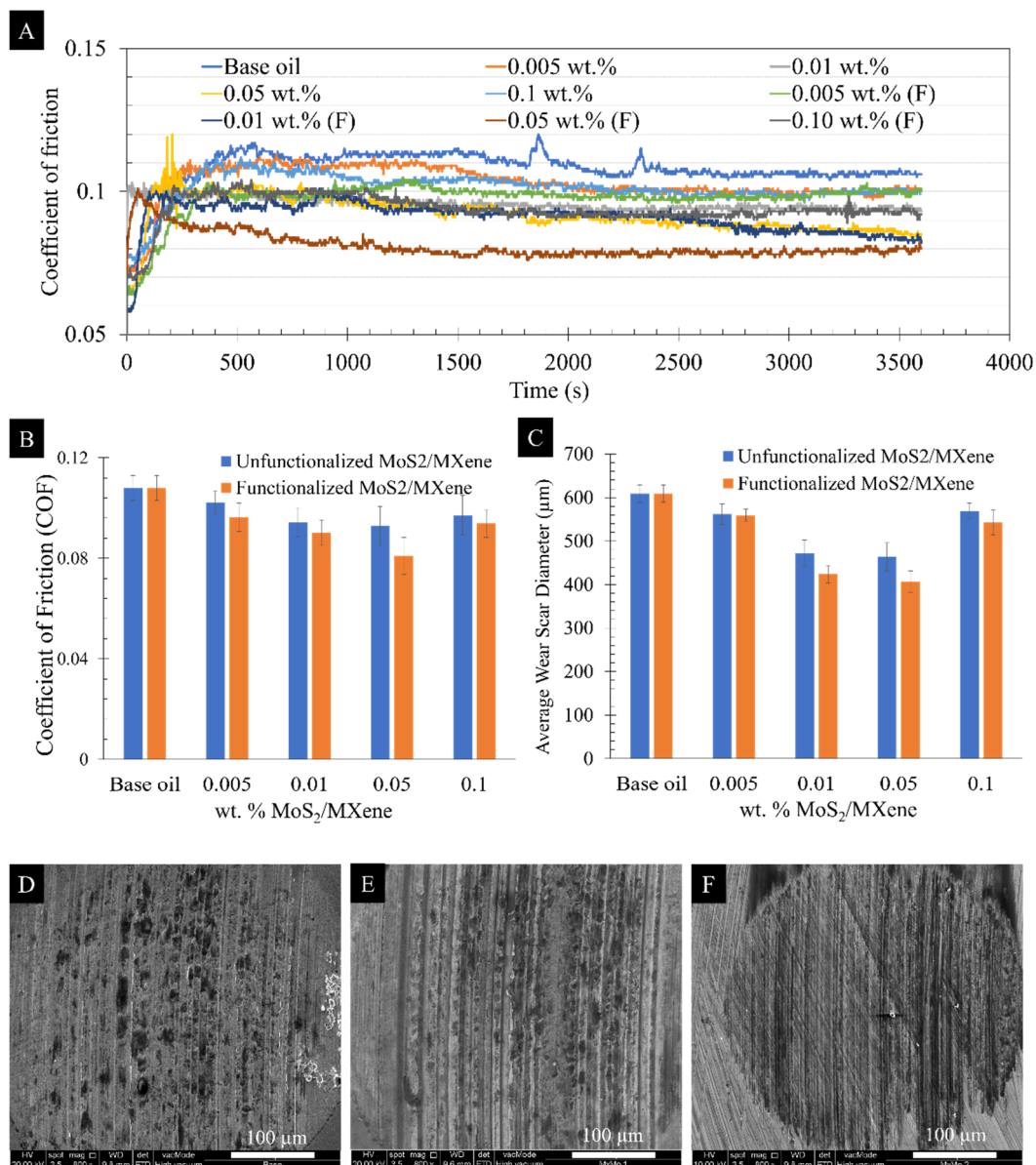


Figure 3. (A) Coefficient of friction (COF) against time for base oil with unfunctionalized MoS₂-Ti₃C₂ and functionalized MoS₂-Ti₃C₂ (indicated by letter F). (B) COF and (C) average wear scar diameter of unfunctionalized and functionalized MoS₂-Ti₃C₂-based nanolubricant. (D–F) SEM images of the wear surfaces of base oil without additive, base oil with unfunctionalized MoS₂-Ti₃C₂ and base oil with functionalized MoS₂-Ti₃C₂, respectively.

It should be noted that reduction in COF of the nanolubricant when added with 0.005 wt.% MoS₂-Ti₃C₂ was insignificant (i.e., 5.1%), which can be due to insufficient concentration of nano-additive to support the formation of a uniform and dense friction film between the sliding pair [30]. It is also noteworthy that functionalized MoS₂-Ti₃C₂-based nanolubricant exhibited significantly lower COF compared to the unfunctionalized counterpart. For instance, adding 0.05 wt.% of functionalized MoS₂-Ti₃C₂ decreased the coefficient of friction by 24.9% when compared to base oil (without additives). However, the COF for lubricants added with both functionalized and unfunctionalized additives showed a declining tendency above 0.05 wt.% MoS₂-Ti₃C₂. This phenomenon can be related to the possible agglomeration of nanoparticles due to strong van der Waals or Coulombic attractive interactions at contact compulsion, which inhibits their performance at the friction interface.

Figure 3C shows the wear scar diameters of MoS₂-Ti₃C₂-based nanolubricant monitored using an optical profilometer, while Figure 3D–F shows the SEM images of wear scar created on the ball bearing during tribological testing. From Figure 3B, it can be seen that the wear scar diameter of the base oil was reduced when added with MoS₂-Ti₃C₂ nanoparticles. The reduction in wear scar diameters was more significant for the functionalized MoS₂-Ti₃C₂-based nanolubricant. For instance, the wear scar diameter of base oil was reduced by 23.8% and 33.2% when added with 0.05 wt.% of unfunctionalized and functionalized MoS₂-Ti₃C₂ nanoparticles, respectively. In our previous study, it was reported that the addition of 0.05 wt.% functionalized MoS₂ reduced the COF and WSD of base oil by 10.3% and 10.6%, respectively [21], significantly lower than COF and WSD reduced in the present study (i.e., 24.9% and 33.2%, respectively) at a similar concentration of functionalized hybrid MoS₂-Ti₃C₂. The excellent abrasive resistance can be attributed to the synergistic role of MoS₂ and Ti₃C₂ nanoparticles, which form a thin lubricating layer between the contact surfaces to reduce contact pressure and frictional torque. These findings were ascertained by the SEM images of the wear scar where surface of ball bearing with base oil without additives exhibited darker concentric grooves (darker furrow is deeper while brighter furrow is shallower) (Figure 3D) while the addition of unfunctionalized MoS₂-Ti₃C₂ nanoparticles (Figure 3E) did not show significant appearance of the dark concentric grooves indicating lesser abrasive wear. When the lubricant was combined with functionalized MoS₂-Ti₃C₂ nanoparticles (Figure 3F), bright and smooth wear tracks were visible, indicating a decrease in the contact surfaces between the steel balls. It is postulated that the planar geometry of MoS₂ nanosheets allows them to penetrate easily and readily slide between the oil surface. Moreover, the nanosheets provide a continuous layer on the sliding surfaces due to their excellent adherence to contacts. This phenomenon is related to the mending effect of MoS₂-Ti₃C₂, where the nanoparticles occupy the scratched, worn surface to avoid direct contact between the two surfaces, reducing the wear scar diameter.

Figure 4 shows the zeta potential and visual observation (for sedimentation) of unfunctionalized and functionalized MoS₂-Ti₃C₂-based nanolubricant after 14 days. Zeta potential measurements which measure the potential difference between the surface of nanoparticles and a stagnant layer of lubricant attached to the particles, are important quantitative indicators to measure the dispersion stability of nanofluids. It accurately represents the magnitude of electrostatic charge between nanoparticles dispersed in the lubricant. In the present study, the zeta potential of both unfunctionalized and functionalized MoS₂-Ti₃C₂-based nanolubricant after 14 days was higher than 60 mV. Previous research has shown that dispersion with a greater zeta potential magnitude (whether negative or positive) is electrically stable, whereas lower zeta potential magnitudes signal probable agglomeration or flocculation in the fluid. Dispersion with zeta potential >60 mV was considered extremely stable, while dispersion with a zeta potential of 40–60 mV was considered to exhibit physical stability and dispersion with zeta potential <20 mV has limited stability with high possibilities of nanoparticle agglomeration in the lubricant [31,32]. As such, zeta potential values obtained in the present study (i.e., >60 mV) indicates the excellent stability of MoS₂-Ti₃C₂ in the lubricant.

It is also evident from the visual observations of nanolubricants where MoS₂ nanoparticles were stable in the nanolubricant after 14 days. However, nanolubricant reinforced with 0.05 wt.% and 0.1 wt.% MoS₂-Ti₃C₂ showed visible sedimentation after 14 days. This observation is ascertained by the zeta potential measurements, which were reduced by 78.8% and 69.6% when added with 0.1 wt.% of unfunctionalized and functionalized MoS₂-Ti₃C₂, respectively. This indicates that at higher concentrations (>0.05 wt.%), there is limited nanoparticle movement which hinders the growth of energy barrier and leads to particle agglomeration and sedimentation.

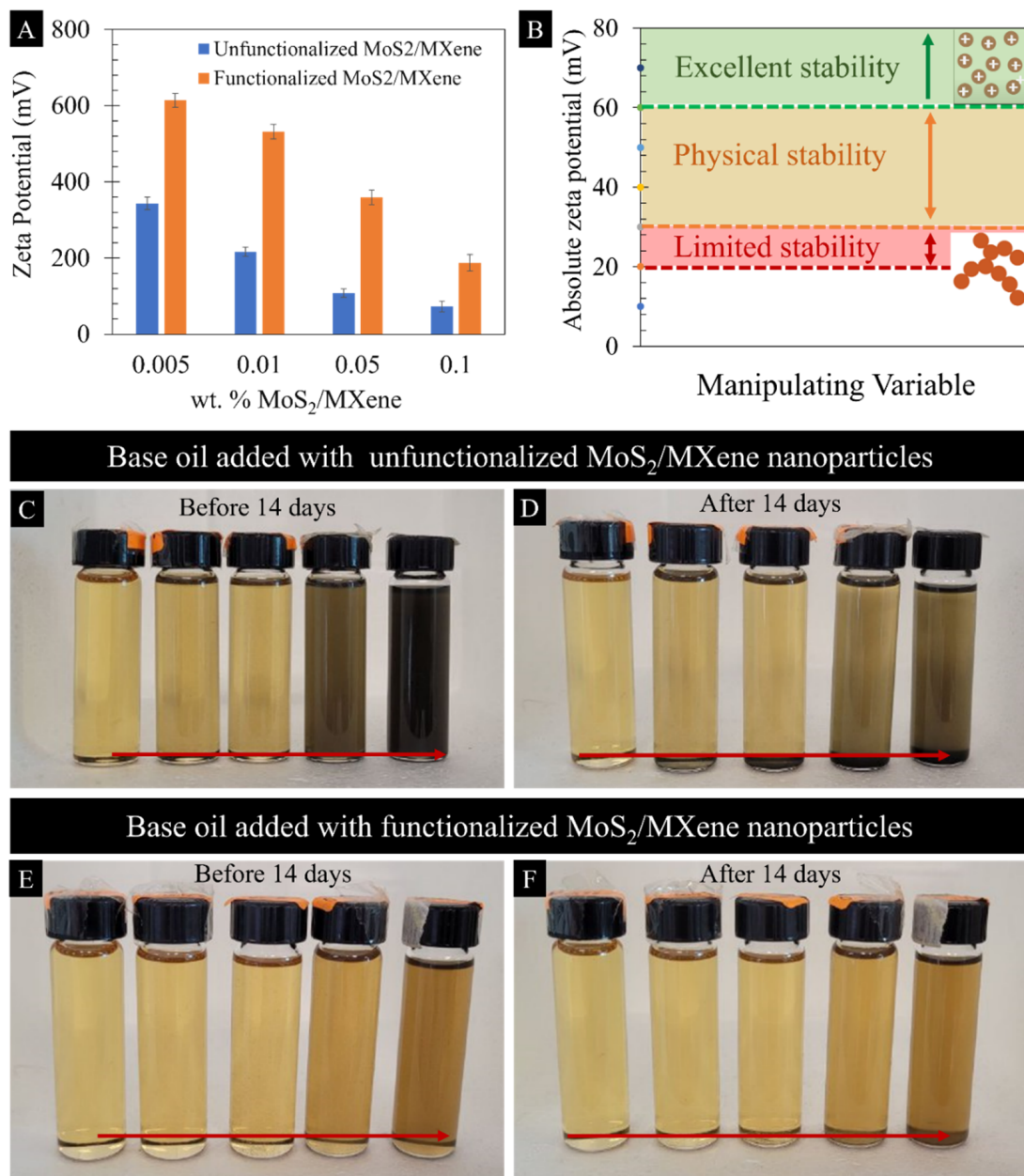


Figure 4. (A) Zeta potential of unfunctionalized and functionalized MoS₂-Ti₃C₂-based nanolubricant (B) Schematic representation illustrating stability and zeta potential ranges (C,D) Visual observation of unfunctionalized MoS₂-Ti₃C₂-based nanolubricant before and after 14 days (E,F) Visual observation of functionalized MoS₂-Ti₃C₂-based nanolubricant before and after 14 days.

3.3. Viscosity Behaviour and Oxidative Induction Time (OIT)

Figure 5 shows the kinematic viscosity of unfunctionalized and functionalized MoS₂-Ti₃C₂-based nanolubricant analyzed at 40 °C and 100 °C according to ASTM D445. Figure 5 shows that kinematic viscosity of all synthesized nanolubricant in the present study conforms to viscosity class SAE 5W40 lubricant, which indicates synthetic, multigrade lubricant with high shear (HS) stable polymer from group III. The decreased kinematic viscosity with an increase in temperature is due to the reduced attractive binding energy between the molecules when temperature rises [33]. As such, from the kinematic viscosity results, it can be ascertained that MoS₂-Ti₃C₂ nanoparticles are effective as viscosity modifiers in the nanolubricant when temperature varies.

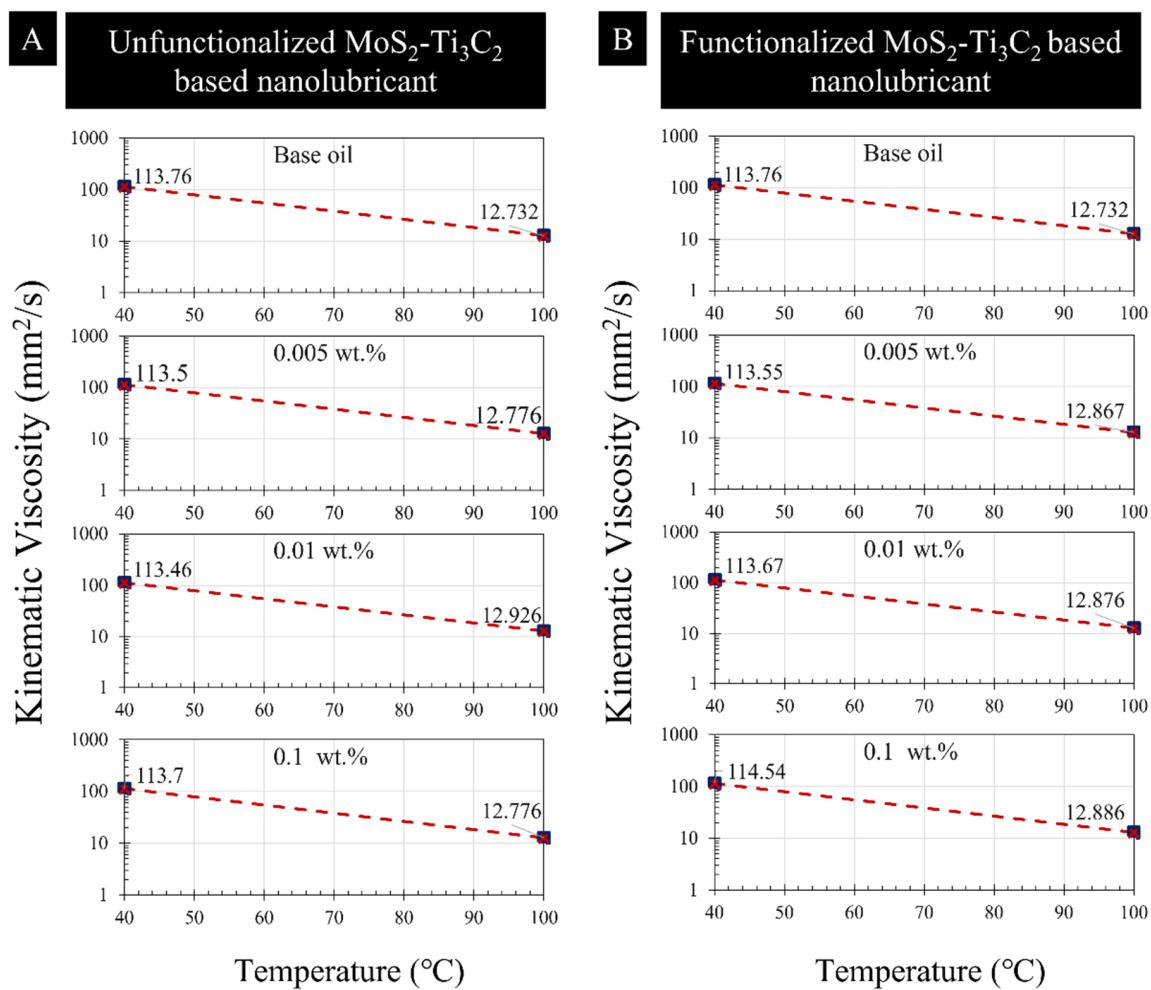


Figure 5. Variation of kinematic viscosity with temperature for (A) unfunctionalized and (B) functionalized $\text{MoS}_2\text{-Ti}_3\text{C}_2$ -based nanolubricant.

The importance of reducing CO_2 emissions from automobiles has urged the need to develop engine oils that exhibit improved fuel-saving performance, which can be envisaged by developing engine oil with high viscosity index (VI). Figure 6 shows the variation in viscosity index with nanoparticle concentration for unfunctionalized and functionalized $\text{MoS}_2\text{-Ti}_3\text{C}_2$ -based nanolubricant. Figure 6 shows that the VI of base oil increased by 3.1% and 4% when added with 0.01 wt.% of unfunctionalized and functionalized $\text{MoS}_2\text{-Ti}_3\text{C}_2$, respectively. Functionalization has modified the surface of the nanoparticles, so they remain well dispersed in the lubricant. Moreover, the higher VI of all $\text{MoS}_2\text{-Ti}_3\text{C}_2$ -based nanolubricant compared to base oil indicates the lower viscosity change in lubricant at fluctuating temperatures where $\text{MoS}_2\text{-Ti}_3\text{C}_2$ particles ensured consistent and stable lubricative properties across a wide temperature range. The $\text{MoS}_2\text{-Ti}_3\text{C}_2$ particles provided excellent resistance to thinning of lubricant film for optimized fuel consumption in the engine. Generally, engine oils tend to be more viscous at a lower temperature, raising drag inside the engine. Engine oil with high VI will have lower viscosity at lower temperatures, which translates into enhanced fuel-saving performance. As such, $\text{MoS}_2\text{-Ti}_3\text{C}_2$ -based nanolubricant synthesized in the present study show great potential for use within the automobile industry.

Figure 6C shows the oxidation induction time (OIT) of the $\text{MoS}_2\text{-Ti}_3\text{C}_2$ -based nanolubricant synthesized in the present study, where the induction time accurately represents their oxidative stability. In the automobile industry, oxidation of lubricants is caused by intense temperature, high load and continuous contact with air. The oxidation process leads

to accelerated engine oil degradation, affecting the performance, innate high efficiency and lifespan. Based on Figure 6C, it can be seen that OIT improved with the addition of $\text{MoS}_2\text{-Ti}_3\text{C}_2$ as an additive in the engine oil, where maximum OIT improved by 17.8% with the addition of 0.01 wt.% functionalized $\text{MoS}_2\text{-Ti}_3\text{C}_2$. The synergistic interaction between molybdenum dialkyldithiocarbamate (MoDTC) and zinc dialkyldithiophosphate (ZDDP) due to MoS_2 production, alongside the antiwear/antioxidant (i.e., ability of phosphate to digest oxides) behaviour and extreme pressure characteristics of ZDDP has been reported previously [34,35]. Generally, lubricants undergo a three-step oxidation process, i.e., (i) initiation to produce free radicals, (ii) propagation, where free radicals combine with oxygen to produce peroxide radicals and (iii) termination stage, where two radicals combine to form a stable molecule. It is postulated that the synergistic effect of MoS_2 with ZDDP promotes hydrogen donation, which stops the radical propagation stage, and increases the OIT [21].

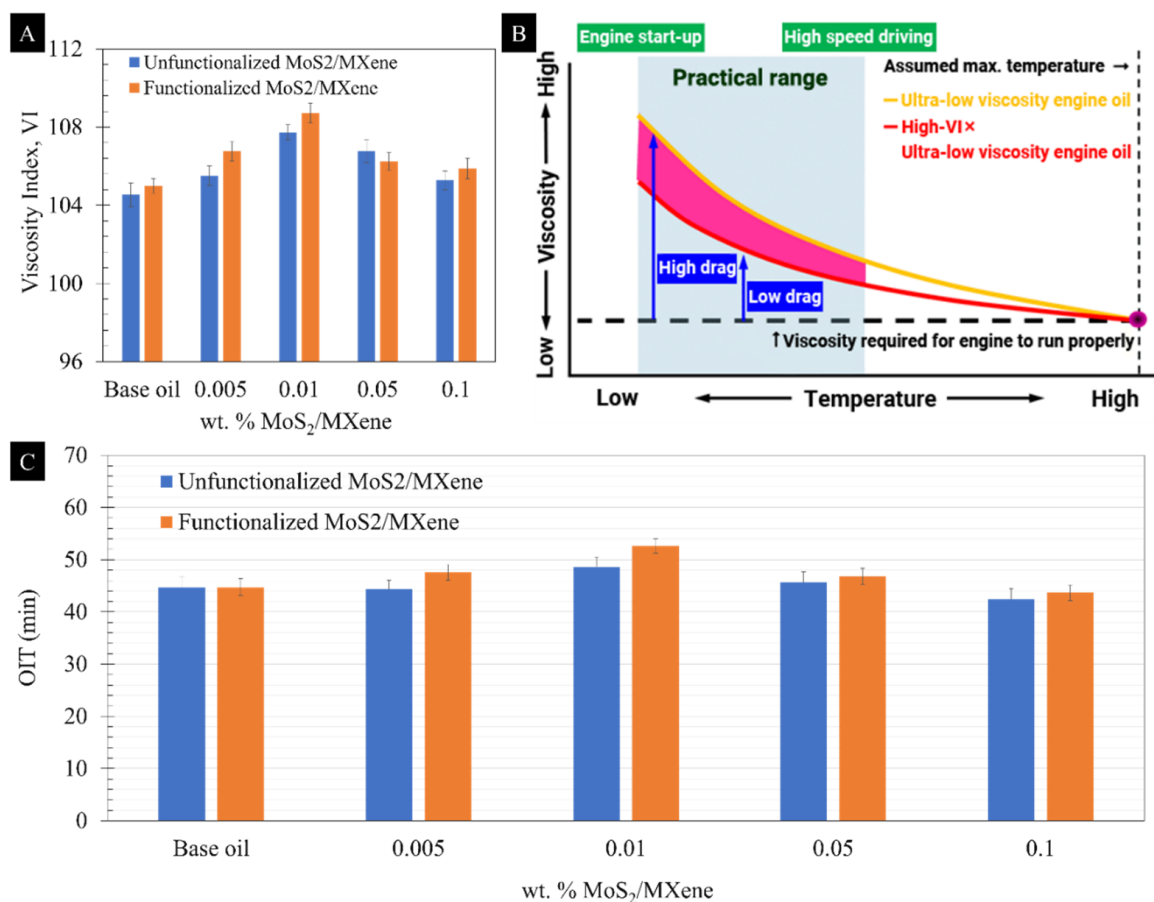


Figure 6. (A) Variation of viscosity index with nanoparticle concentration for unfunctionalized and functionalized $\text{MoS}_2\text{-Ti}_3\text{C}_2$ -based nanolubricant (B) Schematic illustration describing relationship between engine oil viscosity and temperature, adapted with permission from ref. [36] (C) OIT analysis of unfunctionalized and functionalized $\text{MoS}_2\text{-Ti}_3\text{C}_2$ -based nanolubricant.

3.4. Noack Volatility

Figure 7 shows the Noack volatility analysis of unfunctionalized and functionalized $\text{MoS}_2\text{-Ti}_3\text{C}_2$ -based nanolubricant synthesized in the present study. Noack volatility (evaporative loss) of engine oils is important to determine the rate of oil evaporation at very high temperatures and additional oil consumption as a result. For instance, when volatility is low, more oil will stay in the engine with its ideal viscosity for a longer duration. However, when volatility is high, oil loss occurs easily, resulting in a viscosity increase, which leads to reduced fuel economy due to an increase in parasitic load. From Figure 7A,B, it can be seen that adding $\text{MoS}_2\text{-Ti}_3\text{C}_2$ nanoparticles up to 0.05 wt.% reduced the Noack

volatility of lubricants. The decrease in volatility was more significant for lubricants added with 0.05 wt.% functionalized $\text{MoS}_2\text{-Ti}_3\text{C}_2$ nanoparticles, where Noack volatility was reduced by 24.6% compared to the base oil. The reduced oil volatility indicates the reduced oil consumption rate, maximal fuel efficiency and enhanced engine performance for a longer duration.

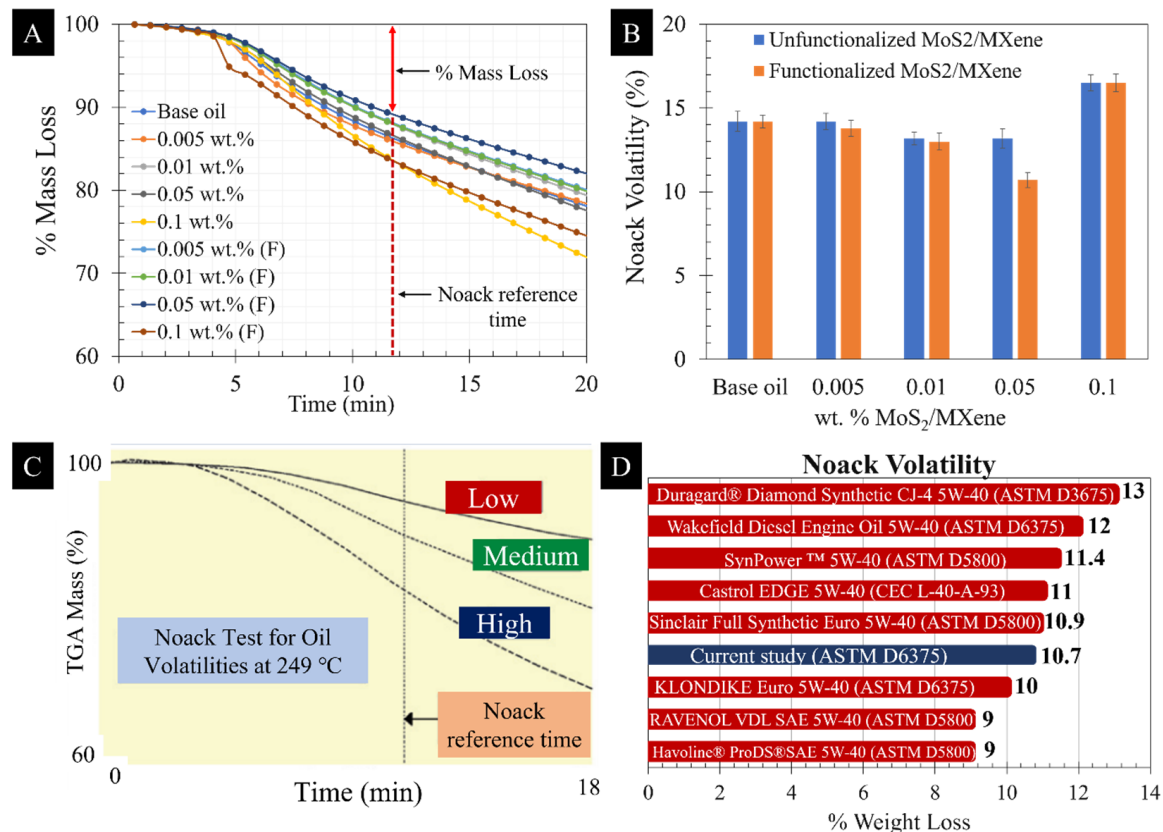


Figure 7. (A) TGA Noack analysis showing mass loss across time $\text{MoS}_2\text{-Ti}_3\text{C}_2$ -based nanolubricant (B) Effect of varying concentrations of unfunctionalized and functionalized $\text{MoS}_2\text{-Ti}_3\text{C}_2$ -based nanolubricant on Noack volatility (C) Schematic illustration showing low, medium and high volatility of lubricants at specified Noack reference time (D) Noack volatility of various commercially available SAE 5W-40 lubricants in comparison to $\text{MoS}_2\text{-Ti}_3\text{C}_2$ -based nanolubricant in the present study (i.e., 0.05 wt.% functionalized $\text{MoS}_2\text{-Ti}_3\text{C}_2$ -based nanolubricant).

Figure 7D shows the Noack volatility of various commercially available SAE 5W-40 lubricants compared to 0.05 wt.% functionalized $\text{MoS}_2\text{-Ti}_3\text{C}_2$ -based nanolubricant synthesized in the present study. Regardless of the testing standard, it is noteworthy that all the lubricants exhibited Noack volatility of <15%; since any volatility >15% is considered high and will not pass the crucial oxidation test, IIG engine test and does not adhere to the requirements of API oil guidelines [37]. On the other hand, General Motors and European automobile manufacturer's association (ACEA) have established specifications to limit maximum Noack volatility at 13%. In the present study, we report Noack volatility of the synthesized $\text{MoS}_2\text{-Ti}_3\text{C}_2$ -based nanolubricant to be 10.7, which is lower than many commercial SAE 5W-40 engine oils such as Duragard® Diamond Synthetic, Wakefield Diesel Engine Oil or Castrol EDGE among others. Although the Noack volatility can be further improved to meet the standards of several commercial engine oils such as Havoline® ProDS® or RAVENOL VDL, it is nonetheless plausible to claim that proper use and further research on functionalized $\text{MoS}_2\text{-Ti}_3\text{C}_2$ -based nanolubricant can allow tremendous synergistic benefits between reduced volatility, excellent abrasive resistance and friction modifier to reduce micro-pitting by minimizing local stresses near the surfaces (i.e., lowered friction).

4. Conclusions

In conclusion, the present study has successfully reported hybrid $\text{MoS}_2@\text{Ti}_3\text{C}_2$ MXene as an effective anti-friction additive with enhanced tribological performance in SAE 5W-40-based engine oil. Amine functionalization showed better dispersibility, stability and tribological behaviour in the engine oil. For instance, the coefficient of friction was reduced by 24.9% compared to base oil with the addition of 0.05 wt.% functionalized $\text{MoS}_2\text{-Ti}_3\text{C}_2$. Similarly, wear scar diameter of base oil was reduced by 23.8% and 33.2% when added with 0.05 wt.% of unfunctionalized and functionalized $\text{MoS}_2\text{-Ti}_3\text{C}_2$ nanoparticles, respectively. Moreover, OIT improved by 17.8% with the addition of 0.01 wt.% functionalized $\text{MoS}_2\text{-Ti}_3\text{C}_2$. Based on Noack's analysis, the volatility of $\text{MoS}_2\text{-Ti}_3\text{C}_2$ -based nanolubricant was 10.7, which is lower compared to many commercial SAE 5W-40-based engine oil. The reduced oil volatility indicates the reduced oil consumption rate, maximal fuel efficiency and enhanced engine performance for a longer duration.

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References

1. Ali, M.; Xianjun, H.; Abdelkareem, M.; Gulzar, M.; Elsheikh, A. Novel approach of the graphene nanolubricant for energy saving via anti-friction/wear in automobile engines. *Tribol. Int.* **2018**, *124*, 209–229. [\[CrossRef\]](#)
2. Holmberg, K.; Andersson, P.; Erdemir, A. Global energy consumption due to friction in passenger cars. *Tribol. Int.* **2012**, *47*, 221–234. [\[CrossRef\]](#)
3. Ali, M.; Xianjun, H.; Turkson, R.; Peng, Z.; Chen, X. Enhancing the thermophysical properties and tribological behaviour of engine oils using nano-lubricant additives. *RSC Adv.* **2016**, *6*, 77913–77924. [\[CrossRef\]](#)
4. Yu, R.; Liu, J.; Zhou, Y. Experimental study on tribological property of MoS_2 nanoparticle in castor oil. *J. Tribol.* **2019**, *141*, 3–7. [\[CrossRef\]](#)
5. Ali, M.; Xianjun, H.; Mai, L.; Qingping, C.; Turkson, R.; Bicheng, C. Improving the tribological characteristics of piston ring assembly in automotive engines using Al_2O_3 and TiO_2 nanomaterials as nano-lubricant additives. *Tribol. Int.* **2016**, *103*, 540–554. [\[CrossRef\]](#)
6. Li, W.; Zheng, S.; Cao, B.; Ma, S. Friction and wear properties of $\text{ZrO}_2/\text{SiO}_2$ composite nanoparticles. *J. Nanoparticle Res.* **2011**, *13*, 2129–2137. [\[CrossRef\]](#)
7. Rasheed, A.; Khalid, M.; Nor, A.B.M.; Wong, W.; Duolikun, T.; Natu, V.; Barsoum, M.; Leo, B.; Zaharin, H.; Ghazali, M. MXene-graphene hybrid nanoflakes as friction modifiers for outboard engine oil. *IOP Conf. Ser. Mater. Sci. Eng.* **2020**, *834*, 012039. [\[CrossRef\]](#)
8. Naguib, M.; Mochalin, V.; Barsoum, M.; Gogotsi, Y. 25th anniversary article: MXenes: A new family of two-dimensional materials. *Adv. Mater.* **2014**, *26*, 992–1005. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Gogotsi, Y.; Anasori, B. The Rise of MXenes. *ACS Nano* **2019**, *13*, 8491–8494. [\[CrossRef\]](#) [\[PubMed\]](#)
10. Gogotsi, Y.; Huang, Q. MXenes: Two-Dimensional Building Blocks for Future Materials and Devices. *ACS Nano* **2021**, *15*, 5775–5780. [\[CrossRef\]](#) [\[PubMed\]](#)
11. Yan, H.; Zhang, L.; Li, H.; Fan, X.; Zhu, M. Towards high-performance additive of Ti_3C_2 /graphene hybrid with a novel wrapping structure in epoxy coating. *Carbon* **2020**, *157*, 217–233. [\[CrossRef\]](#)
12. Nguyen, H.; Chung, K. Assessment of tribological properties of Ti_3C_2 as a water-based lubricant additive. *Materials* **2020**, *13*, 5545. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Zhang, D.; Ashton, M.; Ostadhosseini, A.; Van Duin, A.; Hennig, R.; Sinnott, S. Computational study of low interlayer friction in $\text{Ti}_n\text{C}_{n-1}$ ($n = 1, 2$, and 3) MXene. *ACS Appl. Mater. Interfaces* **2017**, *9*, 34467–34479. [\[CrossRef\]](#)
14. Liu, Y.; Zhang, X.; Dong, S.; Ye, Z.; Wei, Y. Synthesis and tribological property of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. *J. Mater. Sci.* **2017**, *52*, 2200–2209. [\[CrossRef\]](#)

15. Gao, J.; Du, C.-F.; Zhang, T.; Zhang, X.; Ye, Q.; Liu, S.; Liu, W. Dialkyl Dithiophosphate-Functionalized $\text{Ti}_3\text{C}_2\text{T}_x$ MXene Nanosheets as Effective Lubricant Additives for Antiwear and Friction Reduction. *ACS Appl. Nano Mater.* **2021**, *4*, 11080–11087. [CrossRef]
16. Vazirisereshk, M.; Martini, A.; Strubbe, D.; Baykara, M. Solid lubrication with MoS_2 : A review. *Lubricants* **2019**, *7*, 57. [CrossRef]
17. Serles, P.; Gaber, K.; Pajovic, S.; Colas, G.; Filleter, T. High Temperature Microtribological Studies of MoS_2 Lubrication for Low Earth Orbit. *Lubricants* **2020**, *8*, 49. [CrossRef]
18. Thachnatharen, N.; Khalid, M.; Shahabuddin, S.; Anwar, A.; Sridewi, N. Tribological analysis of advanced microwave synthesized Molybdenum disulfide (MoS_2) as anti-friction additives in diesel engine oil for military vehicles. *Mater. Today Proc.* **2022**, *62*, 7243–7247. [CrossRef]
19. Gradt, T.; Schneider, T. Tribological performance of MoS_2 coatings in various environments. *Lubricants* **2016**, *4*, 32. [CrossRef]
20. Numan, A.; Rafique, S.; Khalid, M.; Zaharin, H.A.; Radwan, A.; Mokri, N.A.; Ching, O.P.; Walvekar, R. Microwave-assisted rapid MAX phase etching and delamination: A paradigm shift in MXene synthesis. *Mater. Chem. Phys.* **2022**, *288*, 126429. [CrossRef]
21. Nagarajan, T.; Khalid, M.; Sridewi, N.; Jagadish, P.; Shahabuddin, S.; Muthoosamy, K.; Walvekar, R. Tribological, oxidation and thermal conductivity studies of microwave synthesized molybdenum disulfide (MoS_2) nanoparticles as nano-additives in diesel based engine oil. *Sci. Rep.* **2022**, *12*, 14108. [CrossRef] [PubMed]
22. Li, X.; Lv, X.; Sun, X.; Yang, C.; Zheng, Y.; Yang, L.; Li, S.; Tao, X. Edge-oriented, high-percentage $1\text{T}'$ -phase MoS_2 nanosheets stabilize Ti_3C_2 MXene for efficient electrocatalytic hydrogen evolution. *Appl. Catal. B Environ.* **2021**, *284*, 119708. [CrossRef]
23. Wang, X.; Li, H.; Li, H.; Lin, S.; Ding, W.; Zhu, X.; Sheng, Z.; Wang, H.; Zhu, X.; Sun, Y. 2D/2D $1\text{T-MoS}_2/\text{Ti}_3\text{C}_2$ MXene Heterostructure with Excellent Supercapacitor Performance. *Adv. Funct. Mater.* **2020**, *30*, 0190302. [CrossRef]
24. Wang, H.; Ma, H. The electromagnetic and microwave absorbing properties of MoS_2 modified $\text{Ti}_3\text{C}_2\text{T}_x$ nanocomposites. *J. Mater. Sci. Mater. Electron.* **2019**, *30*, 15250–15256. [CrossRef]
25. Wei, S.; Fu, Y.; Liu, M.; Yue, H.; Park, S.; Lee, Y.; Li, H.; Yao, F. Dual-phase $\text{MoS}_2/\text{MXene}/\text{CNT}$ ternary nanohybrids for efficient electrocatalytic hydrogen evolution, Npj 2D. *Mater. Appl.* **2022**, *6*, 25. [CrossRef]
26. Liu, Y.; He, Y.; Vargun, E.; Plachy, T.; Saha, P.; Cheng, Q. 3D Porous Ti_3C_2 MXene/ NiCo-MOF Composites for Enhanced Lithium Storage. *Nanomaterials* **2020**, *10*, 10040695. [CrossRef]
27. Mao, X.; Zou, Y.; Xu, F.; Sun, L.; Chu, H.; Zhang, H.; Zhang, J.; Xiang, C. Three-Dimensional Self-Supporting Ti_3C_2 with MoS_2 and Cu_2O Nanocrystals for High-Performance Flexible Supercapacitors. *ACS Appl. Mater. Interfaces* **2021**, *13*, 22664–22675. [CrossRef]
28. Radhika, P.; Sobhan, C.; Chakravorti, S. Improved tribological behavior of lubricating oil dispersed with hybrid nanoparticles of functionalized carbon spheres and graphene nano platelets. *Appl. Surf. Sci.* **2021**, *540*, 148402. [CrossRef]
29. Bustillos, J.; Montero, D.; Nautiyal, P.; Loganathan, A.; Boesl, B.; Agarwal, A. Integration of graphene in poly(lactic) acid by 3D printing to develop creep and wear-resistant hierarchical nanocomposites. *Polym. Compos.* **2018**, *39*, 3877–3888. [CrossRef]
30. Feng, P.; Ren, Y.; Li, Y.; He, J.; Zhao, Z.; Ma, X.; Fan, X.; Zhu, M. Synergistic lubrication of few-layer $\text{Ti}_3\text{C}_2\text{T}_x/\text{MoS}_2$ heterojunction as a lubricant additive. *Friction* **2022**, *10*, 2018–2032. [CrossRef]
31. Mukherjee, S. Preparation and Stability of Nanofluids—A Review. *IOSR J. Mech. Civ. Eng.* **2013**, *9*, 63–69. [CrossRef]
32. Zainon, S.; Azmi, W. Recent progress on stability and thermo-physical properties of mono and hybrid towards green nanofluids. *Micromachines* **2021**, *12*, 12020176. [CrossRef] [PubMed]
33. Salameh, T.; Kumar, P.; Sayed, E.; Abdelkareem, M.; Rezk, H.; Olabi, A. Fuzzy modeling and particle swarm optimization of $\text{Al}_2\text{O}_3/\text{SiO}_2$ nanofluid. *Int. J. Thermofluids* **2021**, *10*, 100084. [CrossRef]
34. Morina, A.; Neville, A.; Priest, M.; Green, J. ZDDP and MoDTC interactions and their effect on tribological performance—Tribofilm characteristics and its evolution. *Tribol. Lett.* **2006**, *24*, 243–256. [CrossRef]
35. Thornley, A.; Wang, Y.; Wang, C.; Chen, J.; Huang, H.; Liu, H.; Neville, A.; Morina, A. Optimizing the Mo concentration in low viscosity fully formulated oils. *Tribol. Int.* **2022**, *168*, 107437. [CrossRef]
36. ENEOS Corporation. Development of Next Generation Engine Oils. *Lubricants* (n.d.). Available online: <https://www.eneos.co.jp/english/company/rd/intro/lubricants/hairyo.html> (accessed on 14 December 2022).
37. Shah, R.; Hope, K.; Aragon, N. Fuel economy considerations: Effect of lube oils and their volatility. *Lube Magazine*, November 2020; pp. 1–4.

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