INVESTIGATING THE INFLUENCE OF PROTIC IONIC LIQUID ON THE TRIBOELECTRICAL PROPERTIES OF TRIMETHYLOLPROPANE TRIOLEATE (TMPO)

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Abstract

Under triboelectric conditions, where tribocharging accelerates lubrication failure, lubricants with enhanced electrical properties are essential. Trimethylolpropane Trioleate (TMPO) oil, derived from esters that possess good lubricating properties and wear performance but is lacking in terms of electrical properties which can be further improved when blended with Ionic Liquid. This study blends 1 – 5 wt% of Protic Ionic Liquid (PIL) into TMPO and evaluate the frictional and wear performances of the blends under 1 – 2 A current conditions to understand the behaviour towards the tribological properties of different blends of material. Electric currents ranging around 1 – 2 A are implemented to the custom-designed ball-on-disc tribometer, with a constant 4.5 V voltage supply and the static resistance are measured. Mechanical wear properties are observed after the tribological test with different samples. The frictional properties of all concentrations of PIL in TMPO showed significant frictional improvements with 1%wt PIL showed 53% better results indicating improvements in frictional properties and wear performance under 2A current conditions, owing to its lowest film resistivity of 0.14 mΩ.

Keywords

Protic Ionic Liquid, Trimethylolpropane Trioleate, Vegetable Oil, Wear Characteristics, Triboelectric, Tribology, Mechanical, Friction

Introduction

Machines today that require precise movements are primarily composed of various gears and rotating parts, which undergo wear and tear over time, decreasing the overall efficiency and reliability of these machines and their components. Lubrication is the most effective method to minimize wear and tear during the operation of machine parts, regardless of whether they are low-load or high-load-carrying machines.

Many mineral-based or petroleum-based lubricants used in the market are non-biodegradable, which negatively impacts the environment [1]. This environmental issue can be addressed by using alternative lubricants, such as greener lubrication options found in ionic liquids or plant-based oils. According to literature reports [2-5], the exploration of greener alternatives should prioritize low-viscosity solutions to reduce viscous friction losses. Additionally, in the context of electrification, the electrical properties of lubricants become crucial [6]. Komvopoulos et al.

have noted that the typical formulation of phosphorus and sulfur elements in lubricants can increase electrical resistance [7]. These considerations highlight the importance of incorporating green additives in base oils to develop fully green lubricants.

Fully green lubricants can counter multiple problems related to lubricant characteristics. Palacio indicates that ionic liquids, including protic and aprotic ionic liquids, are good alternatives to green lubricants [8]. Protic Ionic Liquids are salts that are liquid at room temperature, formed by combining different formulations of Bronsted Acid and Bronsted Base, whereas Aprotic Ionic Liquids are used in the lubrication industry typically as base oils [9]. The chemical and physical properties of Ionic Liquids can be tuned by mixing different acids and bases [10]. Various protic ionic liquids generally exhibit lower conductivity, suggesting that the choice of blend will require protic ionic liquid if electrical conductivity properties are desired [11]. Current drawbacks of vegetable oil-derived lubricants include low oxidative stability, low thermal stability, and poor corrosion protection, which can be improved with chemical modifications [12].

According to Wilmar International, Trimethylolpropane Trioleate (TMPO) has excellent lubrication properties with a high viscosity index, thermal resistance, and biodegradability [13]. However, while promising as lubricants, TMPO often exhibits higher viscosity levels that may result in increased frictional losses, questioning their suitability as a base oil [14]. TMPO has also been reported to be unsuitable for electrification applications. Given the lubrication performance of TMPO, this study explores the use of Protic Ionic Liquids (PIL), as additives to improve the electrical properties of the lubrication blend. Additives in lubricants can affect conductivity and oxidation levels [15]. Surface charges influence the behaviour of polar additives [16]. Interface liquid lubricants provide stable DC output and reduce wear, supporting the use of electric current in lubrication [17]. Thus, it is crucial to develop a lubricant blend that provides excellent lubrication performance while ensuring its capability to meet electrical requirements for modern applications.

Therefore, this study aims to investigate the influence of Protic Ionic Liquid, specifically [Oley][Oleic], on the triboelectric properties of TMPO. Additionally, this study will help understand the impact of electrification on the tribological and electrical properties of the lubricant blend. The choice of [Oley][Oleic] as the PIL is mainly due to its cost-effective and simple production process. TMPO is chosen as the main lubricant because it is produced via the esterification of oleic acid, which is one of the precursor chemicals in producing the PIL. Oleic acid itself was chosen to be studied due to its stable dispersibility [18, 19].

EXPERIMENTAL SECTION

Material and Sample Preparation

In this study, trimethylolpropane trioleate (TMPO) oil was purchased from Wilmar Oleochemical, China. The Ionic Liquid (PIL) was produced using oleic acid (CAS no. 112-80-1) and oleylamine (CAS no. 112-90-3), both obtained from Sigma-Aldrich. The neutralisation process followed previous work involving stirring of oleic acid and oleylamine in a 1:1 equimolar ratio using a magnetic stirrer at 400 rpm for 24 hours at room temperature, forming a product denoted as [Oley][Oleic] [20], referred to as PIL in this paper. The process is shown in Figure 1.

Figure 1: Producing [Oley][Oleic]

For the PIL-TMPO blend, PIL is added into TMPO according to the weightage and mixed using a magnetic stirrer for 15 minutes before being sonicated in a water bath at 60 °C for two hours, using SONICA® Ultrasonic Cleaners as in Figure 2. This process is to ensure homogeneity between PIL and TMPO.


Figure 2: Sonicator

For the friction test, the disks used were AISI 304 stainless steel disks (Ø 50 mm, 1 mm thickness, 2B finishing) and the balls used were AISI 52100 steel balls (Ø 6 mm). The disk and ball have a respective arithmetic surface roughness (Ra) of 0.3 and 0.15 µm, measured using a surface profilometer, MeterTo MR220. Before each test, the disk and ball underwent a cleaning process including rinsing with water, ultrasonic cleaning in acetone, and soaking in ethanol for four hours. The disk was air-dried for 30 minutes to ensure ethanol evaporation. This pre-treatment procedure enhanced the surface's wettability of the disk [21, 22].

Viscosity and Density of TMPO Blended with [Oley][Oleic] Measurement

The viscosity testing is conducted using the Brookfield Viscometer DV-ii +pro under temperatures of (25 °C), 40 °C, 60 °C, and 100°C following ASTM D445. In terms of the density, the equipment utilized is the DMA4100M density tester which was conducted following ASTM D4052 under temperatures of 15 °C, 25 °C, 35 °C, and 45 °C, respectively.

Friction Testing

Friction tests were conducted using a purpose-built ball-on-disc tribometer as in Figure 3. A grounded electrical current flow path was incorporated into the tribometer through the point contact between the ball and the disk.

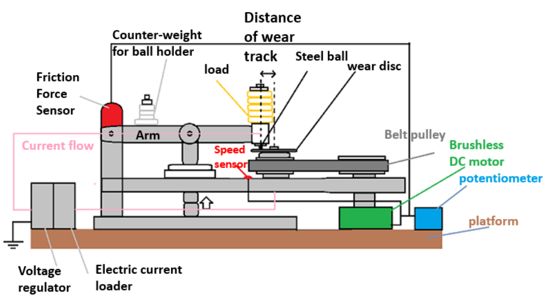


Figure 3: Purpose-built tribometer

The samples were evenly spin-coated onto the disk before each of the friction tests and the thin film formation from the spin-coating technique is expected to give friction results of mixed to boundary lubrication regimes. A new set of ball and disk pairs was used for each test configuration. The test conditions are tabulated in Table 1.

Table 1: Test conditions

	Values	Unit
Load	0.8 – 1.6	N
Rotational speed	500	rpm
Supply voltage	4.5	V
Current	1.0 – 2.0	A

It is to be noted that each configuration was run for around 255 seconds to cover a distance of 200 m. Each test was repeated three times with a repeatability margin of less than 5% standard deviation. At the end of the test, the ball scar diameter and wear track width were measured using an optical microscope.

Results and Discussion

Viscosity and Density of TMPO blended with PIL

The viscosity and density of the blended samples are tabulated in Table 2. For all samples, the temperature increase will cause a decrease in both kinematic viscosity and density, respectively. This is due to thermal expansion occurring between molecules that weaken the molecular bonds allowing the fluid to flow more easily.

Table 2: Properties of TMPO blended with PIL

Sample	Density (g/cm^3)		Viscosity (cSt)	
	@40°C	@100°C	@40°C	@100°C
Neat TMPO	0.903	0.875	44.31	9.14
+ 1wt%	0.904	0.864	24.54	4.38
+ 3wt%	0.903	0.863	27.38	5.44
+ 5wt%	0.903	0.862	24.30	3.81
Neat PIL	0.869	0.828	242.63	20.84

*wt% represents the weightage of PIL added into neat TMPO; PIL – [Oley][Oleic]

The addition of small concentrations of PIL into TMPO reduces the overall viscosity of the blend, despite PIL having a high viscosity. These changes suggest that blending TMPO with PIL could reduce friction when the lubricated contact operates in a hydrodynamic lubrication regime, where friction is mainly proportional to the lubricant bulk viscosity.

Frictional Performance

Figure 1 shows the measured friction over 255 seconds of duration for the TMPO under 1.0 N normal loading.

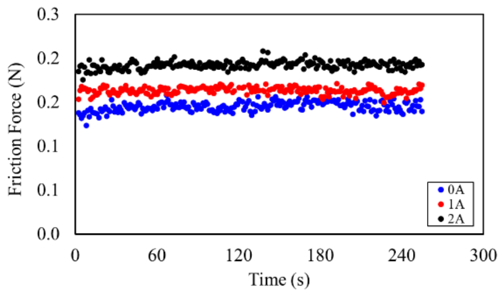
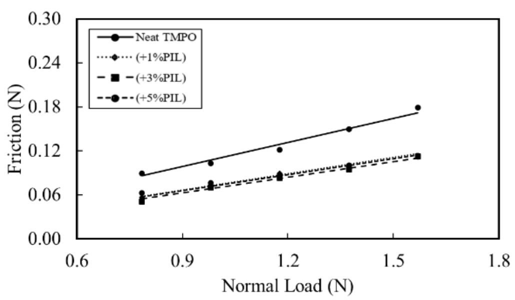


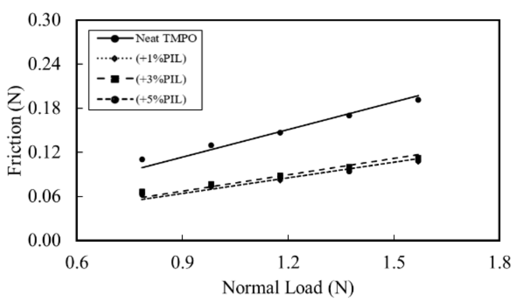
Figure 4: Friction force against testing period for TMPO under 1.0 N loading

The friction force is observed to remain consistent throughout the test even under transversed current conditions, demonstrating a saturated friction behaviour with a deviation rate below 10%. Thus, the vibrations are negligible and do not interrupt the current flow confirming the effectiveness of the tribometer to deliver stable and consistent measurement. The measured friction forces for all lubricant blends are time-averaged for subsequent analysis.

Figure 5 shows the relationship between the friction force and normal load for all samples under 500 rpm rotational speed. Generally, the friction force increases when the current increases. For all cases, the friction force data has a coefficient of determination (R^2) value above 0.95, showing good linear regression fit and following Amonton's Law of friction. It is to be noted that the results have less than 5% standard deviation, thus the error bars are excluded due to their insignificance.



(a)



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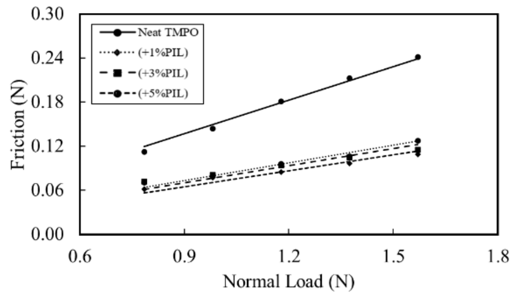


(c)

Figure 5: Friction force against normal load for (a) 0 A (b) 1 A and (c) 2 A current conditions

The addition of 1 to 5 wt% PIL to TMPO significantly reduces the friction force, highlighting the effectiveness of PIL as a friction-reducing additive at low concentrations. This is due to the distinct molecular structure possessed in protic ionic liquid where the ionic charges and polar groups improve the ability to adhere to surfaces, creating consistent and stable films on contact surfaces [23]. This reduction suggests that even minimal amounts of PIL can enhance the lubricating properties of TMPO, making it a promising approach for improving the performance of lubricants in various applications.

Figure 6 represents the value of the coefficient of friction between the samples at different current conditions. The coefficient of friction for the blended materials is calculated from the slope of the measured friction force against the normal load.

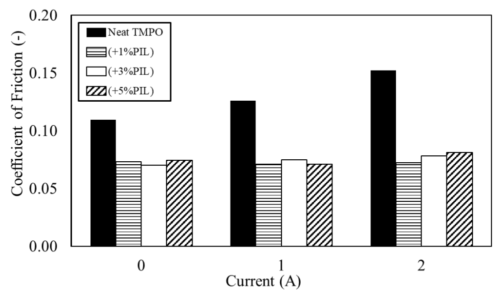


Figure 6: Coefficient of friction for all samples under all current conditions

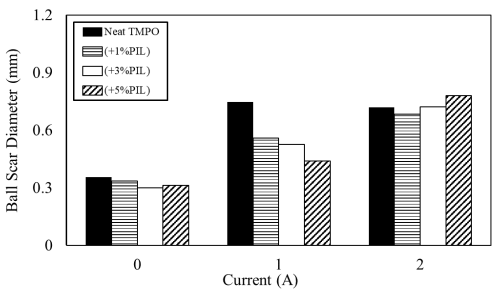
The coefficient of friction for neat TMPO increases up to 38% with higher current, from 0.11 (no current) to 0.15 (2 A). In contrast, the friction for TMPO samples with added PIL remains consistent. Without electrical current, the 3 wt% PIL blend has the lowest coefficient of friction (0.070), while the 1 wt% and 5 wt% samples show similar results. At 1 A, the 1 wt% and 5 wt% PIL samples have a lower coefficient of friction (approximately 5%) than the 3 wt% sample. When the current is increased to 2 A, the 1 wt% PIL sample achieves the lowest coefficient of friction at 0.07 (53% better than neat TMPO), whereas the 5 wt% PIL sample exhibits the highest coefficient of friction at 0.081. TMPO mixture with 1 wt% PIL provides more consistent friction performance, maintaining a coefficient of friction close to the one without current.

It is to be noted that under triboelectric conditions, the synergistic combination of oleic acid and oleylamine as ionic liquids improves the polarity of the lubricant [22]. Therefore, under triboelectric conditions, incorporating PIL improves the overall friction.

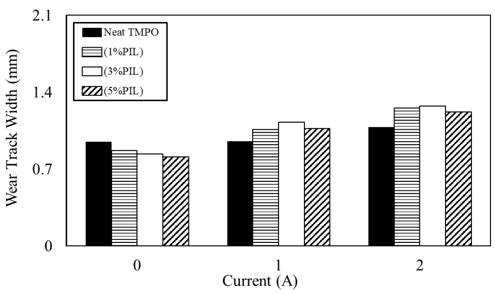
Wear Measurement

Figure 7 shows the ball scar diameter and the wear track width of the disk for all samples under all current conditions. The ball scar diameter and wear track width reduce when TMPO is blended with PIL in the absence of electrical current.

Generally, the ball scar diameter and wear track width increase with increasing current. The ball scar diameter of the PIL blends is lower than neat TMPO when the 1 A of current is traversed. Conversely, under 1 A current, all concentrations of PIL blended with TMPO exhibited larger wear track width. This could potentially be attributed to greater material transfer from the steel ball because of a larger wear scar diameter.



(a)



(b)

Figure 7: Measurement for (a) ball scar diameter and (b) wear track width for all samples under all current conditions

Adding 1wt% of PIL into TMPO maintains show better ball scar diameter which is 25.2% and 4.9% better at 1 A and 2 A conditions, respectively. According to Fry et. Al (2020), the existence of a polar amine group in [Oley][Oleic] improves the adsorption of the molecules to the surfaces [24], even with the presence of current, hence reducing the wear.

Interpreting Friction and Wear Measurement

From the friction and wear measurements, it appears that the addition of PIL results in lower friction and smaller wear scar diameter. The most significant improvement is seen when adding 1 wt% PIL to TMPO, which reduces friction by up to 53% and wear by up to 5% at 2 A electrical current.

During the friction test, voltage drops occur when an electrical current is applied through the ball and disc contact. The lubricant film introduces an additional layer of electrical resistance when spin-coated, contributing further to the voltage drop. This increased electrical resistance or reduced conductivity from the film can also lead to internal heating, potentially reducing the lubricant viscosity and the film's load-carrying ability, subsequently increasing friction.

As an initial assessment, Table 3 displays the voltage drop achieved before and after spin-coating the steel discs with the tested lubricant samples, isolating the electrical properties of the spin-coated films. The voltage drop values are used to calculate the resistance of the discs using Ohm's law, revealing the amount of resistance generated by the spin-coated samples. It is to be noted that the voltage supply throughout the system is 4.5 V.

Table 3: Voltage drop and film resistance under 1 A and 2 A current

Sample	Voltage Drop (V)		Resistance (mΩ)	
	1 A	2 A	1 A	2 A
Neat TMPO	0.49	0.96	0.49	0.48
+ 1wt%	0.34	0.28	0.34	0.14
+ 3wt%	0.42	0.43	0.42	0.22
+ 5wt%	0.34	1.26	0.34	0.63

In Table 3, it is observed that 1 wt% PIL exhibits lower electrical resistance compared to neat TMPO and other PIL concentrations. The resistance of this mixture drops by as much as 69% with a 2 A electrical current compared to neat TMPO. This significantly lower resistance or improved conductivity corresponds to the much-reduced friction observed with 1 wt% PIL concentration. However, it is noted that while the presence of PIL in TMPO has a significant influence on friction, its effect on wear is marginal.

Conclusion

This study investigates the rheological, frictional, and wear properties of TMPO blended with [Oley][Oleic] protic ionic liquid at concentrations up to 5 wt%. The findings reveal several significant insights:

- Blending a small concentration of [Oley][Oleic] into TMPO decreases the viscosity, which could be beneficial for contact operating at a hydrodynamic lubrication regime.
- 5%PIL blend shows the greatest friction reduction under no-current conditions when tested at mixed/boundary lubrication regimes.
- Under 2A, 1%PIL blend protects the contact surfaces the most and has desirable CoF value showing potential and suitability for high current applications.

Overall, key findings demonstrate the potential of [Oley][Oleic] as an additive to enhance the rheological and triboelectric properties of TMPO due to the unique ionic bonding and polarity of protic ionic liquid that improves the conductivity of the lubricant and creating stable lubrication film. It is recommended that future studies should explore different ionic liquids and higher electrical current conditions to further enhance the performance and applicability of these blends.

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