DETERMINATION OF THE EFFECTS OF TPPT ON THE ANTI-WEAR PERFORMANCE OF VEGETABLE OIL AND POLYOL ESTERS

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ABSTRACT

Design of green process is the key points of industries for sustainable energy and environmental protection. Replacement of petroleum derived lubricants, which are extensively used to reduce wear and friction in the mechanical systems, with bio-lubricants is one of the crucial steps for achievement of this criteria. Vegetable oils and polyol esters are promising feedstocks for bio-lubricant formulations. Although vegetable oils are abundant and they have low cost, they have limited utilization since their low temperature behavior and thermo-oxidative stability are poor. On the other hand, polyol esters have high thermal and oxidative stability. These base fluids can be formulated with extreme pressure (EP) and anti-wear (AW) additives in metal working application for better machining performance. Triphenyl phosphorothionate (TPPT) is one of the promising environmentally friendly anti-wear additives that is used in biodegradable lubricant formulations. Canola vegetable oil is commonly used in industrial application due to its high annual production. Trimethylolpropane trioleate (TMPTO) and pentaerythritol tetra-oleate (PE-TO) polyol esters have wide acceptance as lubricant base fluid due to their excellent lubricity and stability. Based on these informations, this study presents an investigation of effect of TPPT on tribological performance of canola oil, TMPTO and PE-TO by using four ball method. For this purpose, wear-scar diameters of pure form of vegetable oil and polyol esters and their formulations with two different amount TPPT compared. As a result, it was determined that low TPPT amount (0.5%) has no effect on anti-wear performance whereas high TPPT amount (2 %) enhanced the tribological performance of formulations. Lowest wear scar diameter was obtained from the formulations of TMPTO with 2 % TPPT.

Keywords: vegetable oil, polyol ester, anti-wear additives

1. INTRODUCTION

Metalworking fluids are crucial products in the machining processes. Primary objective of metalworking fluids is to minimize the friction at the work–tool interface and serve a cooling agent so prevention of energy and heat loses. Also, they protect machines against to corrosion. Thus, service life of machinery parts can be extended and production efficiency can be increased [1]. Global demand of metal working fluids is increasing day by day as result of rapid growth of industrialization. However, conventional metalworking formulations consist of petroleum products which are toxic, non-biodegradable and harmful on environment. Also, petroleum reserves have been depleting. In this regard, finding alternative lubrication fluids based on renewable sources and decreasing dependency on petroleum products has gained much interest to protect environment and overcome the energy crisis [2]. Development of biolubricants is a reasonable approach to solve environmental concerns and achieve sustainability objectives [3]. There are various biodegradable feedstocks to produce bio-lubricants such as vegetable oils and polyol esters [4].

Vegetable oils are attractive raw materials for green and sustainable metal working fluids due to their non-toxicity and high availability. In addition, their high viscosity index and flash point provide a utilization over a wide temperature range. Furthermore, they have excellent lubricity as a result of presence of long chain fatty acid and polar groups in their structure [5]. Besides advantages vegetable oils, they can easily polymerize since their oxidation and thermal stability are low. Therefore, they cannot be used in the industry effectively. Polyol esters are another option for biolubricants. They synthesized with attaching of an alcohol to fatty acids and hydrogen atom on the β-carbon atom is eliminated. Trimethylolpropane trioleate (TMPTO) and pentaerythritol tetra-oleate (PE-TO) are the most popular alternatives among polyol esters. TMPTO is obtained via esterification of trimethylolpropane and oleic acid and as result of moderate price of trimethylopropane [6,7], TMPTO is widely used in the metal working applications. It has higher oxidative stability and better low temperature properties compared to vegetable oils. It has high viscosity index and good lubrication properties [7]. On the other hand, PE-TO is obtained as a result of reaction of pentaerythritol with oleic acid. Recent studies show that pentaerythritol esters have better thermal and oxidative stability and more enhanced lubricity than other polyol esters [8]. In line with all above information, vegetable oils are advantageous feedstocks with their low cost and abundancy and polyol esters are effective sources with their superior physico-chemical properties. Comparison of the machining performance of these base fluids can provide a comprehensive study to literature.

Vegetable oils and polyol esters have good tribological performance however performance of these base fluids can be insufficient in the harsh working condition. Uses of additives is required to enhance the anti-wear capabilities of base lubricants [9]. Zinc dialkyldithiophosphates (ZnDTPs) are commonly used in lubricant formulations as anti-wear agents for many years. Otherwise, they cause serious hazard on environment and human health because of presence of heavy metal zinc in their structure. In this regard, it is aimed that decrease of utilization of ZnDTPs in the formulations and zinc free additives has gained much interest in industrial applications. Triphenyl phosphorothionate (TPPT) is an ecofriendly anti-wear additive and has high thermal stability, that is favorable alternative to ZnDTPs. Sustainable metal working application can be attained with formulation of TPPT additive with biodegradable base fluids [10].

There are various methods in order to test machining performance of metal working fluids. Their tribological performance can be analyzed with four ball method. It is an advantageous method to analyze anti-wear performance. because it is simulation of real operation by providing lubricated steel-steel contact [11].

In this study, machining performance of the canola oils and trimethylolpropane trioleate (TMPTO) and pentaerythritol tetra-oleate (PE-TO) were investigated using the Four Ball test method. Also, these base fluids are formulized with two different amount TPPT (0.5% and 2 %) to determine the effects of TPPT on the anti-wear performance of vegetable oil and polyol esters. Furthermore, surface morphology of balls was analyzed with 3D microscope.

2. EXPERIMENTAL METHOD

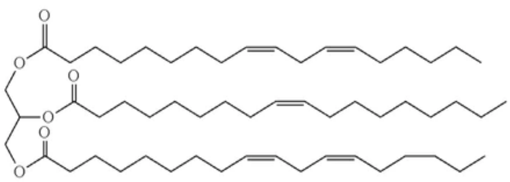
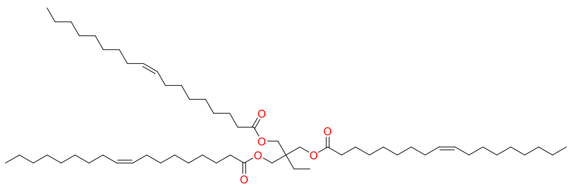
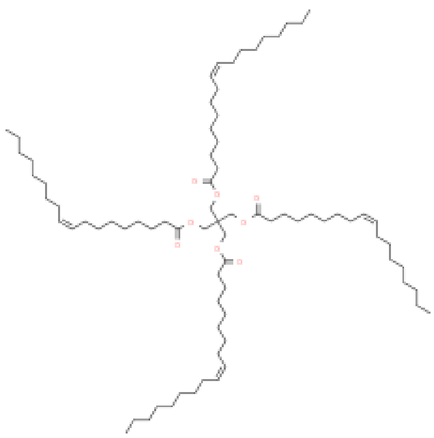
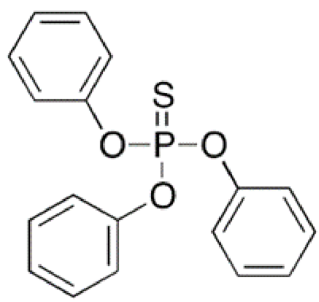
In this study, canola vegetable oil, trimethylolpropane trioleate (TMPTO) and pentaerythritol tetra-oleate (PE-TO) polyol esters are used as base fluids. Their physicochemical properties were given in Table 1.

Table 1. Physicochemical properties of base fluids.

Test Parameter	**Test Method**	**Canola Oil**	**TMPTO**	**PE-TO**
Kinematic Viscosity (40°C, cSt)	ASTM D 445	46	46	65
Kinematic Viscosity (100°C, cSt)	ASTM D 445	10	9,2	14
Viscosity Index	ASTM D 2270	212	187	225
Flash Point (°C)	ASTM D 92	≥ 190	≥ 270	≥ 280
Pour Point (°C)	ASTM D 97	≤-18	≤-42	≤-25

Molecular structures of canola oil, TMPTO, PE-TO and TPPT were given in Table 2. Triphenyl phosphorothionate (TPPT) is used as anti-wear additives in the formulations.

Table 2. Molecular structures of canola oil, TMPTO, PE-TO and TPPT.

 CANOLA OIL	 TMPTO
 PE-TO	 TPPT

Composition of formulations was given in Table 3.

Table 3. Composition of formulations by mass percentage. Numbers in parentheses represent mass percent

No	Formulation Composition	No	Formulation Composition
1	Canola Oil (100:0)	6	PE-TO+TPPT (99.5:0.5)
2	TMPTO (100:0)	7	Canola Oil+TPPT (98:2)
3	PE-TO (100:0)	8	TMPTO+TPPT (98:2)
4	Canola Oil+TPPT (99.5:0.5)	9	PE-TO+TPPT (98:2)
5	TMPTO+TPPT (99.5:0.5)		

Anti-wear performance of canola oils and trimethylolpropane trioleate (TMPTO) and pentaerythritol tetra-oleate (PE-TO) and their formulations with TPPT were studied by Four Ball Test according to ASTM 4172 standard test method. At the end of the four-ball test, wear on the balls is measured and surface morphology was analyzed by helping of 3D microscope.

2.1 Four Ball Test

Three steel balls with 12.7 mm diameter are clamped together. It is covered with test sample and heated to75°C. Fourth steel ball with 12.7 mm diameter is pressed with a force of 40 kgf (392 N) into the cavity formed by the three clamped balls for a three-point contact. During the test, top ball contacts with three other balls, it is rotated at 1200 rpm for 60 minutes. Test condition was given in Table 4 and scheme of test method was illustrated Figure 1.

Table 4. ASTM D 4172 Parameters

Test Parameter	Test Condition
Speed	1200±60 rpm
Temperature	75 ± 2 °C
Load	40 ± 0,2 kgf
Duration	60 ± 1 dk
Ball	ANSI-E-52100 Çelik-12,7mm

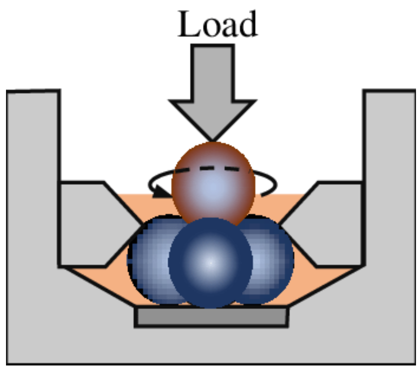


Figure 1. Scheme of Four Ball Test

2.2 3D Microscope

3D microscope is used so that measuring the surface morphology of the worn balls as a result of the four ball test for evaluation more effectively. Thus, it will be possible to detect performance differences that cannot be determined by a conventional microscope. Using 3D Microscop round areas of balls can be measured in the x, y, z coordinates in micron size and high resulation images can be captured. Figure 2 shows the 3D microscope.

Figure 2. 3D microscope

3. RESULTS AND DISCUSSION

3.1. Anti-wear Performance of Formulations

Wear-scar diameters results of pure form of vegetable oil and polyol esters and their formulations with two different amount TPPT were given in Table 5. It was determined that base fluid have similar tribological performance. Wear scar diameter of canola oil, TMPTO and PE-TO decreased slightly with addition of 0.5% TPPT. It was noted that addition of low amount of TPPT is not enough for improvement of anti-wear performance. On the other hand, increase amount of TPPT decreased significantly wear scar diameters. Best anti-wear performance was obtained from the formulation of TMPTO with 2% TPPT.

Table 5. Wear Scar diameters of formulations

Formulation No	Formulation	Wear Scar Diameter (mm)
1	Canola Oil	0.650
2	TMPTO	0.759
3	PE-TO	0.723
4	Canola Oil+0.5% TPPT	0.638
5	TMPTO+0.5% TPPT	0.740
6	PE-TO+0.5% TPPT	0.730
7	Canola Oil+2% TPPT	0.413
8	TMPTO+2% TPPT	0.328
9	PE-TO+2% TPPT	0.430

3.2. Surface Morphology Analysis

Surface morphology of worn balls was analyzed with 3D microscope. High resolution images of wear scars were obtained. As shown in figure 3 and figure 4, wear scars of pure form of vegetable oil and polyol esters are quite significant. On the other hand, wear on the balls became insignificant with addition of 2% TPPT additive. Numerical results were confirmed by helping of these images.

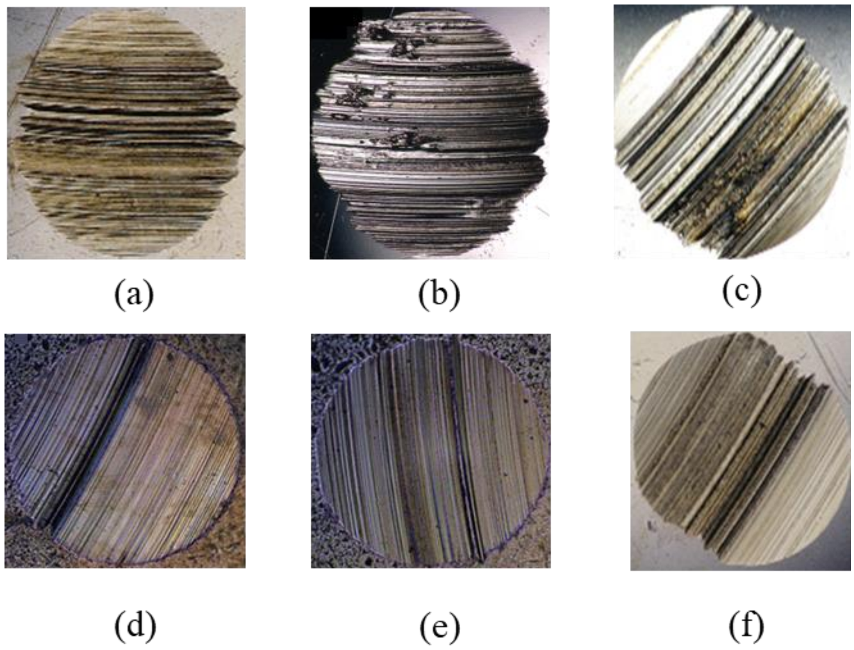


Figure 3. 2D Images of worn balls (a)Canola Oil, (b) TMPTO, (c)PE-TO, (d) Canola oil+2% TPPT, (e) TMPTO+2% TPPT, (f) PE-TO+2% TPPT)

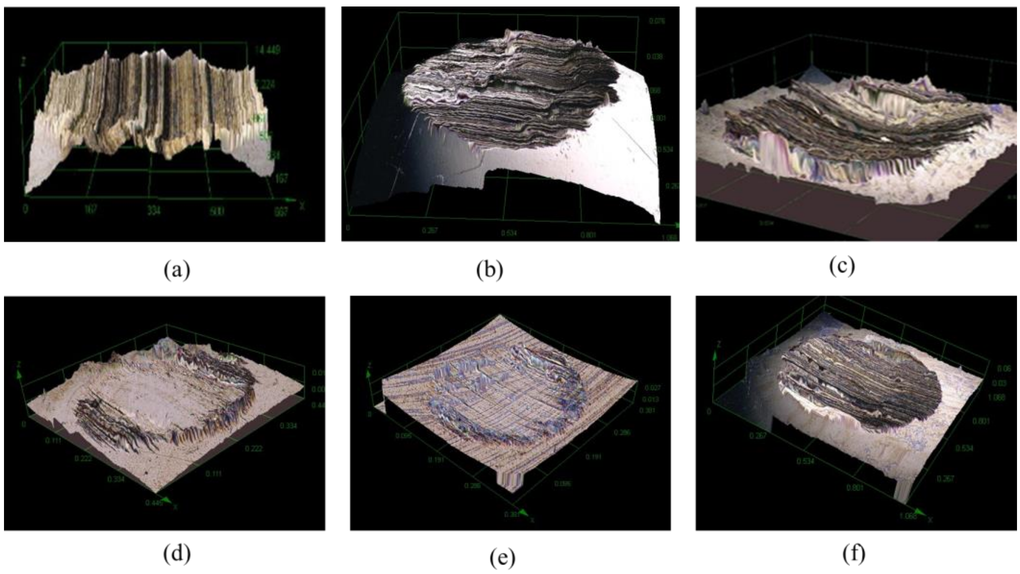


Figure 4. 3D Images of worn balls ((a)Canola Oil, (b) TMPTO, (c)PE-TO, (d) Canola oil+2% TPPT, (e) TMPTO+2% TPPT, (f) PE-TO+2% TPPT)

3.3. Evaluation of Results

In this study, tribological performance of three environmentally friendly base fluids were studied and the effect of the TPPT additives on their ant-wear performance were evaluated. Studies were carried out using the ASTM D 4172 Four Ball Test method. Wear scar diameters were measured and they were visualized by 3D microscope. Comparison of the pure form of canola oil and polyol esters was given in the Figure 4. Besides similar tribological performance of all base fluids, canola oil has slightly better anti-wear performance.

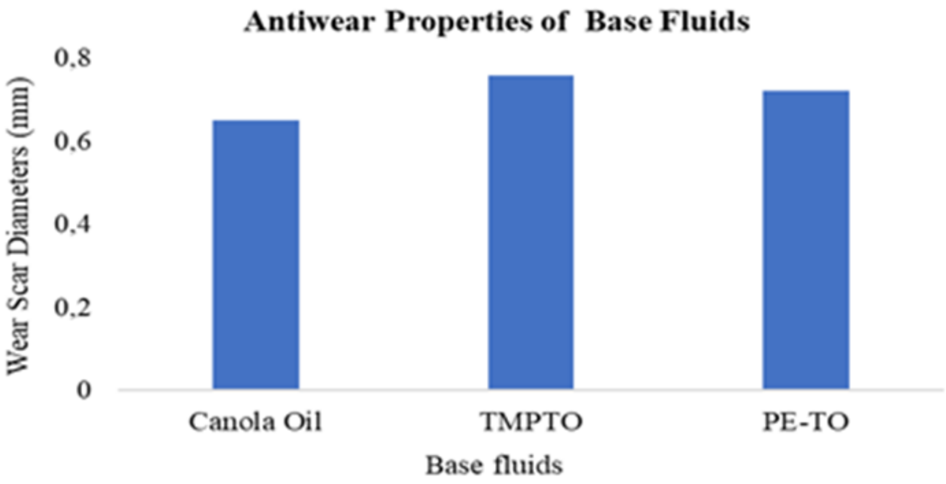


Figure 4. Comparasion Anti-wear Performance of Base Fluids

Comparison of TPPT effect was given in Figure 5. Studies were performed with two different amounts of TPPT which are 0.5% and 2%. It was ascertained that there was any improvement on the anti-wear performance of base fluids with 0.5% TPPT addition. Wear scar diameters of lubricant formulations decreased significantly with increasing TPPT amount from 0.5 to 2%. When TPPT was %2 in the formulations, anti-wear performance of polyol esters showed the highest improvement percentage than canola oil as shown in the Table 6.

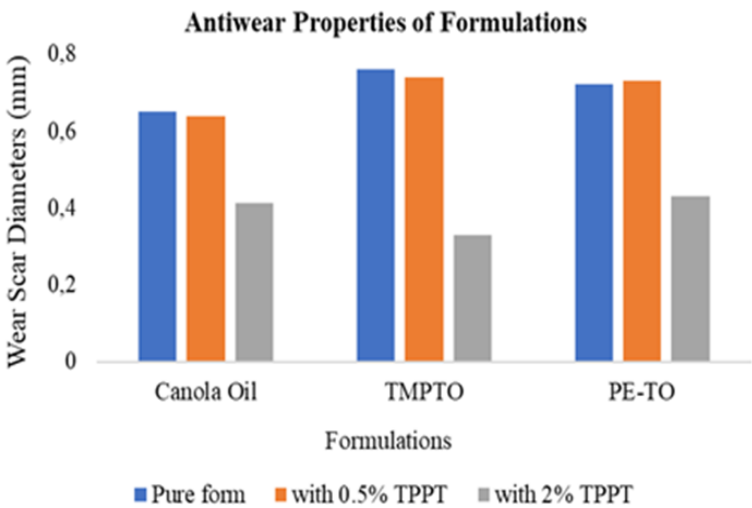


Figure 5. Anti-wear Performance of formulations

Table 6. Improvement Percentage

Base fluids	Canola Oil	TMPTO	PE-TO
Improvement (%)	36.5	56.8	39

The following inferences can be made from the above results:

- Studies with pure form of vegetable oils and polyol esters demonstrated that all base fluids have similar tribological performance. All wear scar diameters were found as above 0.6 mm. Wear scar diameter of canola oil was lowest whereas TMPTO had highest wear scar diameter.
- TPPT is an ecofriendly anti-wear additive that can be used in the biodegradable lubricant formulations. This study demonstrated that amount of TPPT used in the formulations has great importance. Its amount should be appropriate to enhance the anti-wear performance of lubricant formulations.
- Anti-wear performance of TMPTO and PE-TO with addition TPPT enhanced more than canola oil.
- Although TMPTO had worst anti-wear performance in the pure studies, highest improvement on the tribological performance was observed from formulation of TMPTO with 2 % TPPT.

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