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Development of Vegetable Oil Based Nano-lubricants

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DEVELOPMENT OF VEGETABLE OIL BASED NANO-LUBRICANTS

A Thesis

by

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ABSTRACT

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Nowadays, the depletion of crude oil reserves in the world and the global concern in protecting the environment from contamination have renewed interest in developing environment friendly lubricants derived from alternative sources such as vegetable oils. Mineral oil is the most common lubricant, however, it also has poor biodegradable properties. Vegetable oils exhibit good viscosity index, flash point, pour point, tribological properties, and are biodegradable. Furthermore, the use of nanoparticles as additives has shown to improve anti-wear and anti-friction properties of the base lubricant. The present research project will evaluate experimentally the rheological and tribological behavior of coconut oil, sunflower oil, and grapeseed oil modified with nanoparticle additives. Three different nanoparticle additives are investigated: silicon dioxide (SiO_2), copper oxide (CuO), and titanium dioxide (TiO_2). For the three conditions, nanoparticles were dispersed at different concentrations within the vegetable oil. The effects of concentration and shear rate on the viscosity were evaluated and the experimental data was compared with conventional models. Wear scars were analyzed using SEM, EDS, and roughness to identify nanoparticle effect. From the experimental results, it was found that wear volume loss and coefficient of friction were lowered. The developed modified vegetable oil nano-lubricants show potential as possible replacements to conventional mineral oils.

DEDICATION

The completion of my master's studies would not have been possible without the love and support of my family. My parents for their constant support and always believing in me. For my brothers and their constant motivational speeches. For my love, Grisy, and her constant support through my undergrad and grad studies. Thank you all.

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CHAPTER I

INTRODUCTION

There has been growing concern over the environmental impact of the use of petroleum-based lubricants in recent years. Every year, about 38 million metric tons of lubricants are used worldwide, and the most common lubricant is mineral oil, which is petroleum-based [33]. Furthermore, depletion of fossil fuels and fluctuation of petroleum prices has driven interest towards biodegradable lubricants. Lubricants play an important role of decreasing friction and wear of mechanical contacts [30]. Friction is described to be the resistance of one surface or object that is developed when two surfaces move relative to each other. In certain machinery friction is required as in clutches, belts, pulleys, and braking systems. However, in machining, piston ring interface and bearing support systems friction is undesirable. If more friction is present more mechanical energy is lost causing the system to use more work to perform the same task.

Before mineral was discovered, vegetable oils were extensively used in machinery. Due to its relatively low cost and good performance mineral oil was been extensively used. In recent years due to price fluctuation, legal issue, and growing concern of environmental health have given biodegradable oil a better scope for lubrication[18]. Recently much focus has shifted towards vegetable oils such as canola oil, sunflower oil, coconut oil, rapeseed oil, jojoba oil, soybean oil, and pongamia oil. Vegetable oils possess high lubricity, high viscosity index, and low volatility, which are excellent lubricating properties [18,38]. Since the main drawback of vegetable oils is poor oxidation, much has been given in improving thermo-oxidation [2]. Oxidation occurs in vegetable oils through free radical mechanism and can be reduced by decreasing free fatty acids.

To improve the lubricant oil properties, additives have been used such as antiwear additives, extreme pressure additives, viscosity control additives, film-forming additives, and deposit control additives [40]. Recently much attention has been given towards nanoparticles, since they possess unique properties when compared to their bulk counterparts. Studies in the use of nanoparticles as additives have shown to reduce friction and wear.

1.2 Problem Statement

Since conventional mineral oil has many drawbacks there exists a demand for an alternative biodegradable lubricant. Current alternative is vegetable oil, but in its current state it has many drawbacks associated with it and more research is needed to improve its properties. The objective the present study was to evaluate the rheological and tribological behavior of coconut, sunflower, and grapeseed oil modified by the addition of SiO_2, CuO, and TiO_2 nanoparticles at different concentrations to improve the tribological properties.

CHAPTER II

LITERATURE REVIEW

2.1 Background on Lubricants

A lubricant is a substance that reduces friction between surfaces in contact[24]. This in return makes the surfaces heat up less and reduce wear present. Lubricants have been implemented for thousands of years. One of the first lubricants were calcium soaps which were used to lubricate chariots axles back in 1400 BC. Lubrication became more important during the industrial revolution where a lot of machinery required lubrication for metal forming. Initially natural oils were used as lubricants, but discovery of petroleum made the switch to petroleum-based lubricants. Since the 1900s the most common lubricant has been mineral oil. Many other forms of lubricants exist today and are shown in Table 1.

Table 1: Summary of different Lubrication oils[14]

Types of Lubricants		
	Types of Oils	**Description**
Vegetable oils	• Coconut Oil • Grapeseed Oil • Sunflower Oil • Palm Oil • Rapeseed Oil	Are described as biolubricants and are renewable. Mostly obtained from plants making them triglyceride esters.
Mineral Oils	• Paraffins • Isoparaffins • Aromatic	Mineral oil comes from crude oil and can be assigned to 4 groups by the American Petroleum Institute.
Synthetic	• Alkylated aromatics • Polyalphaolefins • Polybutens • Esters Diesters • Polyol Esters	Synthetic oil is petroleum derived that is modified with synthetic hydrocarbons.

Current technology demands for a sustainable and more environmentally friendly lubricant. In the past years the use oil has increased and eventually will reach its peak as shown by wood [40] in Figure 1. When the peak is reached in the 21st century there will be a catastrophically depletion of the world's oil. Furthermore, general concern of toxic lubricants has promoted research to biodegradable lubricants. Much interest has been given towards vegetable oils since they are renewable and do not contaminate the environment. Furthermore, vegetable oils possess many sought out properties such as good lubrication in contact area, high flash point, high biodegradability, and low volatility [2,9,26]. The high polarity of vegetable oils allows them to be useful boundary lubricants [2].

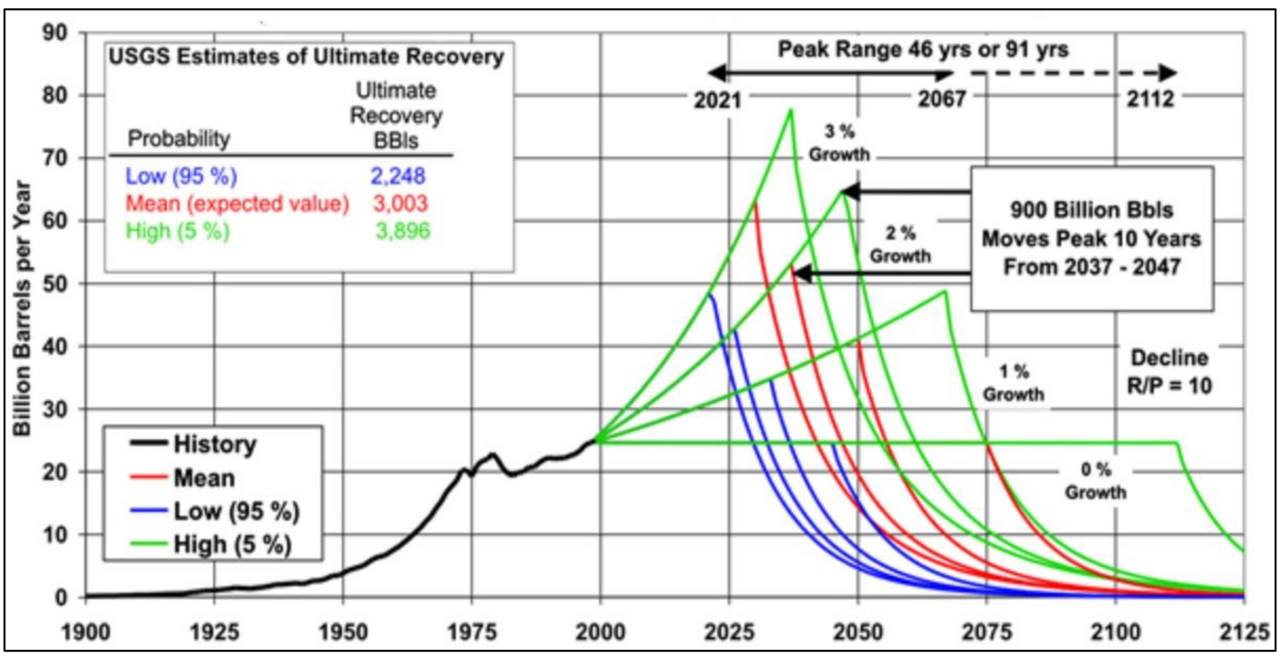


Figure 1: Oil consumption per billion barrels versus year [40].

2.2 Vegetable Oils

As shown in the previous sections there is much need for an alternative lubricant to replace current mineral and synthetic options. Vegetable oils have spiked much interest in recent years in due to them being biodegradable in nature and non-toxic.

Vegetable oil comes in liquid form and is extracted form cash crops and plants. Most vegetable oil is made up of triglycerides, which are glycerol molecules consisting of three long chain fatty acids that are connected via ester linkages at the hydroxy groups[10]. A representation of these triglycerides chains is shown Figure 2.

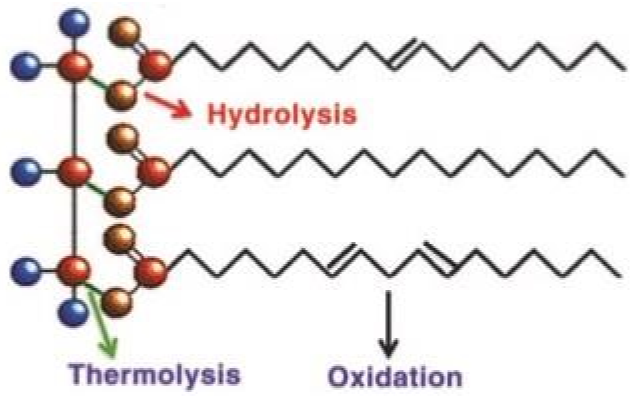


Figure 2: Composition of Triglycerides [16].

Most of the fatty acids found within vegetable oils are between 14 to 22 carbons long. Furthermore, the level of saturation varies depending on the fatty acids. Fatty acids such as oleic acid is absorbed by hydrocarbon solutions at the surface metal tool. This attraction to metal surface and vegetable oil has been assumed to be the reason for enhanced lubricating characteristics in vegetable oil[35]. Other common fatty acids found within vegetable oils are Palmitic fatty acids, Stearic fatty acids, Linoleic fatty acids, and Linolenic fatty acids. Depending of the vegetable oil the percentage composition of the fatty acid will differ. For example, sunflower oil has 53.8% Linoleic fatty acid composition meanwhile Groundnut has only 10% composition. For a full list of common vegetable oils and their corresponding fatty acid composition, see Table 2. Note that “nd” represents that the fatty acid composition was not determined. These fatty acids are what give vegetable oils their unique properties depending on what fatty acid they have the most. For example, vegetable oil high in oleic acid tend to have better oxidative stability.

Table 2: Properties of Some Vegetable Oils [6,27].

Vegetable Oils	Double Bonds	Percentage of Fatty Acids					
		Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)	Palmitic (16:0)	Stearic (18:0)	Lauric (12:0)
Rapeseed	3.8	56.0	26.0	10.0	4.0	2.0	nd
Coconut Oil		6.0	1.6	1.0	nd	2.7	47.7
Sunflower Oil	4.7	37.2	53.8	1.0	5.2	2.7	0.02
Grape Seed		14.3	74.7	0.15	6.6	3.5	0.01
Corn Oil	4.5	25.4	59.6	1.2	10.9	2.0	nd

Although vegetable oils seem to suitable replacement for conventional mineral oil, there are many limitations and drawbacks associated to vegetable oil that have not made it possible. Some of the current disadvantages associated with the use of vegetable oil is that it performs worse when compared with mineral oil, low thermal stability, low oxidative and hydrolytic stability, and poor low temperature performance[34,3]. Recently most new research is focused on fixing the drawbacks of vegetable oils via chemically modification as shown by butanethiol [5], or by the addition of nanoparticles.

2.2.1 Coconut Oil

During the pre-mineral oil coconut oil was widely used in gas engines. Coconut oil is considered one of the most stable oils. Coconut oil belongs to the lauric oil groups. Lauric acid is the most abundant fatty acid found in coconut oil. Coconut oil has 90% saturated acids which have been found to be antioxidant. N.H. Jayadas and Prabhakaran [18] showed that coconut oil had good lubricant properties such as high viscosity index, high flash point, good lubricity, and low evaporative loss.

2.2.2 Sunflower Oil

Sunflower oil was initially used as grease and diesel fuel substitutes. Sunflower main fatty acid is linoleic with a concentration of 53.8 % as shown in Table 2. Most of the research done on sunflower has been to improve its oxidation properties. Minami conducted pin-on-disk experiments and came to the conclusion that high oleic sunflower oil performed well without additives at 50°C, and that addition of stearic acid increased performance at higher loads [25]. Therefore, sunflower has potential in being a biodegradable nontoxic lubricant replacement.

2.2.3 Grapeseed Oil

Although grapeseed oil has existed for 1000s of years little research has been done exploring tribological performance of Grapeseed oil. Grapeseed most abundant fatty acid is linoleic acid at 74.7% concentration. Grapeseed can be found in great abundance in Brazil therefore, making it a viable solution to substitute conventional mineral oil if performance is comparable to mineral oil. Serra in 2017 compared base grapeseed oil with mineral oil and found that in physical properties such as flash point and pour point grapeseed performed better, but in wear test mineral oil had less wear [28].

2.3 Feedstock Considerations.

To consider vegetable oil as replacement to conventional mineral oil it has to be able to keep up with the demand needed. Currently there exists over 350 different crops that vegetable oil can be extracted from [26]. Out of the long list of vegetable oil the popular feedstock oils are coconut, sunflower, canola soybean, castor, peanut oil, and jatropha oil, with a lot more oils to consider that can be used to substitute conventional mineral oil. Vegetable oil can either be edible or non-edible, and ideally finding use for a non-edible vegetable oil would be ideal. This non-edible oil would have little to no influence on current cost of vegetable oil or production.

Such oils that are considered non-edible are castor, rice bran, jatropha and many more. These, non-edible could be grown in a land next to edible crops, therefore no interference would happen to edible vegetable oil [32]. For this paper three vegetable oil will be considered which will be coconut, sunflower, and grapeseed. Although these vegetable oils are among the edible category the great abundance available allows them to be considered as replacement to conventional mineral oil.

2.4 Addition of Nanoparticles

To improve the lubricant oil properties, additives have been used such as antiwear additives, extreme pressure additives, viscosity control additives, film-forming additives, and deposit control additives [39]. Recently much attention has been given towards nanoparticles, since they possess unique properties when compared to their bulk counterparts. Studies in the use of nanoparticles as additives have shown to reduce friction and wear.

This reduction in friction is due to the nanoparticles due to their extremely small size allows them to slip into the contact areas of the two metals. Mending effect, rolling effect, polishing effect, and protective film mechanisms have been proposed to describe the role of nanoparticles in lubricant oil, and is shown in Figure 3. Peng and co-workers found that by adding SiO_2 and diamond nanoparticles in liquid paraffin friction decreased when compared to plain liquid paraffin oil [29]. Hernandez studied the effect of adding ZnO, CuO, and ZrO_2 nanoparticles in polyalphaolefin and found friction and wear decreased due to the nanoparticles acting load-bearings [16]. Although nanoparticles have proven to enhance lubricant properties the current issue is compatibility as stated by Gulzar and co-workers [15]. After some period of time, nanoparticles tend to sediment making the lubricant no longer uniform.

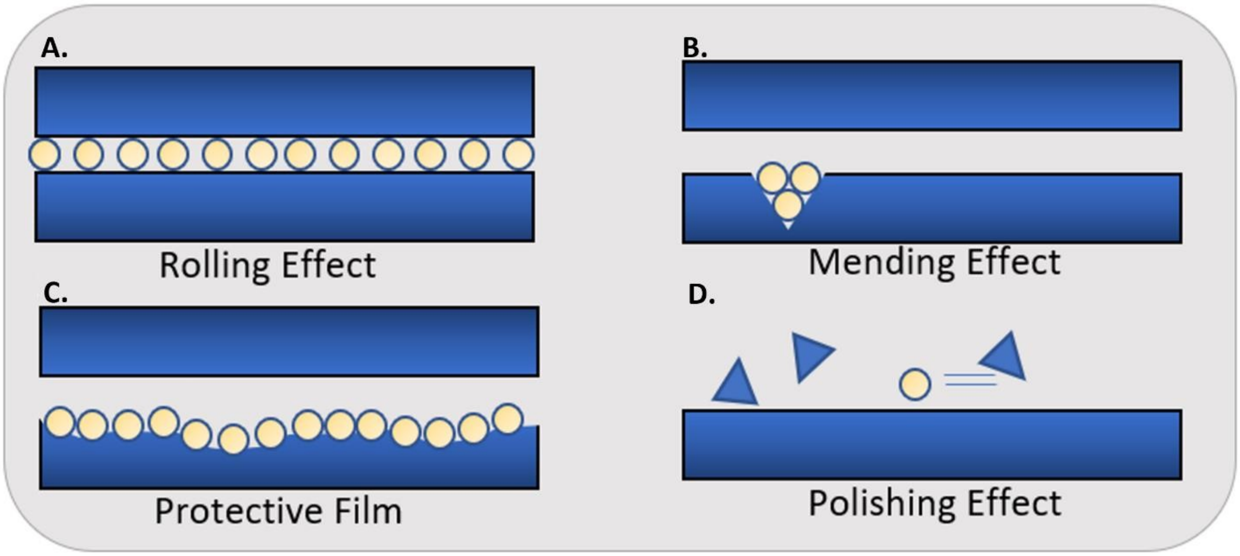


Figure 3: Role of Nanoparticles in Vegetable based Lubricants.

2.4.1 Types of Nanoparticles

Since base oil have many drawbacks, in recent decade increased attention to nanoparticles such as metals, metal oxide, metal sulfide, metal borate, metal carbonate, carbon compounds, and SiO_2. Each nanoparticle has their unique chemical and physical properties. When evaluating a nanoparticle, it is important to answer three questions. What lubrication mechanism is at play from Figure 3? What is the importance of the chemical composition and its effect on the tribological performance? Lastly, what elements available from nanoparticles are positive for nano-lubrication [7]?. Figure 4 shows some nanoparticles that have been previously studied and it can be concluded that the most studied nanoparticles are metal oxide and metals consuming 26% and 23% respectively of total percent. For this specific study, the focus was mainly on three nanoparticles since we wanted to explore the effect of Titanium oxide of 18nm, Silicon dioxide 20-30nm, and Copper oxide 40nm on the tribological performance since no previous research existed of these vegetable oils with these specific nanoparticles.

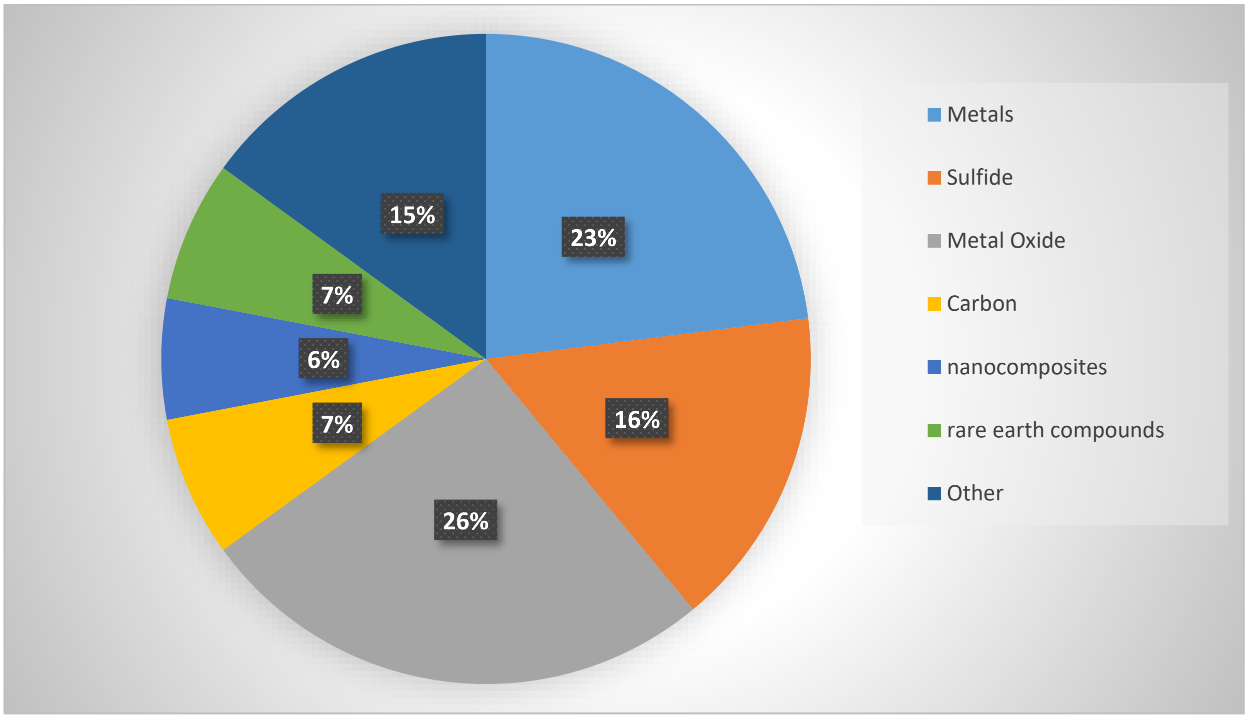


Figure 4: Statistics of Nanoparticles studied as lubricant additives (Reconstructed from [7]).

2.4.2 SiO_2 as Nanoparticle lubricant additive

Silicon dioxide belongs to the other group of lubricant additives and is one of the most common additives used to improve lubricant base performance, since it easily obtained and cheap[29]. As mentioned before Peng found that by the addition in liquid paraffin the friction was lowered when compared to base oil by itself. Other research was done Li and coworkers where they studied surface modified SiO_2 [22]. They found that by modifying the surface the suspension of nanoparticles in oils improved. Dambatta and co-workers studied the tribological performance of SiO_2 in nanofluids specifically in the area of minimum quantity lubrication[8]. Evaluating the surface finish and grinding forces Dambatta and co-workers were able to find that an optimal level of SiO_2 exists, and that by adding nanoparticles friction was reduced through a tribofilm at surface. Therefore, SiO_2 has been studied before and shows promising results if mixed with vegetable oils.

2.4.3 CuO as Nanoparticle lubricant additive

CuO nanoparticles belong to the metal oxide group. Research has shown CuO has the potential to reduce friction and wear improving tribological performance when compared to base oil. Wang and co-workers explored the antiwear and repairing performance of lubricant enhanced with CuO nanoparticles [36]. Wang concluded that the wear scar and friction reduced by 34% and 32% respectively when analyzed by friction and wear test machine. The effects of CuO in Poly-alpha olefin 8 and GL-4 oil were also analyzed using a optimal SRV 4 tester and extreme pressure by a four-ball testing machine by Peña-Parás a and coworkers [29]. They concluded that the addition of CuO helped improve the carrying capacity likely due to the tribosintering of the nanoparticles. Furthermore CuO had more effect in PAO 8 oil improving tribological performance. Therefore, the addition of CuO nanoparticles have shown positive results increasing the tribological performance of base oils. One thing to note is that the nanoparticle will react different in different base oil so performance will differ as the base oil is changed.

2.4.4 TiO_2 as Nanoparticle lubricant additive

Titanium oxide like CuO belongs to the metal oxide group. The metallic nanoparticles have unique chemical and physical properties. Metal oxides have been found to improve lubrication performance through a lubrication film known as a tribo-film, rolling effect due to the nature of semispherical shape nanoparticles, and rolling effect. For example, Kao and Lin found that the addition of spherical titanium oxide nanoparticles into paraffin oil reduced the friction coefficient by the rolling effect and surface repairing effect also known as the mending effect [20]. Other studies have shown that the addition of TiO_2 improved load carrying capacity, reduced friction, and wear when compared to the base oil [4,21,39].

2.6 Application

If successful, the applications for biodegradable lubricants is vast. For our three selected vegetable oils the temperature and potential oxidation will be limiting factors. Sectors where vegetable oil modified with nanoparticles can be used are cutting fluids, refrigerant systems, engine piston seals, bearings and much more. In cutting fluids, the purpose of the lubricant is protecting the tool meanwhile ensuring the product surface is not damage. For refrigerant systems the lubricant role is to protect the pump from damaging itself through excessive friction and wear. In piston seals the purpose of the lubricant is to ensure the surface of the piston is protected to ensure no leakage occurs by damaged piston walls. Furthermore, it is important to note that close systems are ideal since open systems will be exposed to the environment making vegetable oils oxidize quickly. Although much research done is preliminary evaluating experimentally vegetable oils in wear testing machines, much improvement to base oil has already been done by the addition of additives and chemical modification. If successful, we can be seeing a world where most components are lubricated by an environmentally friendly biodegradable lubricant.

2.7 Energy Considerations

For big corporation companies, optimizing for maximum profit is the main goal. Replacing conventional mineral oil with vegetable-based oil may cause an impact on the energy used by the manufacturing equipment. During the machining portion the cutting tool experiences wear and friction, and this factors affect the power consumption and surface finish [23]. Energy consumption is not only lost in manufacturing equipment. For lubricants their applications include transportation such as cars, truck, and buses. Furthermore, power generation also requires lubricants. Therefore, minimizing friction and wear is important since in return consumption of energy will lower, CO_2 emissions will lower, and economic expenditure will occur [17]. Studies have shown 23% of the worlds energy is consumed by tribological contacts and 20% of it is to overcome friction [23].

CHAPTER III

EXPERIMENTAL SETUP AND PROCEDURE

3.1 Nano-Lubricant Preparation

In the present study, SiO_2, CuO, and TiO_2 nanoparticles from US Research Nano Co. (Houston, TX, USA) were dispersed in commercially available sunflower, grapeseed, and coconut oil in different concentrations to formulate the nano-lubricants. The main properties of the lubricant and selected nanoparticles are shown in Table 3. Density of the oil was measured on a weight to volume basis using a 25 mL flask and a Mettler Toledo XS205DU electronic balance (Mettler-Toledo LLC, Columbus, OH, USA) to an accuracy of 0.01 mg. The morphology of the particles was verified using Field Emission Scanning Electron Microscope (FE-SEM) ZEISS SIGMA VP (Carl Zeiss SBE, Thornwood, NY, USA) shown below in Figure 5.

Figure 5: Scanning Electron Microscope[42].

Nano-lubricants then were prepared by the adding of 0.25, 0.50, 0.75, 1.00, and 1.25 wt % nanoparticles into the vegetable lubricant using the Mettler Toledo XS205DU electronic balance shown in Figure 6.

Figure 6. Mettler Toledo electronic balance.

Ultrasonication was followed for 5 min with a 120-Watt sonic dismembrator shown in Figure 7 with a frequency of 20 kHz to ensure uniform dispersion and good suspension stability. The vegetable oils were then immediately tested using the modified tribotester to ensure stability of the nanoparticles within the vegetable oil.

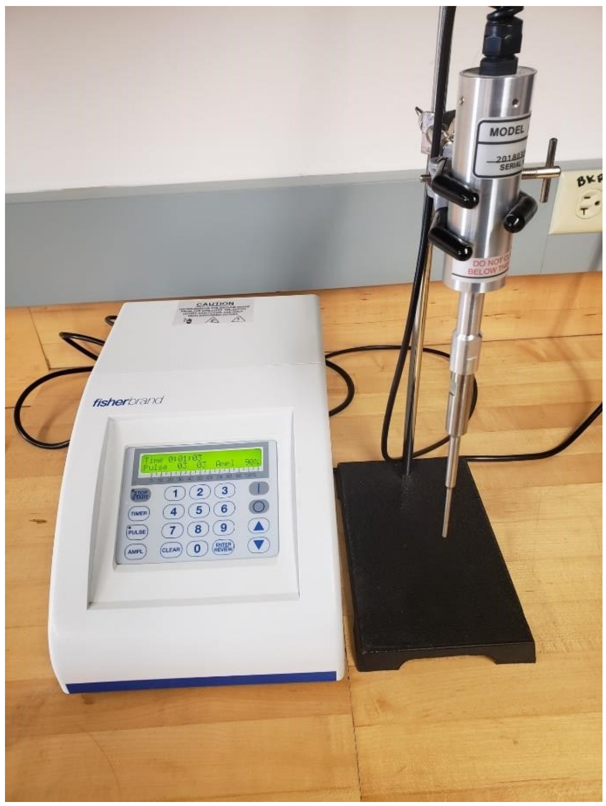


Figure 7: Ultrasonic Mixer.

Table 3: Material Properties.

Material	**Properties**
Lubricant	
Sunflower oil	Density (40°C): 0.90 g/cm^3 Viscosity (40°C): 35 mPas
Grapeseed oil	Density (40°C): 0.92 g/cm^3 Viscosity (50°C): 25.27mPas
Coconut oil	Density (40°C): 0.92 g/cm^3 Viscosity (40°C): 26 mPas
Nanoparticles	
Silicon dioxide	Chemical Formula: SiO_2, Purity: 99.5% Particle size: 20-30 nm
Copper oxide	Chemical Formula: CuO, Purity: 99% Particle size: 30-40 nm
Titanium oxide	Chemical Formula: TiO_2 (anatase), Purity: 99.9% Particle size: 18 nm
Specimens	
Cylinders	AISI 304 steel, d = 12.7 mm, l = 14 mm, hardness: 60 HRC
Blocks	AISI 304 steel, dimensions: 14 x 6.35 x 6.35 mm, hardness: 128 HRB
Rings	AISI 52100 steel, d = 40 mm, hardness: 60 HRC

3.2 Rheological Measurements

The rheological properties of SiO_2 and TiO_2 nanoparticles in sunflower, grapeseed, and coconut oil were evaluated by means of a commercial rheometer HAAKE RS-150 RheoStress (Haake Instruments, Inc., Paramus, NJ, USA) with a special plate (double parallel plates) spindle shown in Figures 8 and 9. The distance between upper and lower plates was 0.5 mm and 0.9 mL of the testing sample was placed on the plate. In this study, viscosities were studied at 22 °C, which was controlled during the measurements. During the rheometer measurements, it is important to make sure the whole surface area of both parallel plates is covered completely before starting the experiment. Furthermore, any vibration or sudden movement would cause error in run, so experiments that had some error were disregarded. The shear rate for all samples was set from 10 to 120 s^{-1}. Each of the runs was repeated 3 times to ensure repeatability.

Figure 8: RS 150 Rheometer.

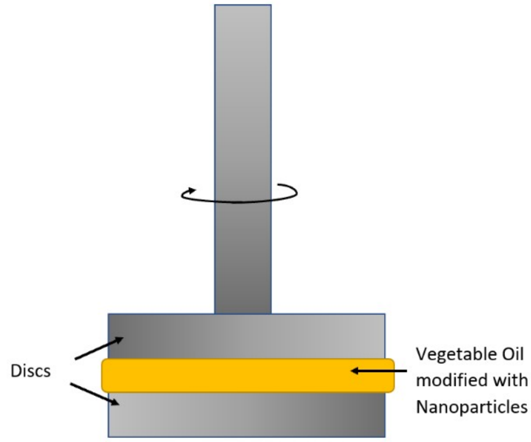


Figure 9: Parallel Plate Configuration.

3.3 Tribological Characterization

The tribological experiments were carried out into two stages: 1. Using a custom made tribotester with cross-cylinders configuration, 2. Using block-on-ring configuration. The characteristics of the tested materials are presented in Table 3. A schematic of the tribotester with cross-cylinder configuration is shown in Figure 10.

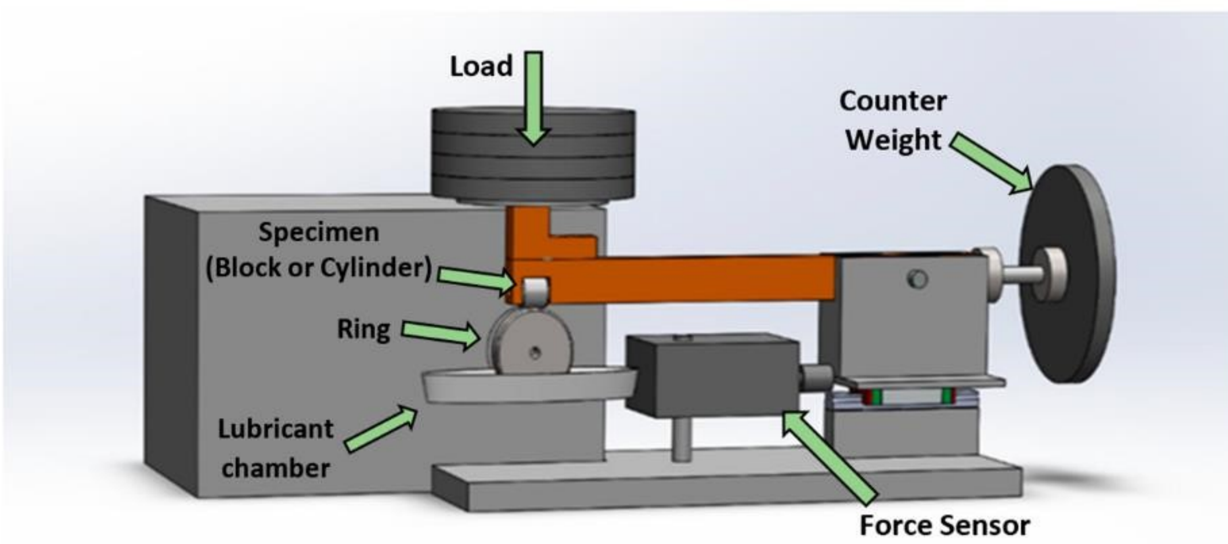


Figure 10: Tribotester with cross-cylinder configuration.

For the tribological experiments using cross-cylinders configuration, all tests were run following the ASTM G-83-96 standard [11] at a temperature of 25 ºC, 300 rpms and 1800s. All concentrations of vegetable oils were tested, and the best were selected for block on ring tribotester based on criteria of lowest volumetric wear. In stage 2, sliding wear tests were performed using the custom made tribotester with a block-on-ring configuration to determine COF based on ASTM G-077-05 [12]. The tribotester with block-on-ring configuration is shown in Figure 11.

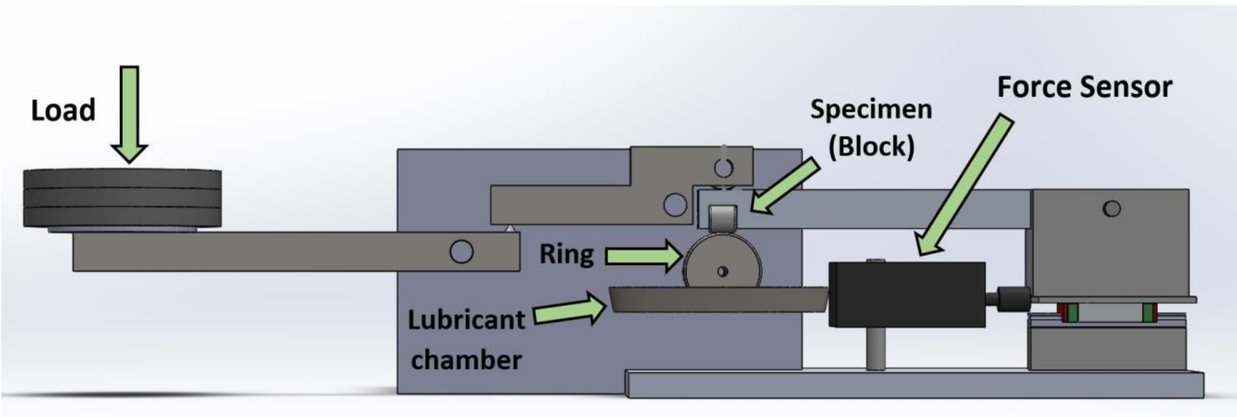


Figure 11: Schematic diagram of the block-on-ring tribotester.

For the block-on-ring experiments the test parameters were as followed, a load of 396N, temperature of 25ºC, 172 rpms, and 1200s. For the evaluation, the nano-lubricants were placed in the oil chamber allowing for constant lubrication, due to the centrifugal force of the rotating bearing. When doing any kind of tribological experiments especially block-on-ring initial setup is crucial. Wear scar must have uniform rectangular pattern, if excessively deviation occurs the run must be disregarded. Therefore, considerable attention was given to initial setup of the contact of the block with the cylindrical bearing. Setup image is shown below in Figure 12.

Figure 12: Block on Ring Initial Setup.

After experiment was over the wear was determined gravimetrically using an electronic balance (Mettler Toledo XS25DU) to an accuracy of 0.01 mg. Before the gravimetric measurements of wear, the cylinders and blocks were washed in soapy water, cleaned ultrasonically in acetone and methanol for 5 minutes each and left in the atmosphere-controlled room for 24 h to dry and thermally stabilize. Using the specific density of 8 g/cm^3 for AISI 304 steel the weight loss was converted into volume loss. For all the experiments the friction force was measured continuously using a Vernier Dual-Range Force Sensor.

3.4 Surface Characterization

Morphology of the wear scars on the worn specimens was analyzed with a Field Emission Scanning Electron Microscope (FE-SEM) ZEISS SIGMA VP (Carl Zeiss SBE, Thornwood, NY, USA) shown in Figure 5. Energy dispersive X-ray spectroscopy analysis was done on the specimen surface before and after the experiments to determine its chemical composition qualitatively and semi-quantitatively. The surface roughness of the specimens before the tribological tests and the surface roughness of the wear scars after the wear tests was measured by means of a Mahr Surf M300C profilometer, shown in Figure 13.

Figure 13: Roughness Tester Mahr 300c.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Morphology

Morphology analysis of the nanoparticles was done in order to better understand its role in the lubrication mechanisms. All images were done with a 50,000X magnification for consistency between images, and to allow comparison. According to the supplier, Silica (SiO_2) nanoparticles should have a diameter of 20-30nm. From the SEM image shown in Figure 14, it is observed that the nanoparticles are closer to 32.20 nm in diameter. Furthermore, the nanoparticles morphology of SiO_2 was fairly spherical in shape.

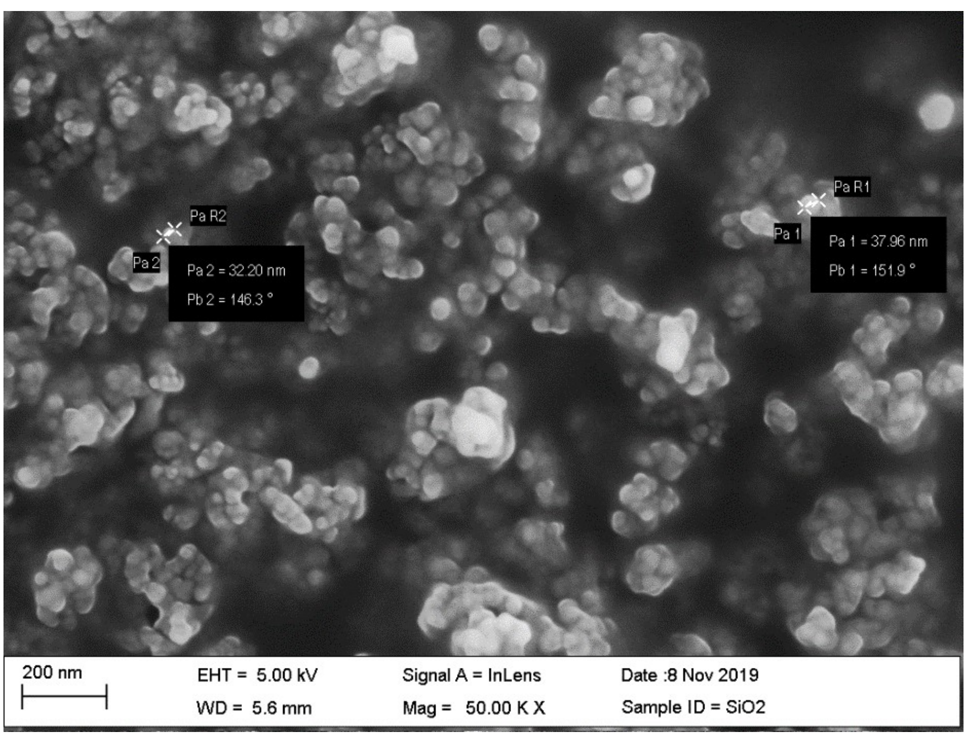


Figure 14: SEM micrograph of SiO_2 nanoparticles at 50,000X.

SEM image for TiO_2 nanoparticles are shown below in Figure 15. SEM micrograph shows the morphology of TiO_2 nanoparticles with particle sizes between 21 and 28nm. Furthermore, it can be observed that the nanoparticles are fairly spherical in shape, similar to SiO_2 nanoparticles.

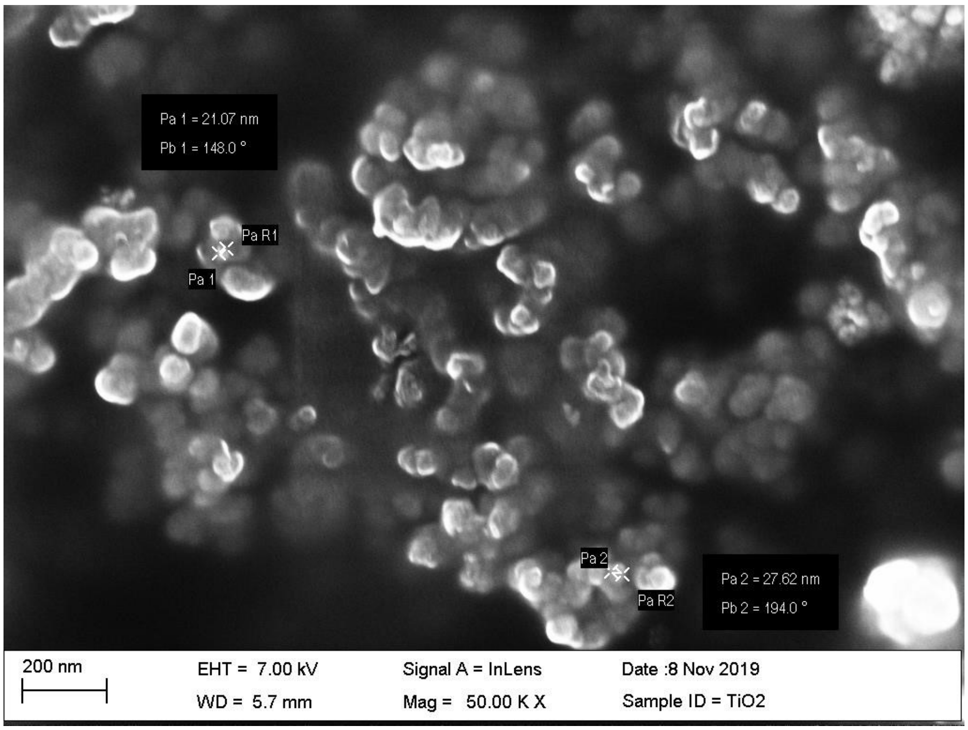


Figure 15: Scanning electron microscopy (SEM) micrographs of TiO_2 nanoparticles at 50,000X.

Figure 16 displays SEM images of the CuO nanoparticles. It is noted that the of size of the nanoparticles ranges between 38nm and 99nm. This particle size is a far greater range than SiO_2 and TiO_2 nanoparticles showed. From the SEM images it is also noted that the shape of CuO varies greatly from being fairly spherical to long oval shaped particles. This variation of nanoparticle morphology can affect the tribology behavior since test results consistency may be affected.

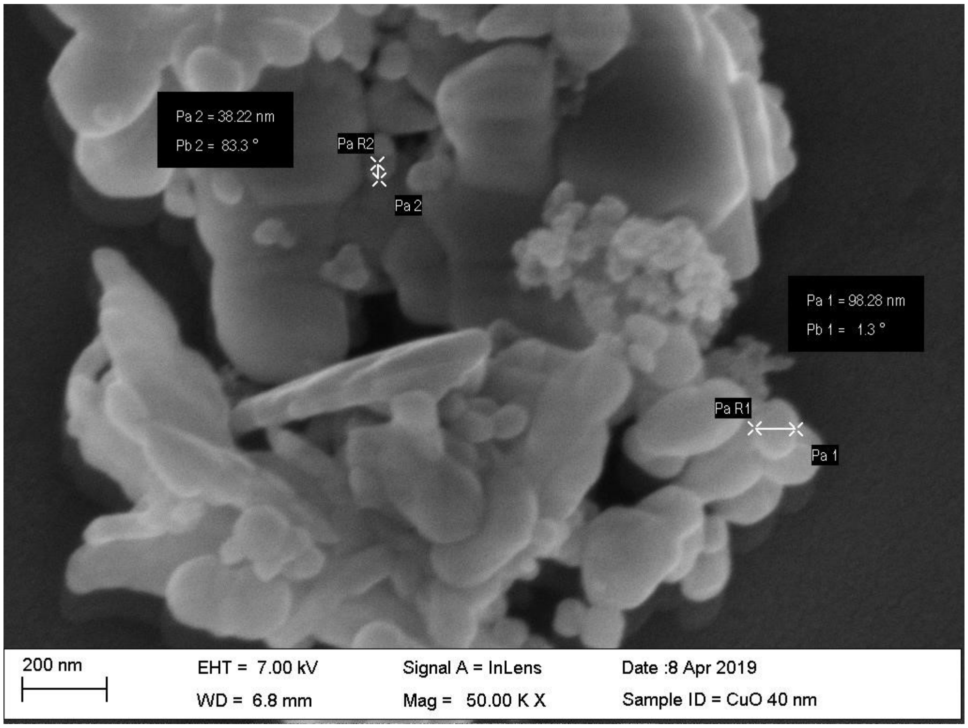


Figure 16: Scanning electron microscopy (SEM) micrographs of CuO nanoparticles.

Overall comparing the three nanoparticles, TiO_2 had the smallest diameter which restates manufacturer claim of the nanoparticles being 18nm. Although the observed diameters are slightly larger in general. This could be due to that the particles are still in clusters and what we are observing are the clusters and not the actual nanoparticles. In order to solve and prevent this issue nanoparticles were dispersed in ethanol and mixed thoroughly in an ultrasonic bath. From the ultrasonic bath it was noted that for-silica clusters existed, and it was hard to distinguish actual individual nanoparticles. Therefore, after initial images the new approach of mixing the nanoparticles was done using the ultrasonic probe mixer. This provided a more efficient way of mixing and allowed to see the nanoparticles better under the SEM. The images above were done using latter method in order to ensure the most possible separation of nanoparticle clusters.

4.2 Rheological Measurements Analysis

In order to better understand the behavior of the vegetable oils with nanoparticles as lubricant additives, rheological properties were studied. Rheological properties were experimentally evaluated for the three vegetable oils with SiO_2 and TiO_2 nanoparticles. Rheological properties for the vegetable-based lubricants are shown through Figures 17-26.

4.2.1 Rheological Analysis of Sunflower oil modified with nanoparticles

Figures 17 and 18 show the effect of different concentrations of SiO_2 (20 to 30nm) nanoparticles on sunflower base oil. It is noted that the base sunflower oil has the lowest viscosity of around of 73 cP. The addition of nanoparticles can alter the viscosity as seen in Figure 17. From Figure 17 it is evident that as the concentration of SiO_2 increases, the measured viscosity increases as well. The highest viscosity observed was of 128 cP at the highest concentration of 1.25% SiO_2. The infinite viscosity range for sunflower oil with SiO_2 nanoparticles is of 70 to 95 cP, which is a good indicate of a good lubricant. This range of viscosity is similar to mineral oil viscosity index of group I which are used for lubricating chainsaw and other cutting machinery.

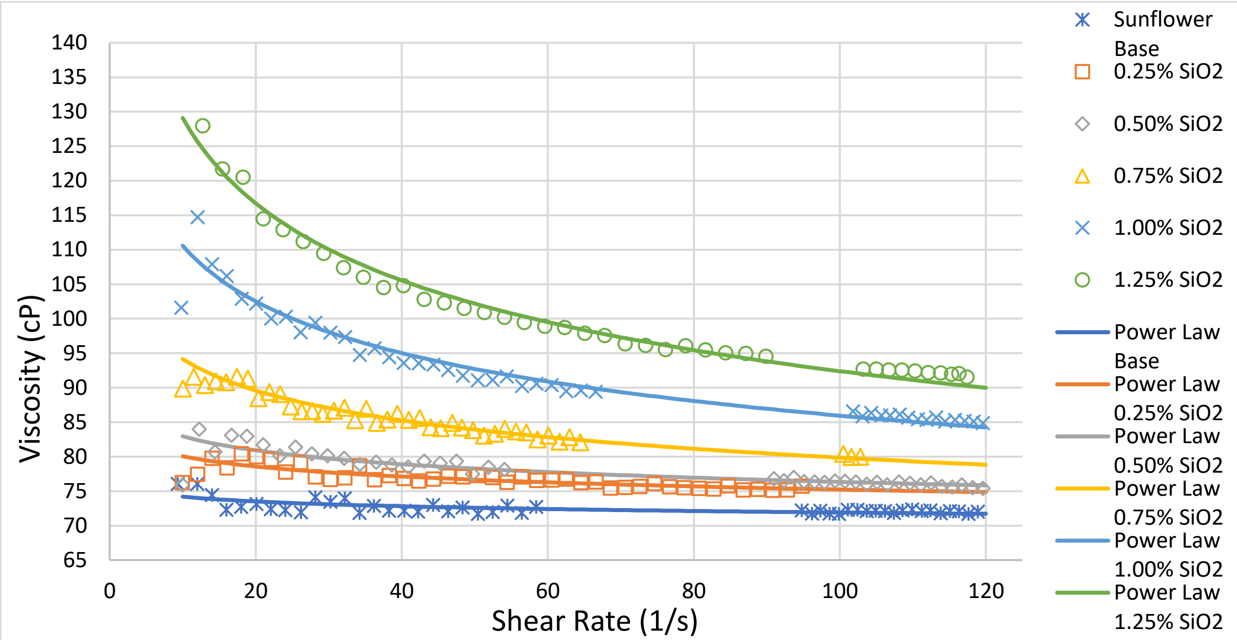


Figure 17: Effect of shear viscosity versus shear rate for SiO_2 dispersion in various weight fractions in sunflower base oil with the power-law applied.

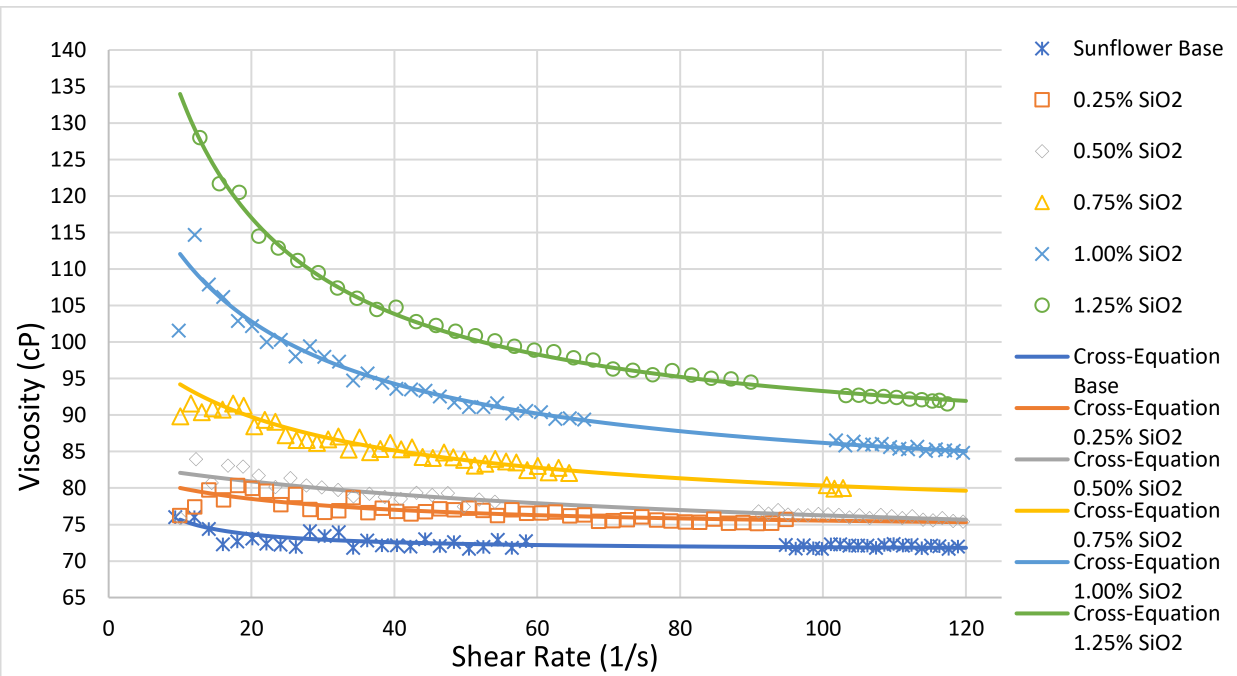


Figure 18: Effect of shear viscosity versus shear rate for SiO_2 dispersion in various weight fractions in sunflower base oil with the Cross model applied.

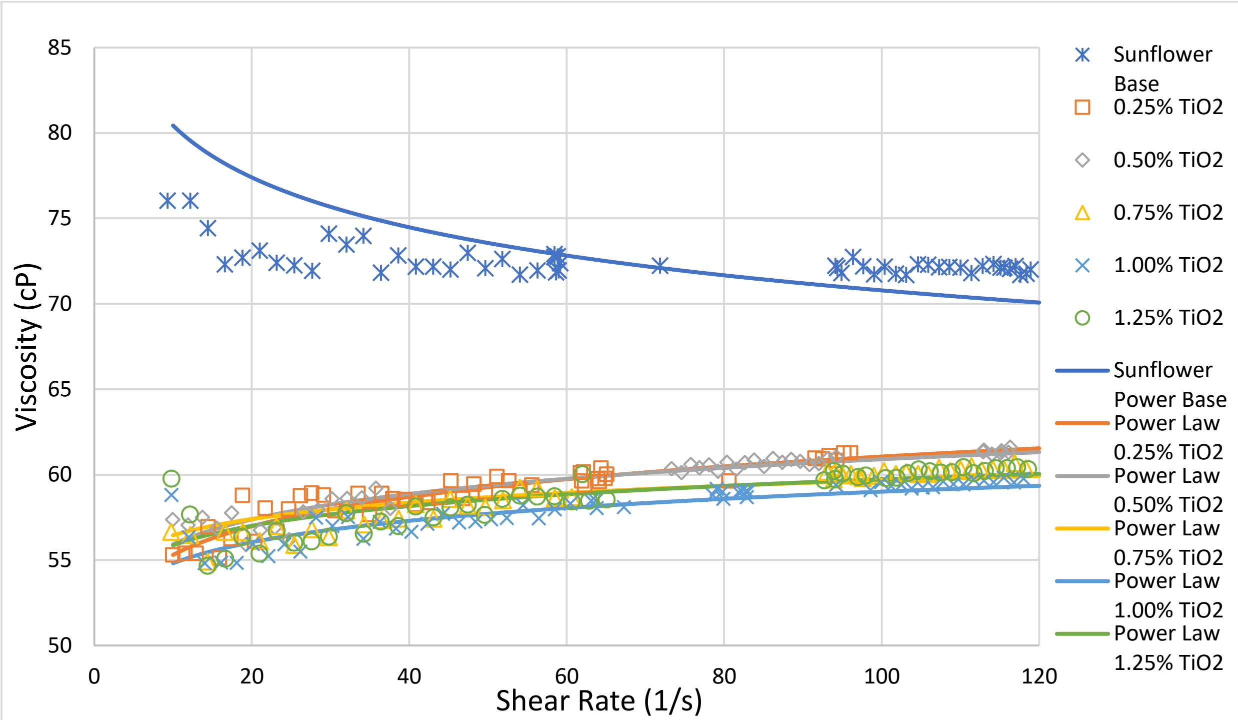


Figure 19: Effect of shear viscosity versus shear rate for TiO_2 dispersion in various weight fractions in sunflower base oil with the power-law applied.

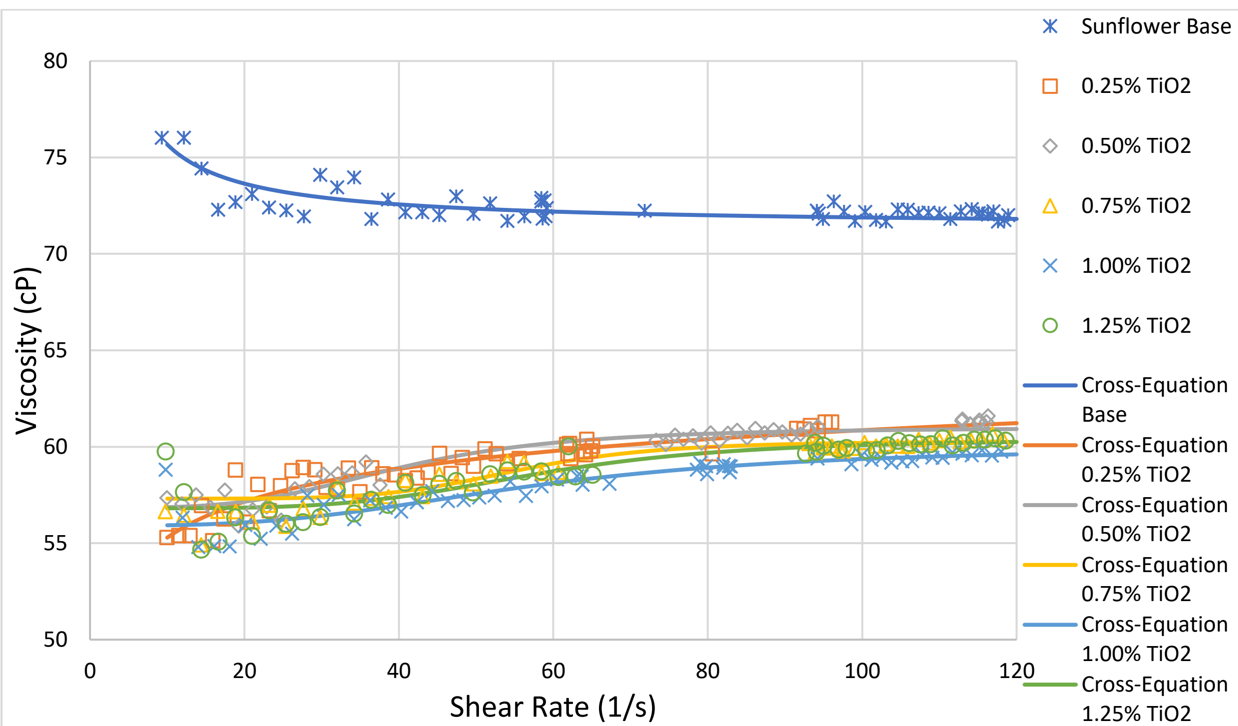


Figure 20: Effect of shear viscosity versus shear rate for TiO_2 dispersion in various weight fractions in sunflower base oil with the Cross model applied.

The effects of TiO_2 nanoparticles in sunflower base oil is shown in Figures 19 and 20. Contrary to SiO_2 nanoparticles, TiO_2 nanoparticles in sunflower oil lowered the viscosity. The viscosity showed similar behavior for 0.25% and 0.50% TiO_2 concentrations. The lowest viscosity behavior was observed at a 1.00% TiO_2 concentration. Similar behavior was also observed at 0.75% and 1.25% TiO_2 nanoparticle concentrations. Although the viscosity decreased with the addition of TiO_2, shear thickening behavior was observed when TiO_2 was added given that the power-law index was greater than 1. Similar results were obtained by Ghasemi et al. when they studied the rheological behavior of (TiO_2) nanoparticles dispersed in an engine lubricant oil [13]. It is well known that the nanoparticle size and concertation can affect the rheological properties of colloidal suspensions such as oil/nanoparticle systems [1].

4.2.2 Rheological Analysis of Grapeseed oil modified with nanoparticles

The rheological behavior grapeseed oil with SiO_2 nanoparticles as lubricant additives is shown in Figures 21 and 22. It is again evident that the viscosity is affected by the concentration of SiO_2 nanoparticles. Grapeseed base oil by itself has the lowest viscosity with an infinite viscosity of around 63 cP. As the concentration of SiO_2 increases the viscosity increases also, which is similar to what happens to sunflower oil viscosity when the same nanoparticle is introduced. Ultimately the highest viscosity recorded was of 96.14 cP at 10 1/s shear rate for 1.25% wt. concentration of SiO_2 nanoparticles. From Figure 22 it is noted that grapeseed oil is shear thinning in nature due to the viscosity decreases as shear rate increases. This shear thinning behavior is more prominent in high concentrations of SiO_2 nanoparticles.

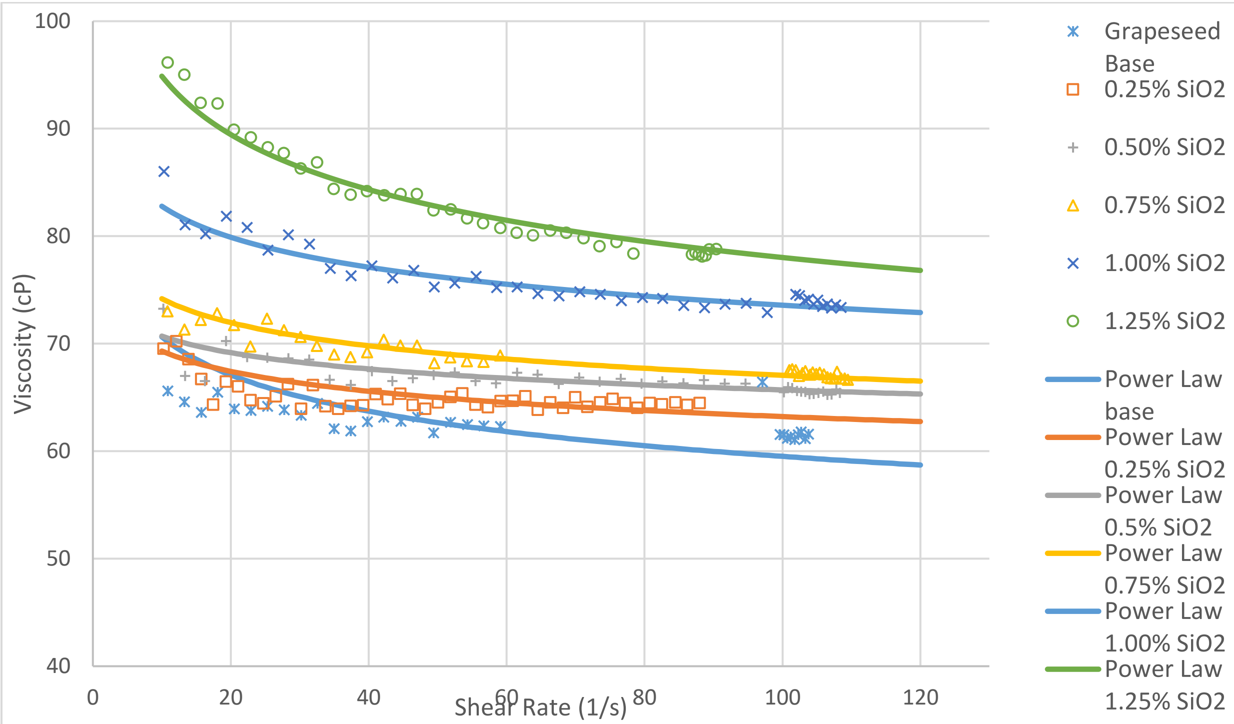


Figure 21: Effect of shear viscosity versus shear rate for SiO_2 dispersion in various weight fractions in Grapeseed base oil with the Power model applied.

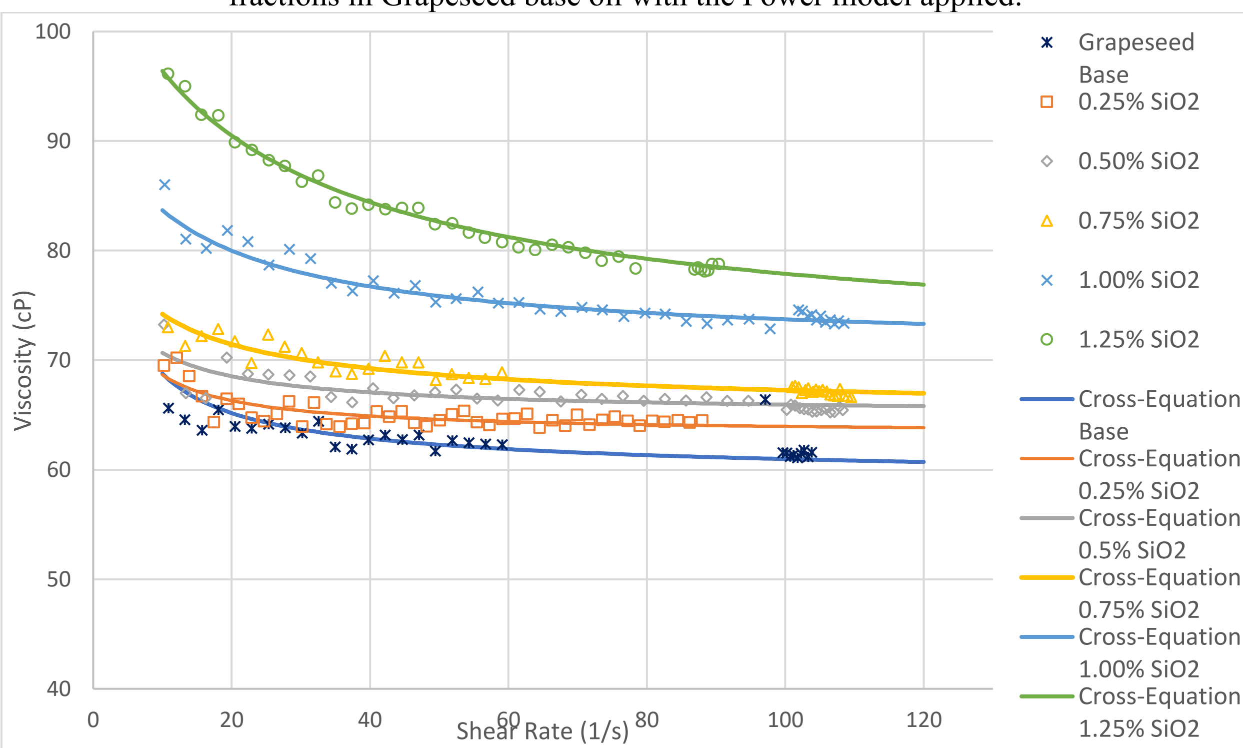


Figure 22: Effect of shear viscosity versus shear rate for SiO_2 dispersion in various weight fractions in Grapeseed base oil with the Cross model applied.

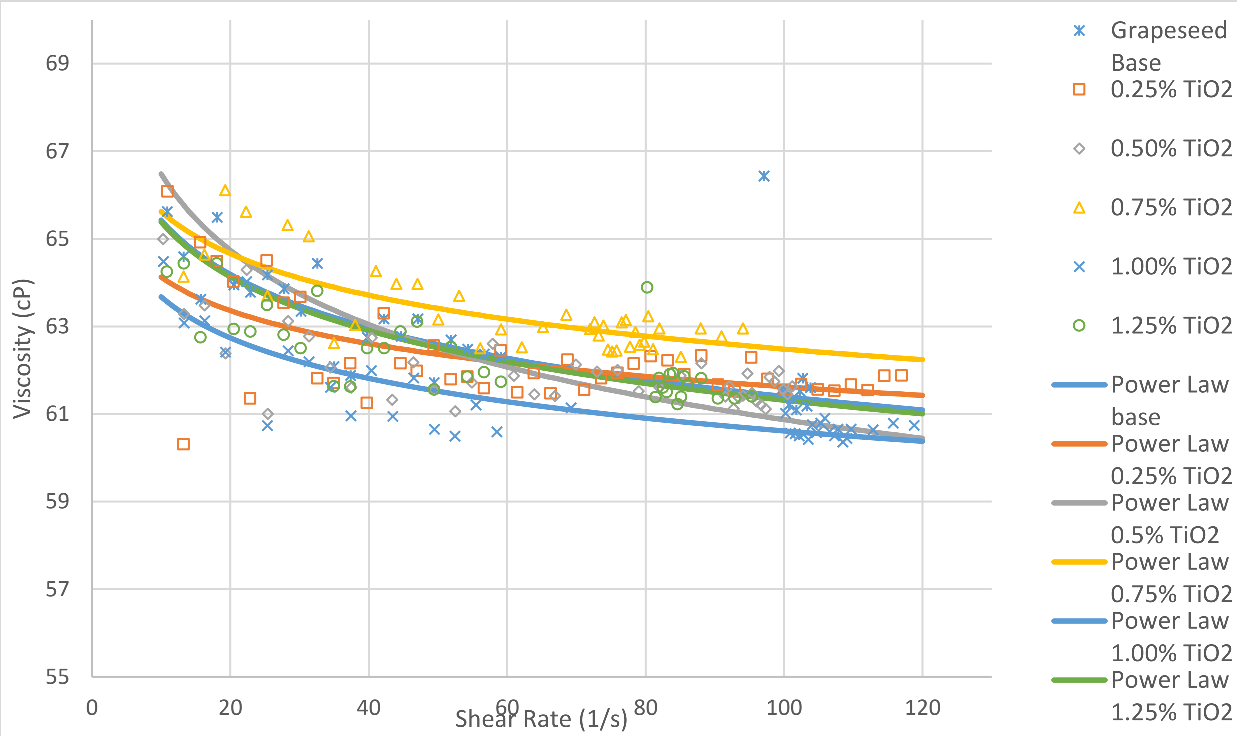


Figure 23: Effect of shear viscosity versus shear rate for TiO_2 dispersion in various weight fractions in Grapeseed base oil with the Power model applied.

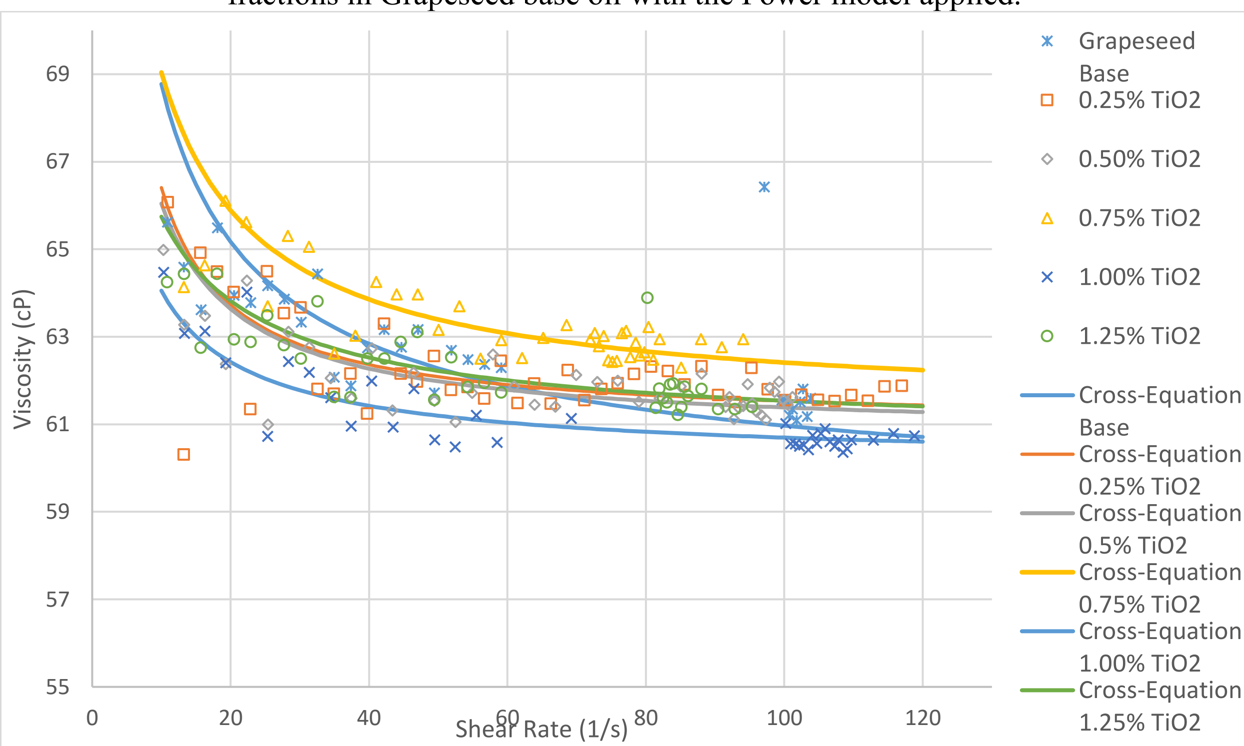


Figure 24: Effect of shear viscosity versus shear rate for TiO_2 dispersion in various weight fractions in Grapeseed base oil with the Cross model applied.

Figures 23 and 24 show the effects of TiO_2 in grapeseed base oil. The titanium oxide particles had little effect on the change of viscosity indicated by the range of the infinite viscosity being from 60 to 63 cP. Although the viscosity was not affected considerably, it can be noted that the highest viscosity is that of 0.75% wt. concentration and the lowest viscosity of for 1.00% wt concentration. Furthermore, viscosity has a shear thinning behavior meaning that as the shear rate increases the viscosity decreases. This behavior is opposite to the shear thickening the TiO_2 nanoparticles caused in sunflower oil.

4.2.3 Rheological Analysis of Coconut oil modified with nanoparticles

The rheological behavior of coconut base oil is shown in Figures 25 - 28. For all coconut rheometer experiments it is noted that initially the viscosity decreases then remains constant as it approaches 120 1/s shear rate. Therefore, the viscosity experiences shear thinning before approaching a constant. Figures 25 and 26 present viscosity at different concentrations of SiO_2 in coconut oil. For concentrations of 0.75% and lower the viscosity steady out at lower values when compared to coconut without additives. For concentrations above 0.75% SiO_2 the viscosity was greater than the base oil and it experienced shear thinning behavior until the end. It is evident that viscosity is dependent of the concentration of SiO_2 in coconut base oil.

Rheological behavior for coconut oil with TiO_2 nanoparticles is shown in Figures 27 and 28. As concentration of TiO_2 increases the viscosity increases also. Initially the viscosity displays some shear thinning as indicated by the power law index of less than one when fitting data into empirical models. At higher shear rates the viscosity remains constant. Therefore, concluding that viscosity behavior of the nanolubricant is dependent of the concentration.

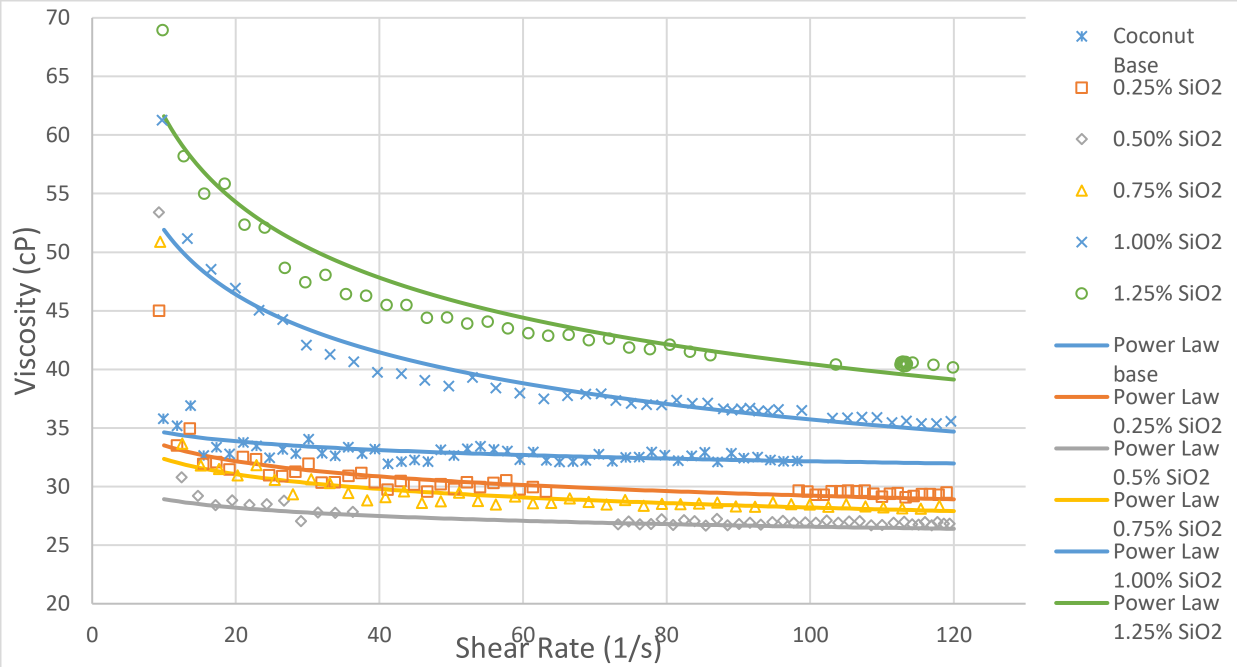


Figure 25: Effect of shear viscosity versus shear rate for SiO_2 dispersion in various weight fractions in coconut base oil with the Power model applied.

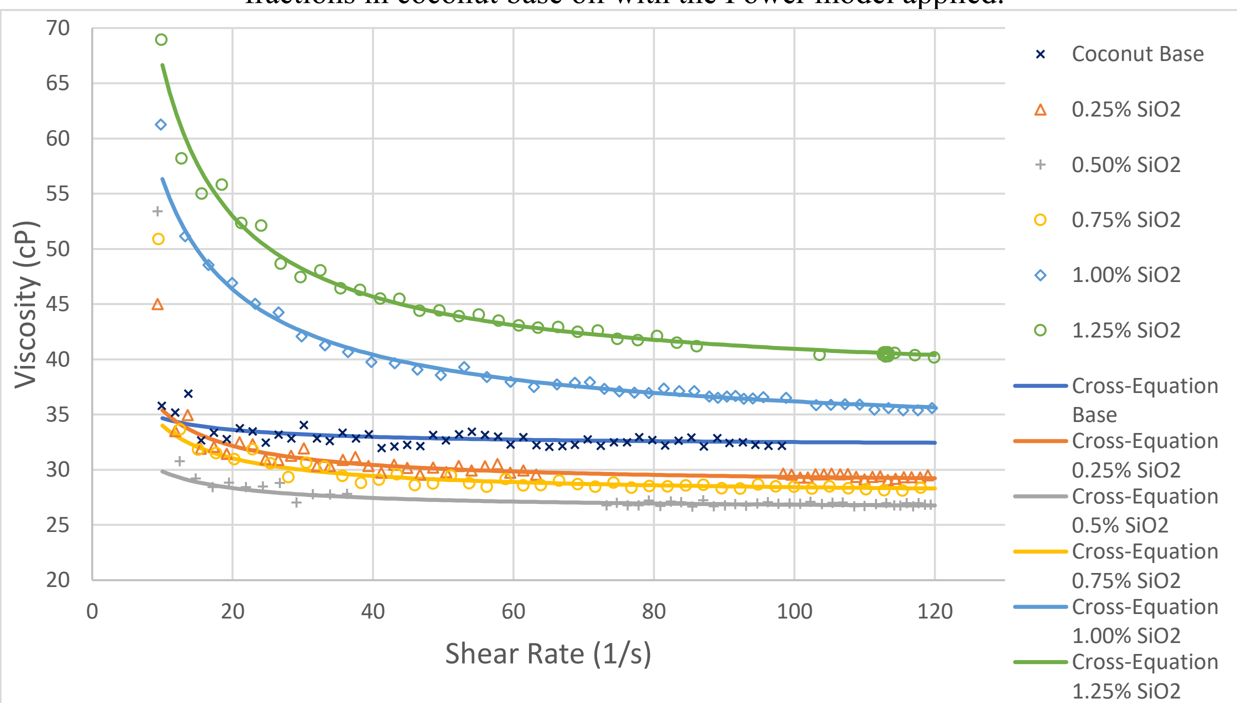


Figure 26: Effect of shear viscosity versus shear rate for SiO_2 dispersion in various weight fractions in coconut base oil with the Cross model applied.

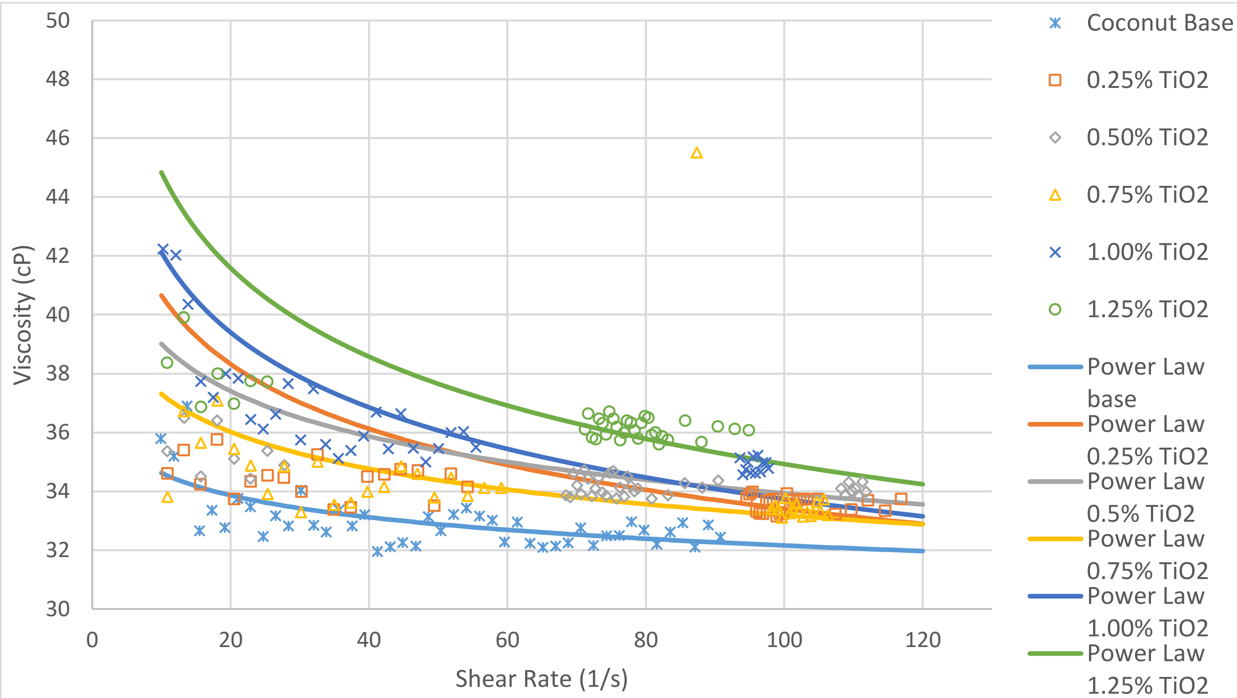


Figure 27: Effect of shear viscosity versus shear rate for TiO_2 dispersion in various weight fractions in coconut base oil with the Power model applied.

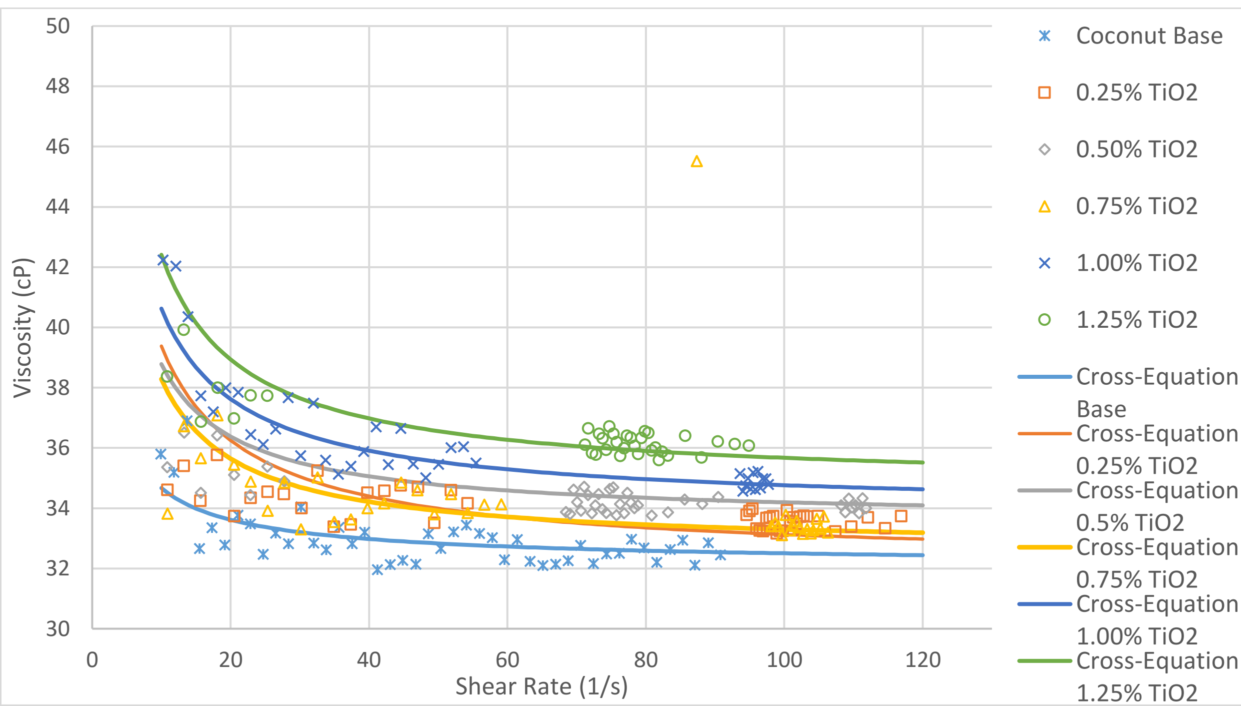


Figure 28: Effect of shear viscosity versus shear rate for TiO_2 dispersion in various weight fractions in coconut base oil with the Cross model applied.

4.3 Rheology Models

Although the rheometer provides the viscosity at the intervals of 10 to 120 1/s shear rate, it is often needed to find the viscosity at another value than the one obtained experimentally. This scenario often occurs where manufacturers need the viscosity at an exact shear rate to calculate the amount of power needed to push the fluid in the tubes. If it is too viscous, then the fluid will not flow and lubricate properly. Therefore, to overcome this obstacle we decided to model the rheological properties using the power and Cross equation model.

4.3.1 Power Model

The simplest model to represent viscosity versus shear rate behavior is the power law. The power law consists two parameter which help express viscosity (η) as shown in equation 1.

$$\eta = K(\dot{\gamma})^{n-1} \tag{1}$$

Where *K* represents the consistency coefficient and *n* the power law index. When $n < 1$ it represents shear thinning behavior, when $n = 1$ it represents a Newtonian fluid, and when $n > 1$ it represents shear thickening behavior. The power law fitted equations are shown on Figures 17, 19, 21, 23, 25, and 27.

4.3.2 Cross Model

To further improve empirical model the cross model can be used. Equation 2 represents the Cross model.

$$\eta = \frac{\eta_0 - \eta_\infty}{1 + (K\dot{\gamma})^n} + \eta_\infty \tag{2}$$

where η_0 represents viscosity at a very low shear rate, η_∞ represents infinite viscosity, *K* is consistency index, and n is the flow behavior index [13].

The Cross-equation fitted data for all the vegetable oils with SiO_2 and TiO_2 are shown in Figure 18, 20, 22, 24, 26, and 28 respectively. The parameters for the empirical models are shown in Table 4. Using the coefficient of determination (R^2) the better empirical model was found to be the cross-equation. The closer the value of R^2 is to 1 the more precise the empirical model is representing the data. A value of 1 means that the data is perfectly represented. Overall, the Cross-equation provided higher R^2 values. This is due to that at higher shear rate values the lubricants behave in a nonlinear fashion. Therefore, the parameters of η_0 and η_∞ are needed to express this behavior. These parameters are not used for the power law and from the past figures it is evident these contributed to the lower R^2 values since it was at the ends that the power law model struggled to represent precise the data points.

Table 4: Regression parameters for some vegetable oils.

Model	Configuration	K	n	R^2	η_0	η_∞	SSE
Power Law	Sunflower Oil w/1.25% SiO_2	0180.4	0.8547	0.8516	N/A	N/A	110.3
Cross Equation	Sunflower Oil w/1.25% SiO_2	.1134	.9874	.8877	190	84.49	8.347
Power Law	Sunflower Oil w/1.00% TiO_2	50.92	1.032	.7395	N/A	N/A	27.16
Cross Equation	Sunflower Oil w/1.00% TiO_2	0.0175	3.3032	.8245	55.91	59.99	18.3
Power Law	Coconut Oil w/ 1.25% SiO2	93	0.8174	0.9192	N/A	N/A	116.1
Cross-Equation	Coconut Oil w/ 1.25% SiO2	271.1	0.9029	0.9841	370	37.27	22.87
Power Law	Coconut Oil w/ 1.00% TiO_2	52.59	0.9036	0.6671	N/A	N/A	25.11
Cross-Equation	Coconut Oil w/ 1.00% TiO_2	1.053	0.92	0.8364	99.52	33.87	17.66

4.4 Tribological Results

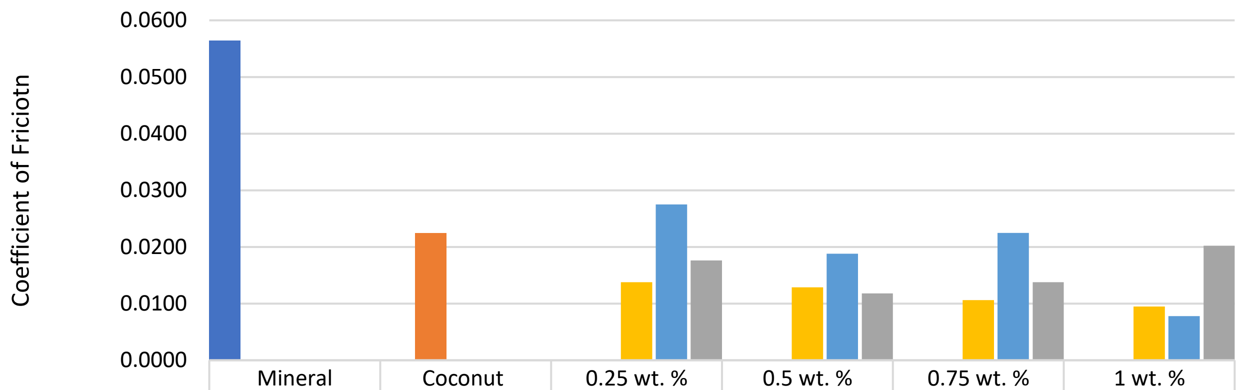
The tribological performance of coconut oil, sunflower oil, and grapeseed oil was assessed with and without nanoparticle additions. The coefficient of friction and wear loss values were found. These values were determined from the tribological tests under block-on-ring and cross-cylinder configuration. Equation 3 was used to calculate the coefficient of friction and is shown below,

$$\mu = F/N \tag{3}$$

Where F is the friction force, N is the normal force applied, and μ is the coefficient of friction. The friction force is calculated using the force sensor as shown in Figures 10 and 11. The normal force is the force applied vertically at the location of the sample. For the tribological tests using cross-cylinder configuration, the normal force was applied using a balancing arm with a counterweight for fine adjustments. Although this configuration worked fine for block-on-ring the maximum force that could be applied was of 40N, which is to small since it will not create a scar in the block samples. Therefore, a modification to the current block-on-ring configuration was needed. The block-on-ring configuration uses moment arms to multiply the force by 26.4 times. This allows for the force to be applied to be of 396N which is almost 10 times as much as before. Using the results from both the cross-cylinders and block-on-ring experiments the final conclusions were obtained.

4.4.1 Preliminary Results Cross-Cylinder

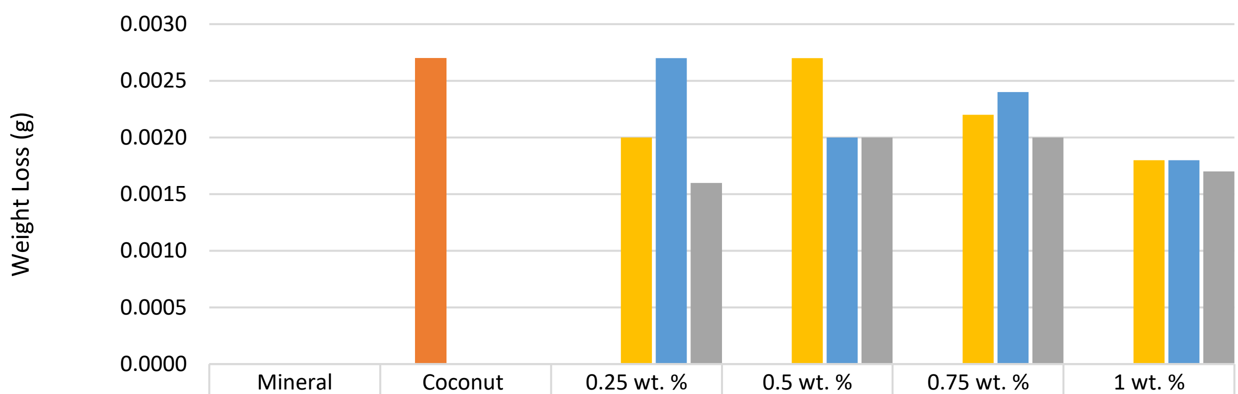
Initially, tribological tests under cross-cylinder configuration were conducted prior to block-on-ring experiments. This was done to screen the vegetable oil tribological performance with SiO_2, CuO, and TiO_2 nanoparticles as lubricant additives. This preliminary data will aid us in the selecting process for block-on-ring tests. Only the best performance vegetable oil and nanoparticles will be allowed to be retested for the block on ring configuration. Figures 29 - 34 show the tribological results obtained using the cross-cylinder configuration.



	Mineral	Coconut	0.25 wt. %	0.5 wt. %	0.75 wt. %	1 wt. %
Mineral	0.0565					
Coconut Control		0.0225				
Coconut SiO2			0.0138	0.0129	0.0106	0.0095
Coconut CuO			0.0275	0.0188	0.0225	0.0078
Coconut TiO2			0.0176	0.0118	0.0138	0.0202

Mineral   Coconut Control   Coconut SiO2   Coconut CuO   Coconut TiO2

Figure 29: COF vs concentration for coconut oil with nanoparticles.



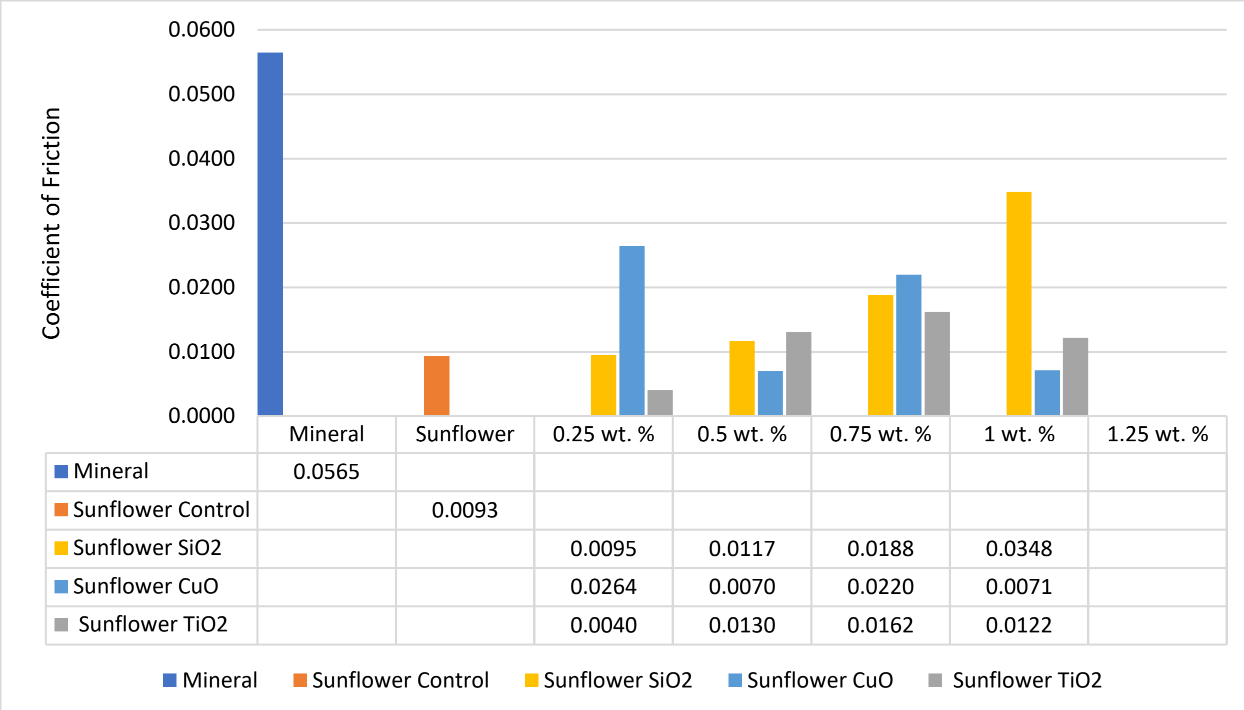
	Mineral	Coconut	0.25 wt. %	0.5 wt. %	0.75 wt. %	1 wt. %
Mineral	0.0000					
Coconut Control		0.0027				
Coconut SiO2			0.0020	0.0027	0.0022	0.0018
Coconut CuO			0.0027	0.0020	0.0024	0.0018
Coconut TiO2			0.0016	0.0020	0.0020	0.0017

Mineral   Coconut Control   Coconut SiO2   Coconut CuO   Coconut TiO2

Figure 30: Weight loss vs concentration for coconut oil.

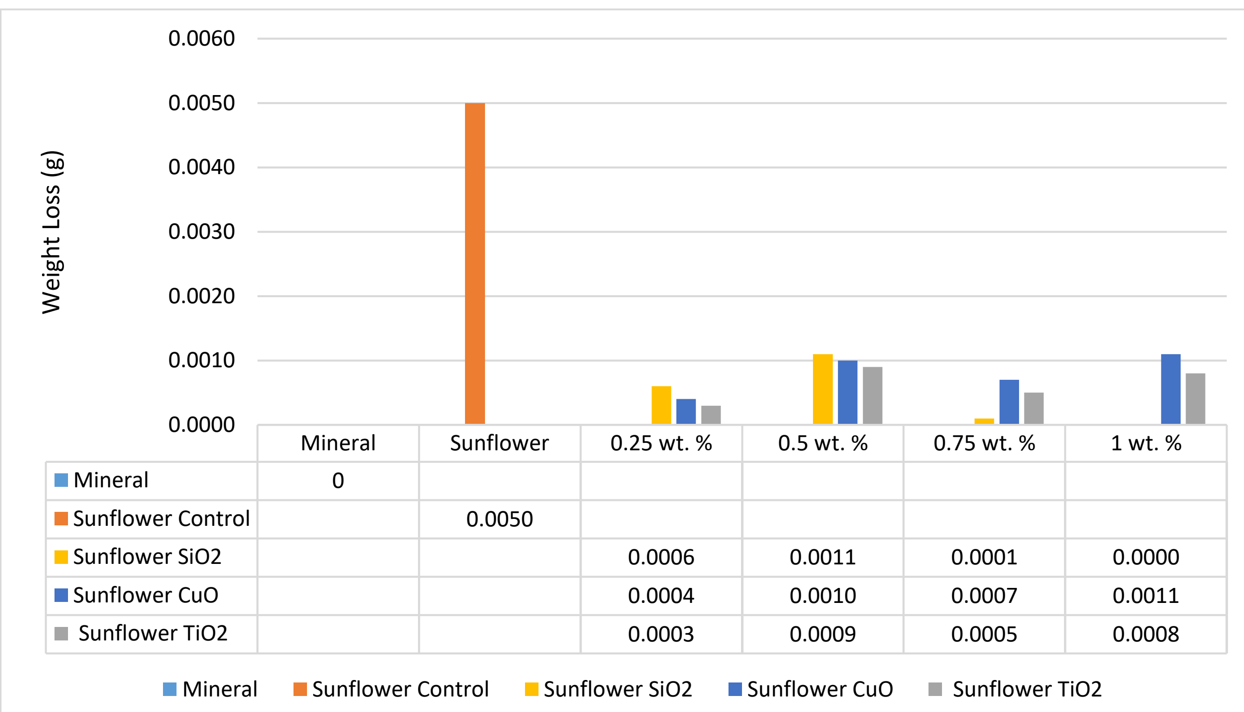
From Figure 29 the first aspect to note is the high coefficient of friction is mineral oil of 0.056. This is relatively high when compared to vegetable oil counterparts. When comparing the performance of the nanoparticles it is noted that at 1.25% concentrations SiO_2 and CuO had the lowest COF. The coefficient of friction of coconut oil was lowered by 57.7, 65.3, and 47.5% by adding SiO_2, CuO, and TiO_2 nanoparticles respectively. When observing the weight loss values of coconut oil in Figure 30 it is evident that mineral oil is superior. Mineral oil weight loss is lower than what the Mettler Toledo balance was able to measure since it reported a value of 0g. Although coconut oil experienced more wear the weight loss was decreased by 33.3, 33.3, and 40.7% by adding SiO_2, CuO, and TiO_2 nanoparticles respectively.

Figure 31 and 32 display the effects of nanoparticles on coefficient of friction and weight loss respectively on sunflower oil. Like coconut oil the COF for the vegetable oil was lower when compared to the mineral oil. As SiO_2 concentration increased the coefficient of friction. For CuO the coefficient of friction was the lowest at 1.25 wt.% concentration. For TiO_2 the lowest coefficient of friction was of 0.0040 for 0.25 wt.% concentration. For weight loss it is observed that the base sunflower oil has the highest weight loss. When analyzing the concentrations, it is noted that sunflower oil performs the best at different concentrations of nanoparticles depending on the particle. The best performance was for 1.00 wt.% SiO_2 where it matched mineral oil weight loss. The next closest was of 0.25 wt.% TiO_2 where the weight loss was of 0.003g. Therefore, sunflower oil performance as base oil is poor for wear protection but can be enhanced 100% by adding nanoparticles. Note this is only for this case study and performance can change due to many variables such as change of speed, load, material, temperature, environment, and many more variables.



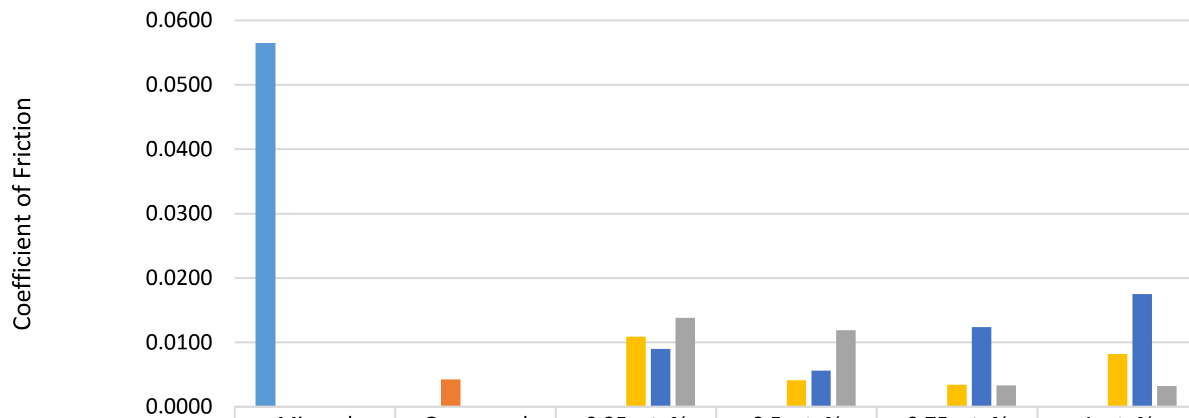
	Mineral	Sunflower	0.25 wt. %	0.5 wt. %	0.75 wt. %	1 wt. %	1.25 wt. %
Mineral	0.0565						
Sunflower Control		0.0093					
Sunflower SiO2			0.0095	0.0117	0.0188	0.0348	
Sunflower CuO			0.0264	0.0070	0.0220	0.0071	
Sunflower TiO2			0.0040	0.0130	0.0162	0.0122	

Figure 31: COF vs Concentration for Sunflower oil.



	Mineral	Sunflower	0.25 wt. %	0.5 wt. %	0.75 wt. %	1 wt. %
Mineral	0					
Sunflower Control		0.0050				
Sunflower SiO2			0.0006	0.0011	0.0001	0.0000
Sunflower CuO			0.0004	0.0010	0.0007	0.0011
Sunflower TiO2			0.0003	0.0009	0.0005	0.0008

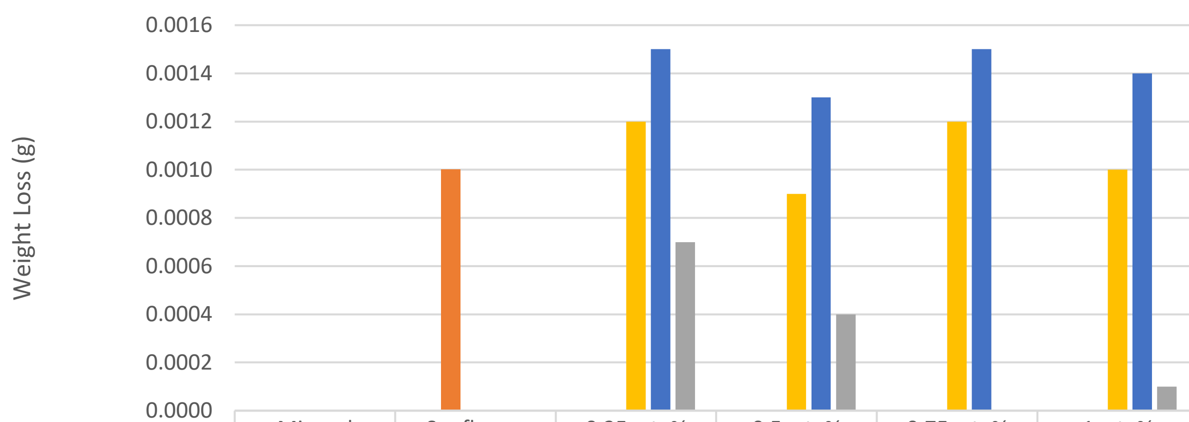
Figure 32: Weight loss vs Concentration for sunflower oil.



	Mineral	Grapeseed	0.25 wt. %	0.5 wt. %	0.75 wt. %	1 wt. %
Mineral	0.0565					
Grapeseed Control		0.0042				
Grapeseed SiO2			0.0109	0.0041	0.0034	0.0082
Grapeseed CuO			0.0090	0.0056	0.0124	0.0175
Grapeseed TiO2			0.0138	0.0119	0.0033	0.0032

Mineral Grapeseed Control Grapeseed SiO2 Grapeseed CuO Grapeseed TiO2

Figure 33: COF vs Concentration for Grapeseed oil for cross-cylinder.



	Mineral	Sunflower	0.25 wt. %	0.5 wt. %	0.75 wt. %	1 wt. %
Mineral	0					
Grapeseed Control		0.0010				
Grapeseed SiO2			0.0012	0.0009	0.0012	0.0010
Grapeseed CuO			0.0015	0.0013	0.0015	0.0014
Grapeseed TiO2			0.0007	0.0004	0.0000	0.0001

Mineral Grapeseed Control Grapeseed SiO2 Grapeseed CuO Grapeseed TiO2

Figure 34: Weight loss vs Concentration for Grapeseed Oil for cross-cylinder.

Figures 33 and 34 display the effect of nanoparticles on grapeseed oil's coefficient of friction and weight loss. Comparable to coconut and sunflower oil, the coefficient of friction for the grapeseed is lower than the mineral oil. For SiO_2 nanoparticles only at 0.75 wt. % did the coefficient of friction lowered. Grapeseed friction increased with CuO nanoparticles and using TiO_2 nanoparticles the coefficient of friction lowered to 0.0033 and 0.0032 using 0.75 and 1.00 wt.% concentration respectively. Overall, the best performance was shown in vegetable oil enhanced with SiO_2 and TiO_2 nanoparticles. But the low weight loss values leave room for error so therefore, using a block on ring test will provide higher loads and more wear that will allow us to see more clearly the bigger picture. The following section will highlight the effects of SiO_2 and TiO_2 nanoparticles in three vegetable oils using a modified tribotester in a block on ring configuration.

4.4.2 Block on Ring Results

From the preliminary runs it was selected that SiO_2 and TiO_2 nanoparticles performed better than CuO nanoparticles. Therefore, due to this reason it was selected that those concentrations be tested in the under block-on-ring configuration. Figures 35 -38 show the tribological results obtained from the block-on-ring experiments for sunflower oil enhanced with the addition of SiO_2 and TiO_2 nanoparticles.

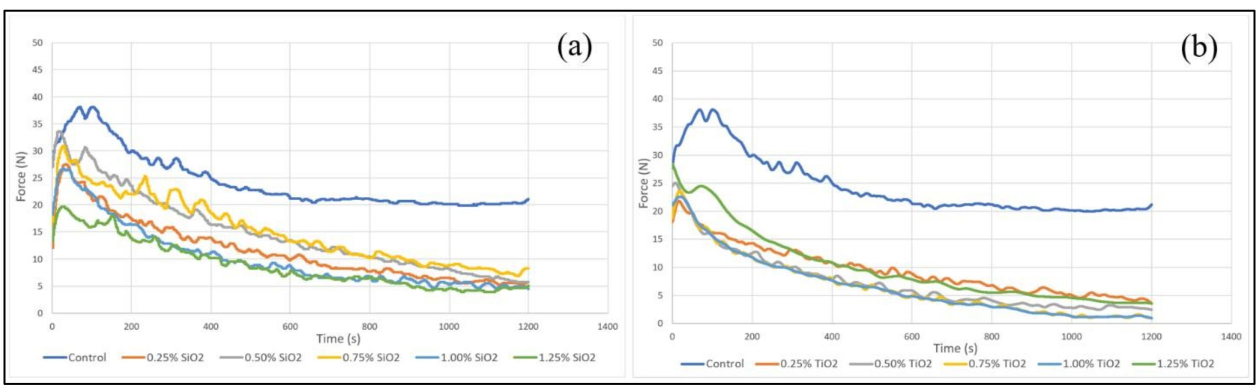


Figure 35: Friction force results for sunflower oil modified with: (a) SiO_2, and (b) TiO_2 nanoparticles.

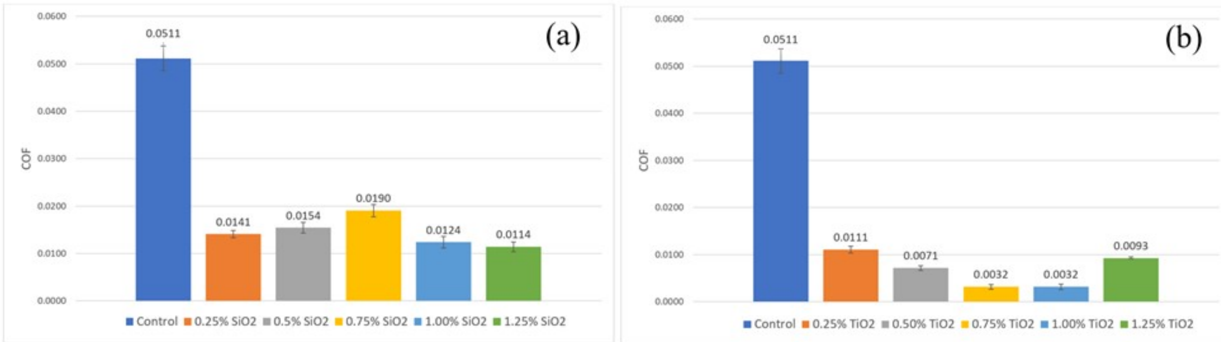


Figure 36: COF results for sunflower oil modified with: (a) SiO_2, and (b) TiO_2 nanoparticles.

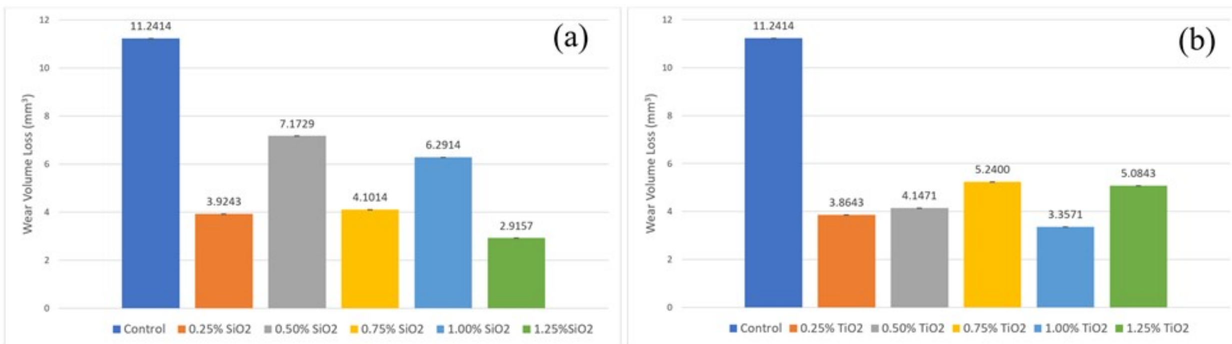


Figure 37: Mean volumetric wear of AISI 304 cylinders lubricated with sunflower oil modified with: (a) SiO_2, and (b) TiO_2 nanoparticles.

The coefficients of friction shown in Figure 36 were calculated in the steady state which is the final times of Figure 35. This was done for all experiments for consistency. Vegetable oils were not compared to mineral oils in this section due that it was not possible for mineral oil to finish the experiment regardless of trials. Mineral oil would immediately have excessive wear characterized by a high-pitched noise and the experiment had to be stopped to ensure safety of equipment. From Figure 35(a), it is noted that the addition of SiO_2 nanoparticles decreases the friction force. The coefficient of friction also lowered with the addition of nanoparticles which is similar to Peng and coworkers findings [30]. For sunflower oil with SiO_2, the coefficient of friction lowered from 0.0511 which corresponds to sunflower without nanoparticles to 0.0141 corresponding to 0.25% SiO_2 concentration, as shown on Figure 36a. From there, the COF increased up to 0.0190 at 0.75% SiO_2 and then afterwards decreased to its minimum of 0.0144 corresponding to a concentration of 1.25% SiO_2. The effect of TiO_2 nanoparticles on the COF is shown on Figure 36b. TiO_2 nanoparticles lowered the coefficient of friction which is an agreement with Saravanakumar and co-workers [32]. As the concentration of nanoparticles increases the COF decreases until the TiO_2 concentration reaches 1.00%, as shown in Figure 36b. By adding SiO_2 and TiO_2 nanoparticles to the sunflower based oil the COF was decreased by 77.69% and 93.73% respectively.

The volumetric wear loss of the AISI 304 stainless steel specimens after the block on ring runs is shown in Figure 37. From Figure 37a it can be observed that as the addition of SiO_2 the volumetric wear decreased initially then increased, but eventually reaching a minimum at the highest SiO_2 concentration of 0.25% SiO_2. Compared to the sunflower base oil without nanoparticle additives, the addition of 1.25% SiO_2 lowered the volumetric wear by 74.06%. Similar to the SiO_2 nanoparticles, the addition of TiO_2 nanoparticles lowered the volumetric wear. At the concentration of 1.00% TiO_2 it can be observed that the volumetric wear decreased by 70.13% compared to sunflower base oil, as shown in Figure 37b.

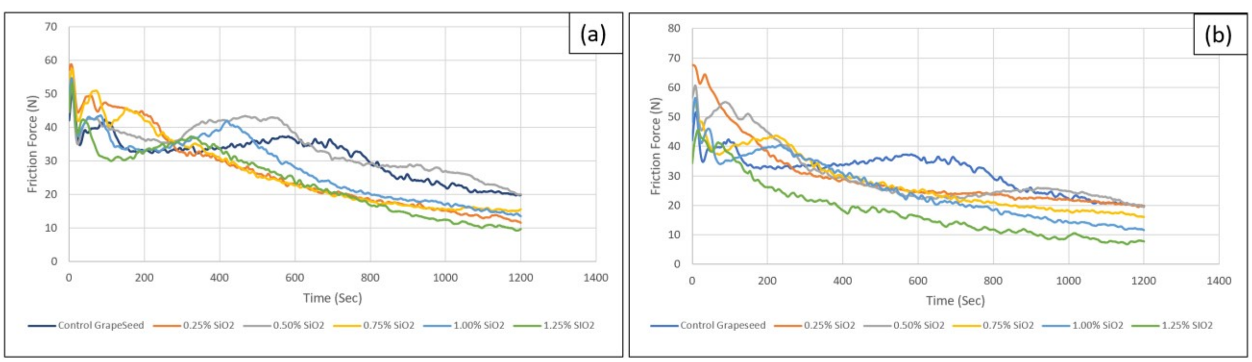
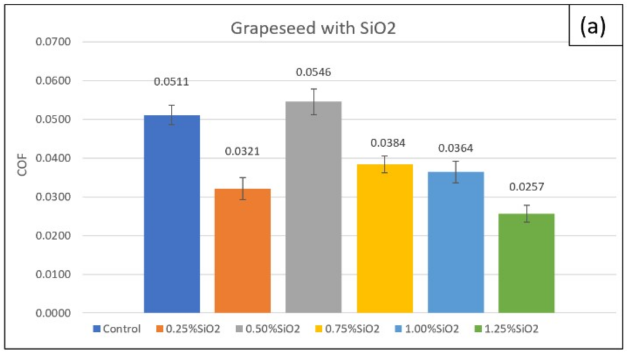


Figure 38: Friction force results for grapeseed oil modified with (a) SiO_2 and (b) TiO_2 nanoparticles.



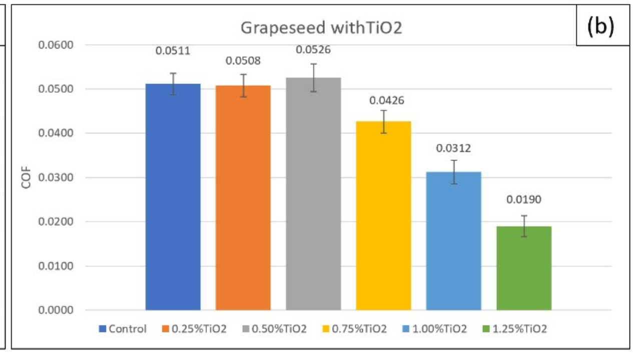
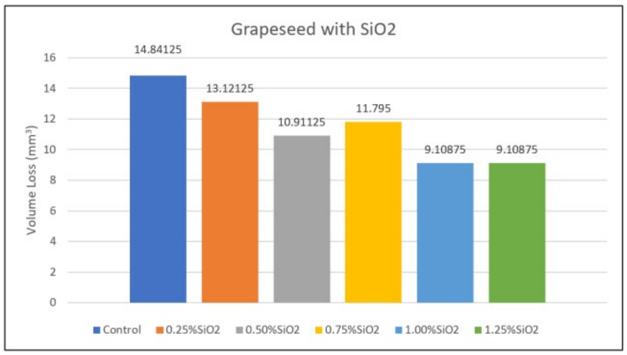


Figure 39: COF results for grapeseed oil modified with: (a) SiO_2, and (b) TiO_2 nanoparticles.



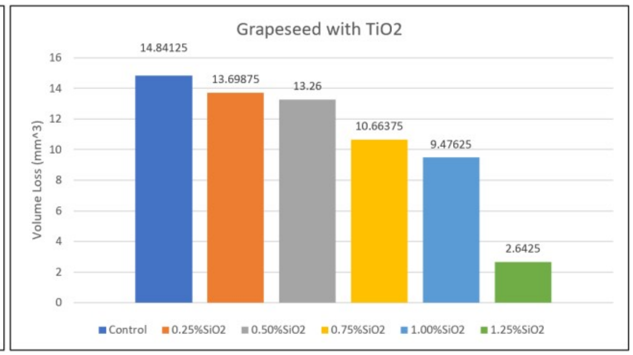


Figure 40: Mean volumetric wear of AISI 304 cylinders lubricated with sunflower grapeseed oil modified with: (a) SiO_2, and (b) TiO_2 nanoparticles.

Figures 38 -40 show the tribological results obtained from the block-on-ring experiments for grapeseed oil enhanced with the addition of SiO_2 and TiO_2 nanoparticles. Figure 38 shows the friction force obtained from the block on ring experiments for grapeseed oil with SiO_2 and TiO_2 nanoparticles. Figure 39 then was obtained from the steady state portion of the Figure 38. From Figure 38a it is noted that for 0.50% and 1.00% SiO_2 concentration there is sudden rise in friction force in between 200 and 600s then proceeds to lower. This rise of friction is not noted in TiO_2 nanoparticles as shown in Figure 38b. The COF of friction is shown if Figure 39 and it shows there exists an optimal concentration of nanoparticles that will lower the friction. For SiO_2 and TiO_2 this optimal concentration is 1.25% which lowered COF by 49.70% and 62.8% respectively. The weight loss was measured and converted to volumetric loss and the values for grapeseed oil are shown in Figure 40. Both the addition of SiO_2 and TiO_2 nanoparticles lowered the volumetric loss by 38.6% and 82.2% respectively. For grapeseed oil the optimal concentration of SiO_2 and TiO_2 nanoparticles exist at 1.25% concentration.

Figures 41 -43 show the tribological results obtained from the block-on-ring experiments for coconut oil enhanced with the addition of SiO_2 and TiO_2 nanoparticles. From figure 41b it is noted that concentration of 0.50 wt% TiO_2 did not finish the experiment from the two trials it ran and therefore the results for COF and volumetric wear loss are not presented. The reason the experiment did not finish is due to the friction increased around 590s causing excessive wear and due to safety concerns the experiment was paused. The addition of SiO_2 nanoparticles lowered the friction meanwhile the addition of TiO_2 nanoparticles increased the friction when compared to coconut base oil. In the other hand the addition of both 0.25 wt% SiO_2 and 0.75 wt% TiO_2 decreased the volumetric wear by 67.51% and 50.13% respectively.

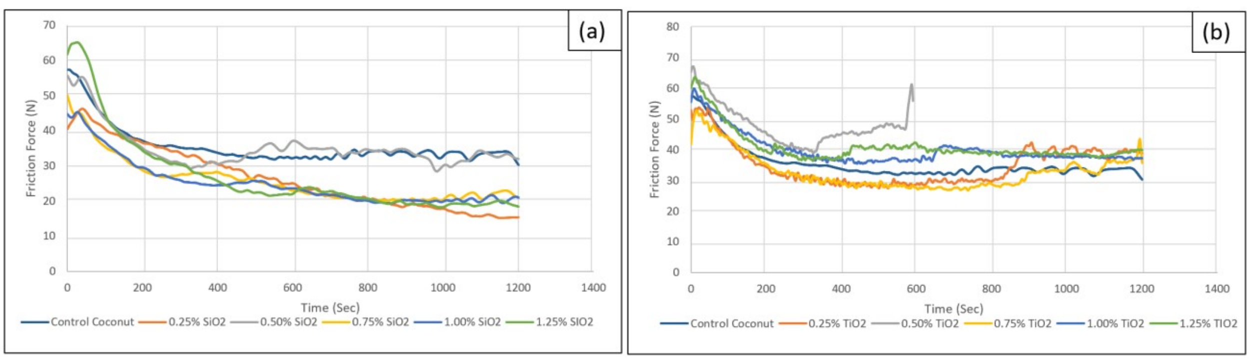


Figure 41: Friction force results for coconut oil modified with (a) SiO_2 and (b) TiO_2 nanoparticles.

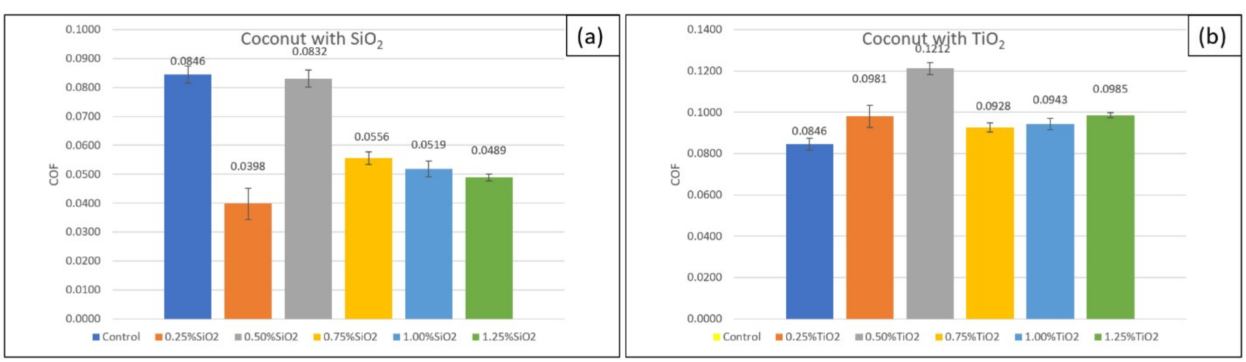


Figure 42: COF results for coconut oil modified with: (a) SiO_2, and (b) TiO_2 nanoparticles.

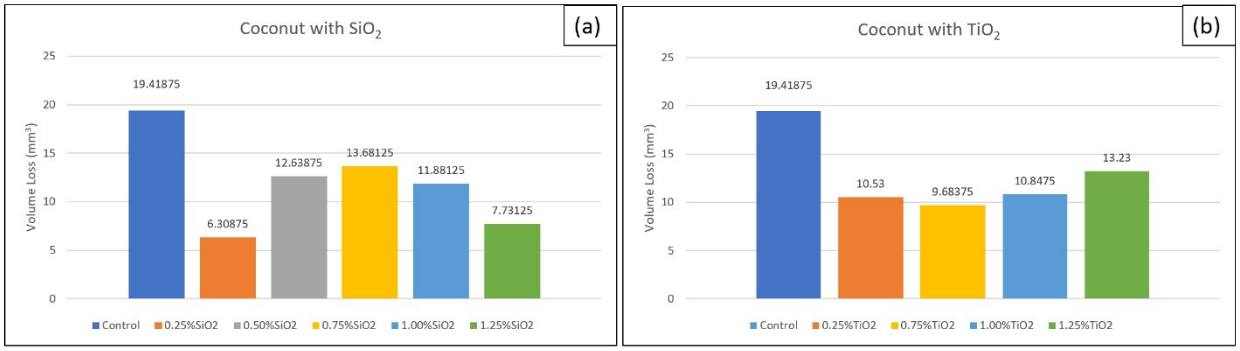


Figure 43: Mean volumetric wear of AISI 304 cylinders lubricated with coconut oil modified with: (a) SiO_2, and (b) TiO_2 nanoparticles.

4.5 Wear Surface Characterization

To further analyze the wear mechanisms, present on the wear scars, SEM and EDS spectra analysis were done. Analyzing all wear scars would be excessive, so only the optimal concentrations and the control for each vegetable oil group were selected. From the previous results in section 4.4 it was concluded that for sunflower oil 1.25% SiO_2 and 1.00% TiO_2 performed the best regarding wear and friction. For grapeseed oil the selected samples were 1.25% concentrations of SiO_2 and TiO_2. For coconut oil the selected samples were 1.25% SiO_2 and 0.75% TiO_2. Micrographs showing the surface morphology of the wear scars produced on the specimens lubricated with sunflower oil are shown in Figure 44. Figure 44a displays wear scar produced on the specimen lubricated with sunflower base oil. The wear scar produced on the specimen lubricated with sunflower with 1.25 wt% SiO_2 displays grooves in the sliding direction and some furrows also. Localized micro pits are also present in Figure 44b. A micrograph of the wear scar produced on the specimen lubricated with sunflower with 1.00% TiO_2 is shown in Figure 44c shows shallow grooves in the sliding direction. Present also are pits and shallow furrow. The shallow grooves allowed for the surface for 1.00 wt % TiO_2 to have the smoothest surface at 0.095 Ra (μm) as shown in Figure 45. Figure 45 displays the surface roughness Ra values obtained using the Mahr 300c profilometer. During the tribological tests using sunflower base oil as lubricant, the surface roughness increased by 121% when compared to the controlled non tested sample. When using nanoparticles, the roughness decreased by 69.9% and 78% using SiO_2 and TiO_2 nanoparticles respectively. This decreasing in roughness by nanoparticles is known as the polishing effect. The polishing effect can be accomplished with the appropriate size, hardness, and volume content, nanoparticles can polish the counterpart surface in a very fine scale[19].

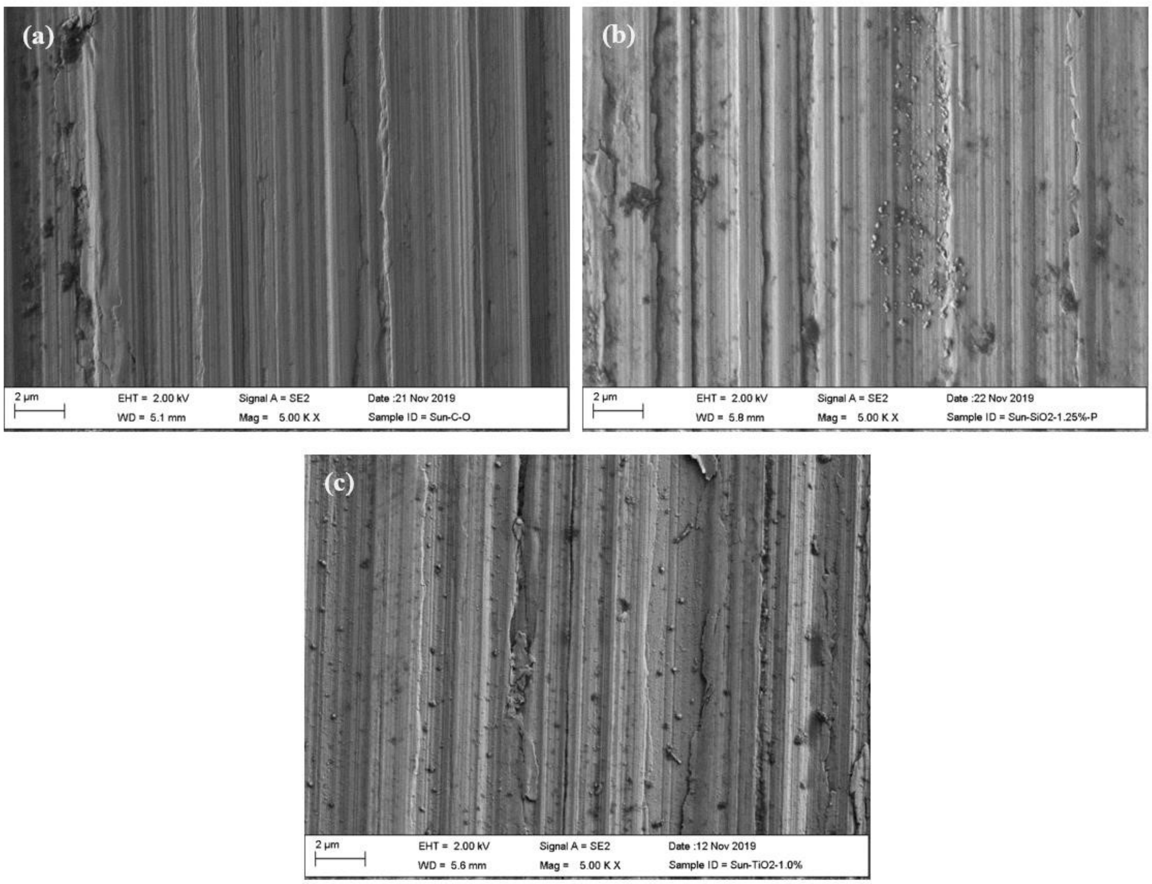


Figure 44: Morphology of wear scars produced during wear tests lubricated with (a) sunflower oil, (b) sunflower oil with SiO_2 nanoparticles at 1.25 wt %, and (c) sunflower oil with TiO_2 nanoparticles at 1.0 wt %.

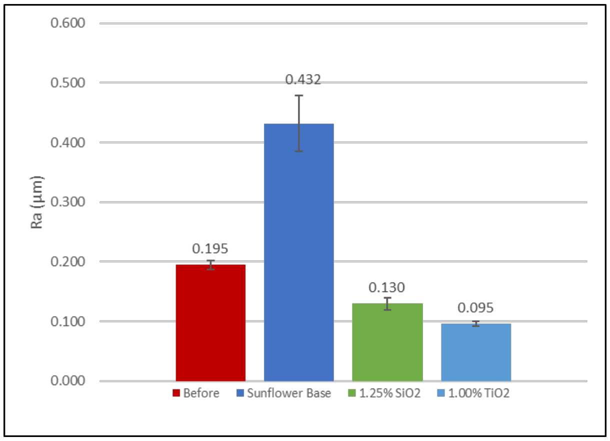


Figure 45: Average surface roughness values (Ra) measured on the wear scars produced during wear testing using sunflower oil as lubricant. Sunflower surface roughness.

SEM micrographs of the wear scars produced on the specimens lubricated using grapeseed oil with SiO_2 and TiO_2 nanoparticles are shown in Figure 46. Surface of the wear track produced on the specimens lubricated using grapeseed oil without nanoparticles is shown in Figure 46a. A micrograph of the wear scar produced on the specimen lubricated using grapeseed with 1.25 wt % SiO_2 nanoparticles is shown in Figure 46b. Figure 46b displays abrasive grooves with a shallow furrow at the left up quadrant. A micrograph of the wear scar produced on the specimen lubricated using grapeseed with 1.25 wt% TiO_2 nanoparticles is shown in Figure 46c and displays shallow grooves with micro-pitting. When comparing the three SEM images, the ones with nanoparticles present shallow grooves which may have been caused by the polishing effect. In the polishing effect the nanoparticles make shallow grooves allowing the particles to pass these new channels. Furthermore, as shown in Figure 47 the surface roughness was lowered when the nanoparticles were added into grapeseed reinstating that the polishing effect mechanism plays a role in lowering friction and wear. The roughness stayed the same when comparing the sample before testing and after testing with grapeseed base. In this case the smooth surface was for the specimen lubricated using grapeseed oil with 1.25 wt % SiO_2 nanoparticles concentration .

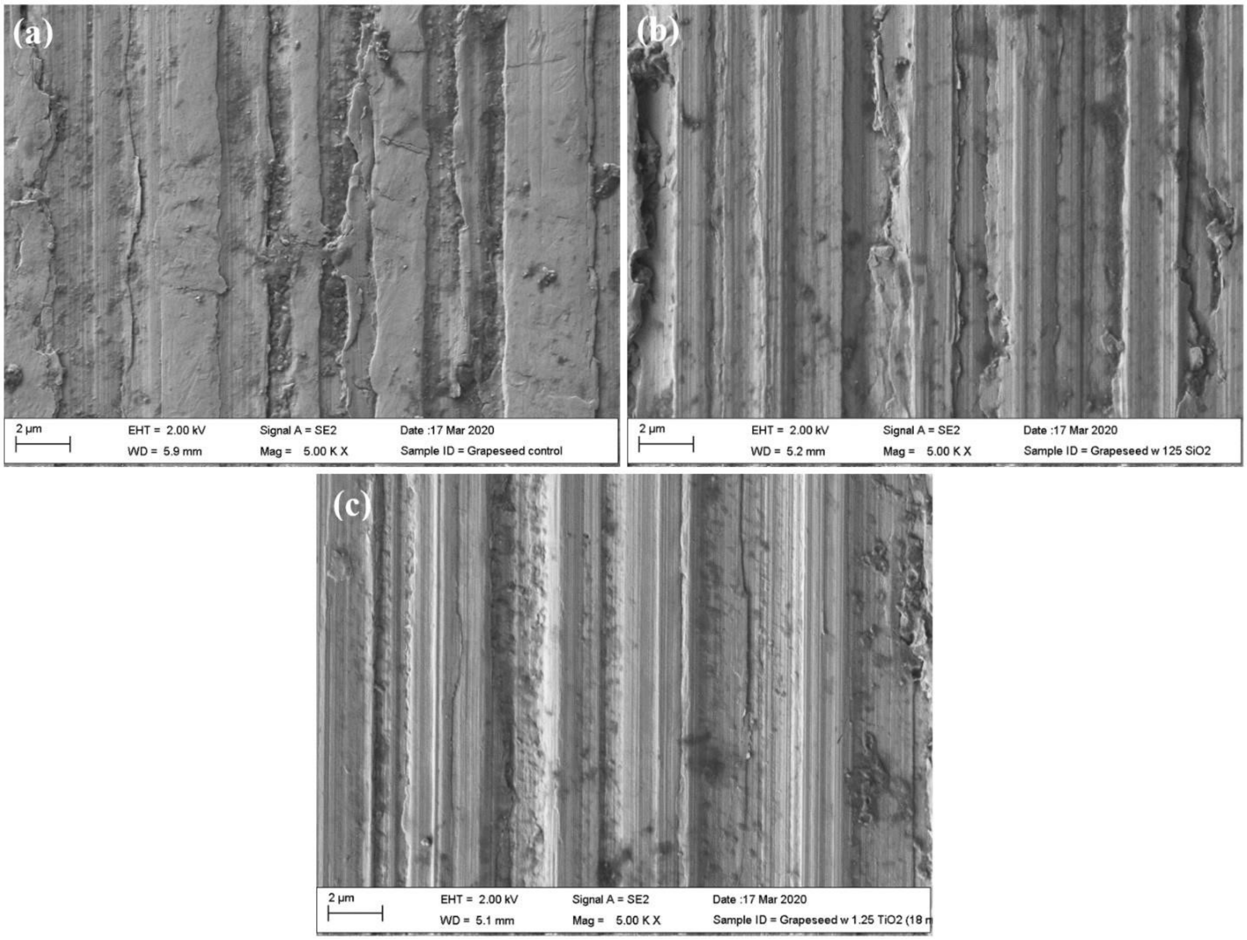


Figure 46: Morphology of wear scars produced during wear tests lubricated with (a) grapeseed oil, (b) grapeseed oil with SiO_2 nanoparticles at 1.25 wt %, and (c) grapeseed oil with TiO_2 nanoparticles at 1.25 wt %.

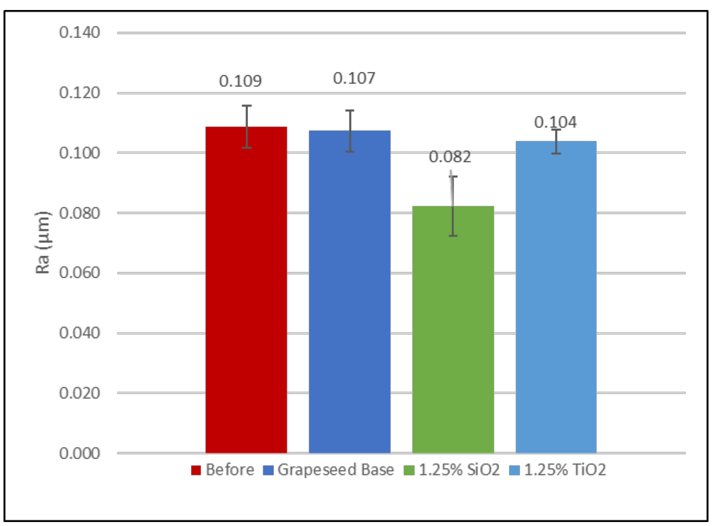


Figure 47: Average surface roughness values (Ra) measured on the wear scars produced during wear testing using grapeseed oil as lubricant. Surface roughness for grapeseed block-on-ring experiments.

SEM micrographs of the wear scars produced on the specimens lubricated using coconut oil are shown in figure 48. From figure 48a shallow grooves are observed in the right quadrant. From the wear scar of coconut oil with 1.25% SiO_2 shown in figure 48b shallow grooves are observed throughout the SEM micrograph. Micro pitting also exists at the center of the micrograph. From visual observation it is noted that the surface appears smoother in the micrograph pertaining to the wear scar of 1.25% SiO_2 concentration in coconut.

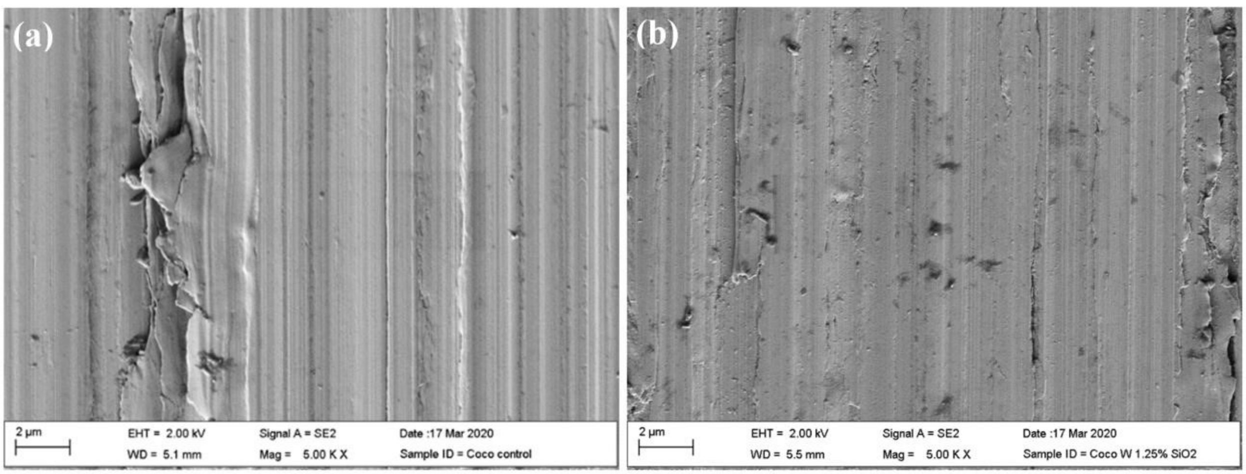


Figure 48: Morphology of wear scars produced during wear tests lubricated with (a) coconut oil, (b) coconut oil with SiO_2 nanoparticles at 1.25 wt %.

To further identify the lubrication mechanisms at play, it is important to perform EDS analysis on the wear surface. Figure 49 shows EDS analysis results for worn surfaces after testing using sunflower oil as lubricant. For the specimen tested using sunflower oil with TiO_2 nanoparticles as lubricant additives, a Ti concentration of 9.31 wt % was found, as shown in Table 5. This is an important discovery, since Ti is not present in the AISI 304 stainless steel chemical composition. This means some of the TiO_2 nanoparticles were placing themselves into the surface of the AISI 304 steel. This mechanism is known as the protective film effect and occurs if the correct amount of pressure, particle size, hardness, and surface finish are present.

For the sunflower lubricants with SiO_2 nanoparticles as lubricant additives, the concentration of SiO_2 did not increase substantially, meaning the protective film effect is not present.

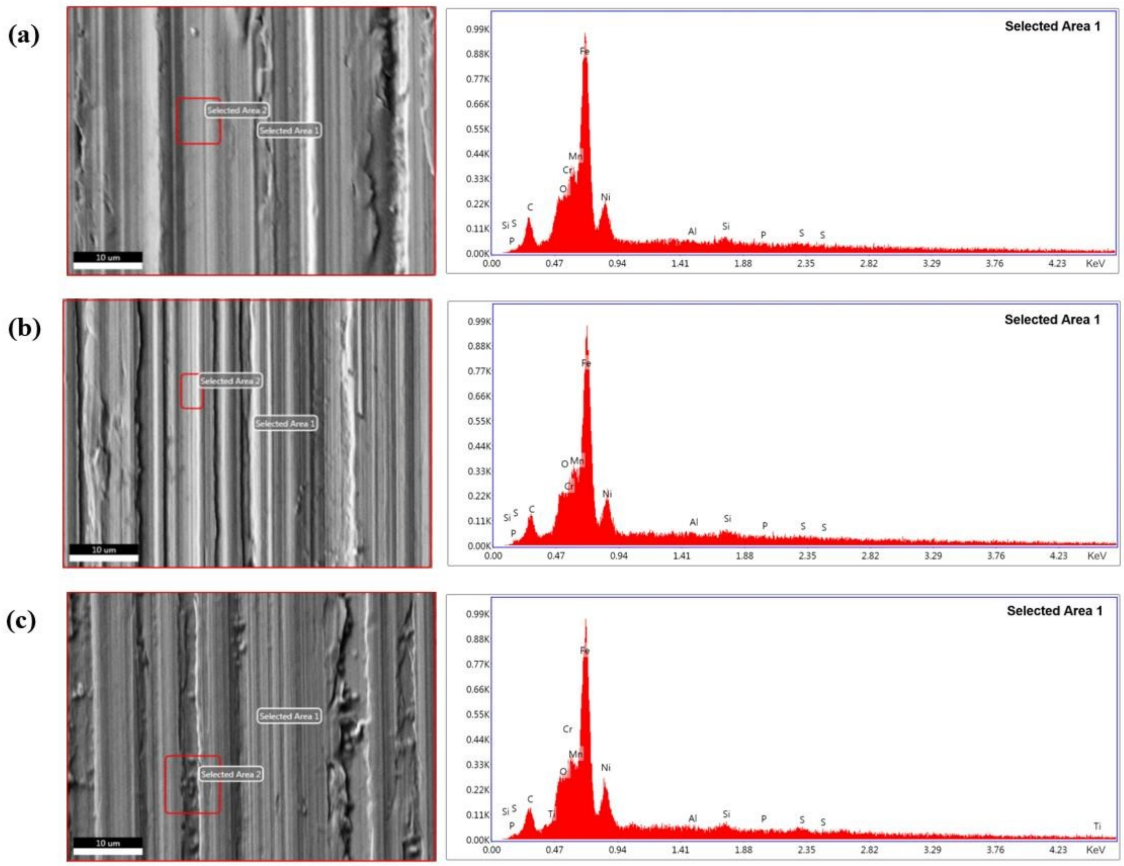


Figure 49: SEM micrograph and EDS spectra of worn surfaces produced during wear tests lubricated with (a) sunflower oil, (b) sunflower oil with SiO_2 nanoparticles at 1.25 wt %, and (c) sunflower oil with TiO_2 nanoparticles at 1.0 wt %.

Table 5: EDS element concentration for sunflower oil

Element	Sunflower Oil (SO) Conc. (Wt %)	SO with SiO_2 1.25% Conc. (Wt %)	SO with TiO_2 1.0% Conc. (Wt %)
C K	9.66	9.70	7.46
O K	3.04	3.44	5.54
Cr L	12.08	11.19	8.65
Mn L	2.92	2.81	4.54
Fe L	56.22	57.20	51.58
Ni L	11.44	11.44	10.77
Al K	0.49	0.56	0.10
Si K	1.53	1.61	0.69
P K	0.98	0.79	0.20
S K	1.66	1.25	1.14
Ti L	0	0	9.31

Figure 50 shows the SEM micrographs and EDS analysis for the worn surfaces after the wear tests using grapeseed as a base lubricant. From the EDS analysis presented in Table 6, it is noted that Ti was present in the wear tests that used grapeseed oil with TiO_2 as lubricant additive. Therefore, the protective film effect is present in this case indicated by the presence of imbedded TiO_2 nanoparticles in the surface. For the grapeseed oil modified with SiO_2 nanoparticles the weightt concentration found of SiO_2 nanoparticles increased from 1.53 to 1.61 wt %. This is not a significant increase therefore there is not a protective film being created with SiO_2 nanoparticles

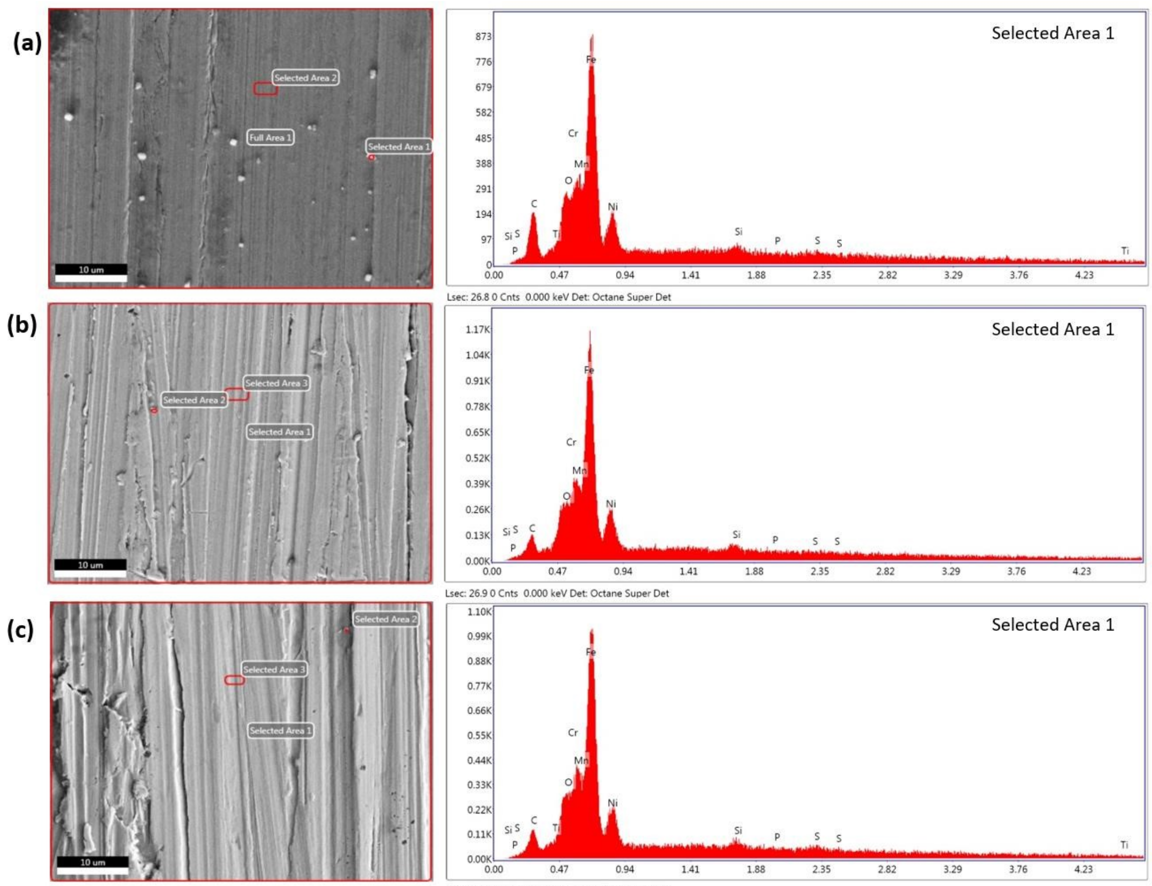


Figure 50: SEM micrograph and EDS spectra of worn surfaces produced during wear tests lubricated with (a) grapeseed oil, (b) grapeseed oil with SiO_2 nanoparticles at 1.25 wt %, and (c) grapeseed oil with TiO_2 nanoparticles at 1.0 wt %.

Table 6: EDS element concentration for grapeseed oil.

Element	Grapeseed Oil (GO) Conc. (Wt %)	GO with SiO_2 1.25% Conc. (Wt %)	GO with TiO_2 1.25% Conc. (Wt %)
C K	24.23	7.44	5.89
O K	3.98	3.36	4.73
Cr L	9.29	12.32	8.94
Mn L	2.74	3.05	4.49
Fe L	50.79	57.84	50.52
Ni L	8.22	12.80	9.64
Si K	0.64	1.47	1.53
P K	0.11	0.65	0.70
S K	0	1.07	1.72
Ti L	0	0	11.82

To further understand the effects of coconut oil in the wear scar EDS spectra was done for the wear scars and the results are shown in Figure 51 and Table 7. When comparing the coconut base oil to coconut with 1.25% SiO_2 it was noted that Si wt% concentration decreased from 0.68 to 0.46%. Therefore, the SiO_2 were not adhering to the surface in such a way that the mending effect or protective film would do. Although from the block on ring results the wear was lowered the mechanism responsible was either the polishing effect or rolling effect.

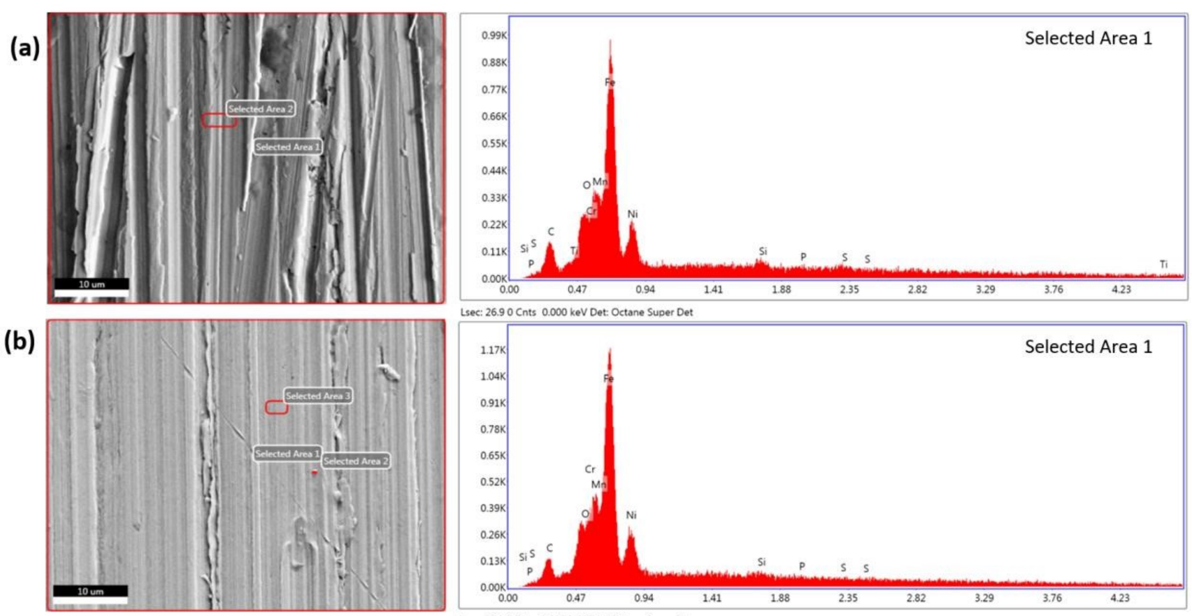


Figure 51: SEM micrograph and EDS spectra of worn surfaces produced during wear tests lubricated with (a) coconut oil, (b) coconut oil with SiO_2 nanoparticles at 1.25 wt %.

Table 7: EDS element concentration for coconut oil.

Element	Coconut Oil (CO) Conc. (Wt %)	CO with SiO_2 1.25% Conc. (Wt %)
C K	8.39	7.54
O K	5.26	3.46
Cr L	8.11	12.40
Mn L	4.69	3.09
Fe L	53.20	60.47
Ni L	9.47	12.17
Si K	0.68	0.46
P K	0.23	0.25
S K	1.14	0.18
Ti L	8.83	0

4.6 Energy Consumption Analysis

In addition to the friction and wear results, energy lost due to friction was calculated from the tribological tests. To calculate the power used by friction the equation below was used,

$$\dot{W} = \frac{Tn}{9549} \tag{3}$$

Where $\dot{W}$ is the power or the time rate of energy transfer (kW), T is the Torque (N.m), and n is rotational speed (rpm). From the steady state coefficient of friction, a prediction of cost savings can be made. The following graphs were made with a scenario of the machine running for 40 hours a week during four weeks per month period in order to find energy consumed by friction. For the cross-cylinder configuration, the torque was calculated using the friction force measured by sensor times a distance of 0.02m which corresponds to the radius of the ring on the tribotester. The rotational speed for the cross-cylinder and block-on-ring configurations were 300 and 172 rpm respectively.

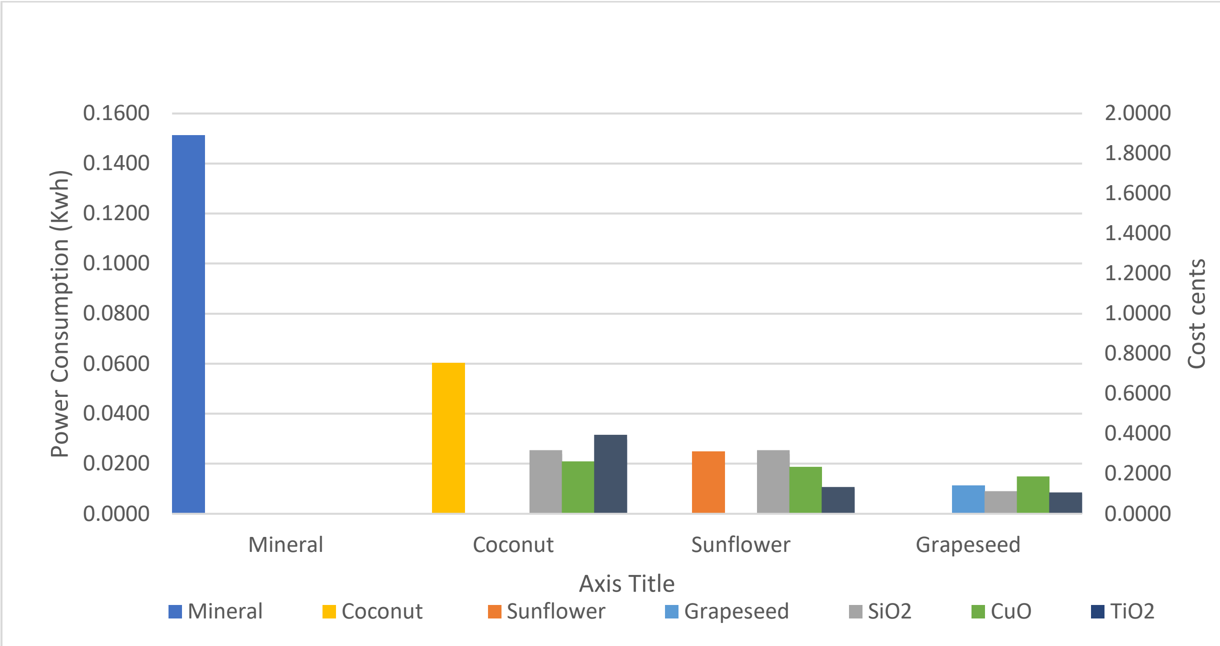


Figure 52: Preliminary Energy consumption and cost using cross-cylinder configuration.

Table 8: Energy consumed and cost values.

Lubricant	**Energy Consumed (KWh)**	**Cost ¢**
Mineral	0.1420	1.8915
Coconut	0.0566	0.7533
Sunflower	0.0234	0.3113
Grapeseed	0.0106	0.1406
CO with SiO_2	0.0239	0.3180
CO with CuO	0.0196	0.2611
CO with TiO_2	0.0297	0.3950
SO with SiO_2	0.0239	0.3180
SO with CuO	0.0176	0.2343
SO with TiO_2	0.0101	0.1339
GO with SiO_2	0.0085	0.1138
GO with CuO	0.0141	0.1875
GO with TiO_2	0.0080	0.1071

Figure 52 displays the scenario and from it is noted that the cost will decrease if the appropriate lubricant is used. The lowest COF from SiO_2, CuO, and TiO_2 concentrations were selected in this energy consumption and cost study. When using mineral oil, the energy consumed by friction for the month period was a total of 0.1420 KWh resulting in a total cost of 1.8915 cents. The cost was calculated assuming the average cost of electricity of 13.32 [43]. By using grapeseed oil with 1.00 wt % SiO_2 the cost was lowered 94.33 %. Although its only cents saved, this would be more since more than one machine will be running at the same time and in the long run the savings would be greater by using the correct lubricant.

Further energy consumption and cost analysis was done for block on ring configuration as shown in Figure 53 and Table 9. When comparing the base oils it was noted that coconut oil friction power consumption was greater at 0.1931 Kwh when compared to sunflower oil and grapeseed oil power consumption of 0.142 Kwh and 0.142 Kwh respectively. Furthermore, it was noted that the addition of nanoparticles will lower the friction energy consumption. When using SiO_2 as an additive in the vegetable base oil the cost in cents decreased by 42.19%, 77.69%, and 49.70% when compared to base coconut oil, sunflower oil, and grapeseed oil respectively. The addition of TiO_2 nanoparticles in coconut oil increased the power consumption by 9.68% meanwhile in sunflower oil and grapeseed oil it decreased it by 93.76% and 62.77% respectively. For these block-on-ring results the lowest friction power consumption was provided by sunflower oil with TiO_2 at 0.0730 Kwh. Also, power consumption of friction is related to application since the range of cost for block-on-ring experiments was greater than the range of cross-cylinder experiments. At higher loads there will be higher friction and that higher friction means more energy is being wasted due to friction. Therefore, using the correct concentration and vegetable oil will result in the lowest friction power consumption values.

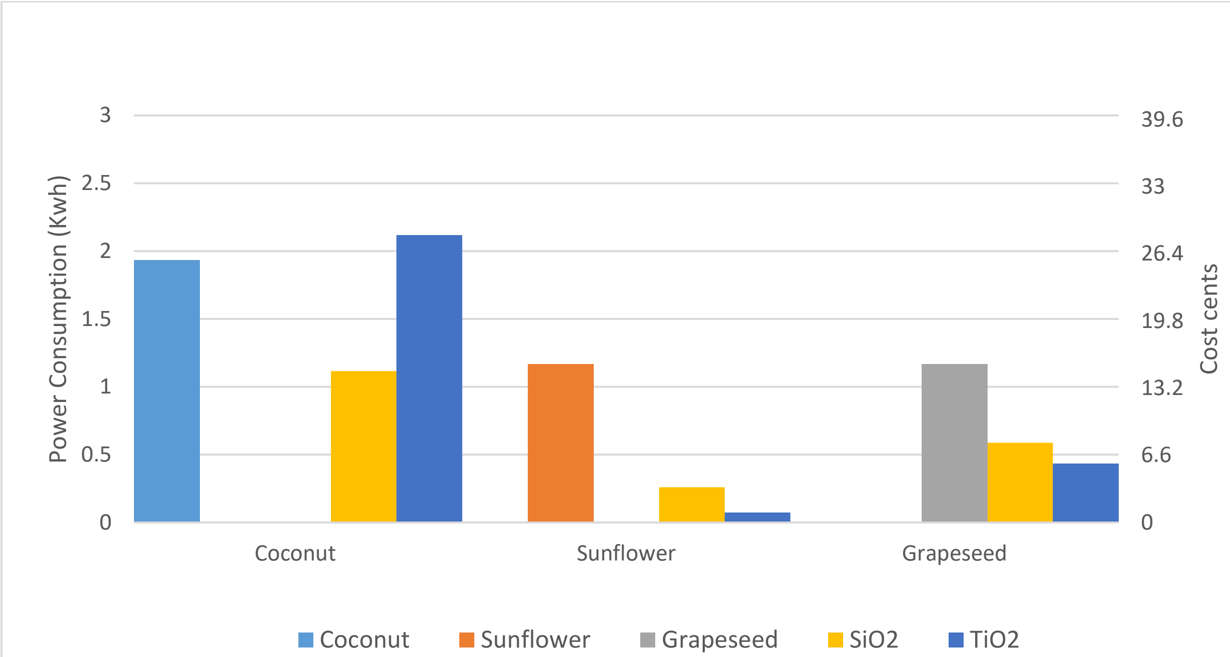


Figure 53: Energy Consumption of Block on ring configuration.

Table 9. Block on Ring Energy consumption values

Lubricant	**Energy Consumed (KWh)**	**Cost ¢**
Coconut	1.9310	25.7211
Sunflower	1.1663	15.5360
Grapeseed	1.1663	15.5360
CO with SiO_2	1.1161	14.8671
CO with TiO_2	0.0730	28.2142
SO with SiO_2	0.260207955	3.4659
SO with TiO_2	0.073040829	0.9729
GO with SiO_2	0.586609161	7.8136
GO with TiO_2	0.433679925	5.7766

CHAPTER V

CONCLUSION

In the present research project, the rheological behavior and tribological performance of sunflower oil, grapeseed oil, and coconut enhanced with nanoparticle additions at different concentrations have been extensively discussed. Based on the research conducted, it can be concluded that:

- The rheological behavior of the nano-lubricant is dependent of the concentration. For SiO_2 nanoparticles the viscosity increased at higher concentration in sunflower oil, coconut oil, and grapeseed oil. The viscosity of sunflower oil decreased when TiO_2 nanoparticle concentration increased. The addition of TiO_2 in grapeseed oil lowered the viscosity at 1.00 wt % concentration.
- Different rheological behavior was observed when analyzing different vegetable oils and nanoparticle additives. All the vegetable oils displayed shear thinning behavior except for sunflower oil with TiO_2 nanoparticles, which presented a shear thickening behavior.
- SiO_2 and TiO_2 nanoparticles were effective additives for incorporation into the sunflower oil; they reduced the COF and wear volume loss by 77.69 and 74.06% and 93.73 and 70.13% respectively.
- SiO_2 and TiO_2 nanoparticles were effective additives for incorporation into the grapeseed oil; they reduced the COF and wear volume loss by 49.70 and 62.8% and 38.6 and 82.2% respectively.

- SiO_2 and TiO_2 nanoparticles were effective additives for incorporation into the coconut oil; they reduced the COF and wear volume loss by 77.69 and 93.73% and 74.06 and 70.13% respectively.
- The protective film and polishing effect mechanisms were found to be present in wear test using TiO_2 as a nanoparticle additive in vegetable oil. For nano-lubricants enhanced with SiO_2 nanoparticles the polishing effect mechanism was found.
- Energy consumption during the cross-cylinder was lower when using the vegetable oils with nanoparticles when compared to mineral oil. If the correct oil and nanoparticle concentration the energy consumption can be lowered by 94.33% in cross-cylinder experiments. Furthermore, energy consumption was concluded to be dependent on application parameters. Higher loads and rpms will result in higher power consumptions.

Vegetable oil enhanced with nanoparticles show great potential as replacing conventional mineral oil. Although vegetable oil still has some drawbacks this study proved that friction and wear can be reduced through tribological experimentation.

5.1 Future Work

This research area is new in the UTRGV and this work has helped set the footwork for more future work. Lubricants can have many important aspects and future work will be exploring different properties such as thermal conductivity among others. Lubricants in real world application not only have to reduce friction and wear, in some scenarios they need to remove heat from components such as in automobile engines. Furthermore, experiments at different temperatures need to be done since vegetable oil properties diminish at high temperatures.

Other future work will be analyzing more vegetable oils and nanoparticles. For the nanoparticles, more nanoparticles need to be analyzed to see if there is better suspension and tribological properties. Nanoparticles also come in many different diameter sizes and shape. Future work will revolve around analyzing the effect of different size nanoparticles in vegetable oil.

When it comes to tribological experimentation tests, future work will be revolved using the modified tribotester, tapping torque tests, and pin on disk experimentations. Furthermore, adding texture to samples such as pre channel grooves and seeing if this has any effect on wear and friction.

Renewability is an important characteristic that will be analyzed in the future. Centrifugal force has shown to be able to remove nanoparticles from the fluid. In conclusion, much more work is needed in order to ensure vegetable-based lubricant is ready for the market to compete against conventional mineral oil.

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APPENDIX A

APPENDIX A

STATE OF THE ART EQUIPMENT AND SOFTWARE

State-of-the-Art Equipment

Equipment	Purpose	Results Obtained
SEM	Microscope to observe nanoparticles, and wear block samples	Nanoparticles morphology was observed and is shown in figure 14 through 16. Wear scars were able to be observed and are shown in figure 44, 46, and 48.
EDS	To know the weight % composition of the samples after the experiment.	Element concentration wt % for the base sunflower, base grapeseed, and base coconut oil and optimal conditions with SiO_2 and TiO_2 and were found found and are shown in table 5, 6, and 7.
Profilometer	Measure the roughness of the block samples before and after the block on ring tests.	Average roughness for the block samples after the block on ring experiments for base sunflower oil, and base grapeseed oil and is shown in figure 45 and 47. The average roughness was also calculated for the block samples corresponding for the optimal concentration of SiO_2 and TiO_2 nanoparticles test runs. The results are shown in figure 45 and 47.
Rheometer	Measure the viscosity at different shear rate of base sunflower oil, base grapeseed oil, and base coconut oil modified with SiO_2 and TiO_2 nanoparticles.	Viscosity was measured from 10 s^{-1} to 120 s^{-1} shear rate for sunflower oil, grapeseed oil, and coconut oil modified with nanoparticles and is shown in figure 17-28.

State-of-the-Art Software

Equipment	Purpose	Results Obtained
Matlab	Fit shear rate vs viscosity data to common simulation models. Filter rheology and block on ring data.	Able to fit rheology data into power law and cross-equation model. Able to filter data in order to fit 50 data points per graph in rheology portion and able to remove noise from block on ring data

BIOGRAPHICAL SKETCH

Vicente Cortes was born in Mission, Texas on August 19, 1996 where he currently resides. He attended school institutions in the Mission Consolidated Independent School District (MCISD) which includes Pearson Elementary, Kenneth White Jr. High, and Mission High School. Vicente attended the then University of Texas – Pan American (now University of Texas – Rio Grande Valley) located in Edinburg, Texas in August 2014 and graduated in May 2018 with his Bachelor of Science in Mechanical Engineering. Throughout his undergrad years, Vicente was a member of Society of Hispanic Engineers, and Aero Club.

In August 2018, he returned to the University of Texas – Rio Grande Valley and received a Master of Science in Mechanical Engineering in May 2020. Since entering the graduate program, Vicente has been employed as a graduate research assistant under his professor, Dr. Ortega, which has allowed him to further his research efforts. Vicente may be reached by email at cortesv07@gmail.com