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Lubrication Performance of Vegetable Oils Modified with Halloysite Clay Nanotubes (HNT) as Lubricant Additives

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LUBRICATION PERFORMANCE OF VEGETABLE OILS MODIFIED WITH HALLOYSITE CLAY NANOTUBES (HNT) AS LUBRICANT ADDITIVES

A Thesis

By

MD ABU SAYEED BISWAS

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ABSTRACT

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Vegetable oil-based nano-lubricants are a great alternative to petroleum-based lubricants because of their less adverse impact on the environment. This work evaluates the tribological performance of sunflower, corn, and peanut oils modified with halloysite clay nanotubes ($Al_2Si_2O_2(OH)_2nH_2O$) as lubricant additives at different concentrations. To analyze the tribological performance of the nano-lubricants, a block-on-ring tribometer was used following the ASTM G-077-17 standard procedure. Characterization of HNT was carried out by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Thermogravimetric Analysis (TGA). The effect of the HNT on the lubrication performance of the newly developed vegetable oil-based nano-lubricants was evaluated, and the experimental data of wear, friction, and temperature was analyzed. The results concluded that sunflower, peanut, and corn oils modified with Halloysite Clay Nanotubes could be a great alternative to mineral and synthetic lubricants.

DEDICATION

The completion of my master's studies would not have been possible without the love and support of my family and close friends. My wife, Shagufta Taufiq Khan , my brother, Hossain Ali, my sister, Masuma Hossain, and all my family and friends who inspired, motivated, and supported me to be able to accomplish this degree. Thank you very much for all the mental support, love, and patience you have provided.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Page

CHAPTER I

INTRODUCTION

1.1 Problem Statement

Lubricants are used in almost all modern moving machinery to run efficiently. About half of this lubricant is leaked into the environment, contributing to pollution. Because of the growing concern for environmental protection, demand for environmentally friendly lubricants is increasing. Vegetable oils are being considered a source of environmentally friendly lubricant due to their anti-wear and fatigue resistance capabilities and better load-carrying capacity compared to mineral oils [1]. To avoid pollution of the environment, it is necessary to use biodegradable lubricants [2]. The biodegradability of vegetable oils is around 95%. [3]. Their ester linkages, which enable oil molecules to physically adhere to metal surfaces and give superior boundary lubricity than nonpolar petroleum-based mineral oil [4], deserve special attention.

1.2 Purpose Statement

To reduce the environmental pollution caused by petroleum-based lubricants, vegetable oil-based lubricants can be used as a great alternative. Not only is there a detrimental impact on the environment, but petroleum-based lubricants are also increasing in price due to a scarcity of sources, which is another reason to consider vegetable oils as a substitute. The use of nanoparticles as lubricant additives is an innovative way to extend the life of vegetable lubricants and reduce wear. In this work, the effect of Halloysite Nanotubes (HNT) as lubricant additives at different concentrations into sunflower, corn, and peanut oils is experimentally investigated. Before adding halloysite nanotubes as lubricant additives, characterization of HNT will be carried out by SEM, XRD, and TGA to determine the physical and chemical properties. The tribological performance of each lubricant will be studied to determine the effect of different HNT concentrations in different vegetable oils. The lubrication performance of the newly developed vegetable oil-based nano-lubricants will be evaluated in a real-world application by means of the tapping torque test.

CHAPTER II

LITERATURE REVIEW

2.1. Lubrication Background

Lubricant is a substance used to reduce friction and wear of the surfaces in contact with the bodies in relative motion. Protective film formed by the lubricants helps to separate the mating surface and thus lessen the wear and friction. The concept of lubricants is not new; it started when humans started using tools. A good lubricant should have a high boiling point, a low freezing point, a high viscosity index, thermal stability, hydraulic stability, corrosion resistance, and strong oxidation resistance. The history of modern lubricants began in Pennsylvania in the nineteenth century with the start of crude oil drilling. With the invention of crude oil, the machine's life was significantly prolonged. As the machine became complicated and sophisticated, such types of lubricating oils were required, which can survive and work in harsh environments incomparable to that past. Along with the rapid advancement of automobiles, aircraft, diesel locomotives, and large vessels, the advancement of lubricating oils was obvious. In the 1920s the use of lubricant additives enhanced lubricating oils' performance and made a revolutionary move in this field. Though the advancement of petroleum oil-based lubricants overshadowed the vegetable oil-based lubricants, environmental pollution is a great concern at present time. To reduce the environmental impact of lubricants, biodegradable vegetable oil is a good choice. The vegetable oil-based lubricants have a higher cost, oxidative and thermal instability and limited temperature applications compared to mineral-based lubricant oils [1-2]. At present, biodegradable properties of vegetable oils are being investigated for their non-toxic and renewable nature and good lubrication characteristics than mineral-based oils [3]. The addition of nanoparticles in justified concentration can improve the lubrication properties in vegetable oils as well as performance [4].

2.2 Vegetable oils as biodegradable lubricant

The use of vegetable oil as lubricating oils started in ancient days. Vegetable oils were the main ingredients of lubricating oils until the nineteenth century as they are easily achievable from the natural source. After the nineteenth century, the requirement for lubricants became very high because of rapid industrialization and putting pressure on the price and availability of vegetable oils and shifted to petroleum-based lubricants. Most of the lubricants released in the atmosphere have a great impact on the atmosphere. Petroleum-based lubricants are less degradable and pose a great threat to the environment when released. That is a strong incentive to provide biodegradable lubricants. Moreover, the rapid rise in the price of petroleum products in recent years, the increased reliance on offshore supplies, the decreasing rate of output from older domestic oil fields, and the decline in the pace of discovering new reserves have prompted governments and individuals to push for renewable energy products as replacements for petroleum products. Based on those stresses, environmental issues, and sustainability, the bio-lubricant industry is rising. Natural vegetable oils are biodegradable and sustainable. The use of vegetable oils as lubricants offers a wide range of advantages such as high biodegradability [5], low pollution of the environment, compatibility with additives [6], low production cost [7], wide production possibilities [8], low toxicity, high flash points, low volatility, and high viscosity indices [9]. Primary drawbacks for their use of vegetable lubricants [10–11] are relatively high freezing points [12] and their low thermo-oxidative stability [13]. Vegetable oils are also a source of fatty acids for polyol esters [14-15]. These polyol-esters are also base oils for environmentally friendly lubricants.

2.2.1 Sunflower oil

Sunflower oil is a non-volatile vegetable oil that is extracted by pressing sunflower seeds. It is biodegradable, readily available, eco-friendly, and can be renewable. Most sunflower oil consists of linoleic acid, oleic acid, polyunsaturated fat, and monosaturated fat which can differ based on the manufacturing process and selective breeding. Due to the high percentage of oleic acid (30%) compare to other vegetable oils, it has high oxidation properties [16]. More on, sunflower has good tribological properties and predominantly polyunsaturated fatty acid composition [17]. The different fatty acid profiles in sunflower oils have an influence on friction and wear. As sunflower oil is mainly composed of less stable monosaturated and polyunsaturated fatty acids, it can be easily susceptible to degradation by heat and air which can easily accelerate the oxidation. The lubrication properties of sunflower oil can improve by the addition of lubricant additives. Table 1 shows important physical properties of sunflower oil.

Table 1: Physical properties of sunflower oil [16].

Specific gravity	**Density(Kg/m^3)**	**Flash Point(^0C)**	**Pour Point(^0C)**	**Viscosity @ 40 °C(mm^2/s)**	**Viscosity @ 100 °C(mm^2/s)**	**Viscosity Index**
0.916	920.0	**254**	-15	**36**	6.7	264

2.2.2 Corn oil

Corn oil is a kind of vegetable oil that can easily be extracted from the germ of corn. Corn oil is less expensive and readily available compare to other vegetable oils and has some good tribological properties. Corn oil consists of linoleic acid, oleic acid, polyunsaturated fat, and monounsaturated fat. Among its fatty acid part, 80% are palmitic acid(lipid number of C16:0), 14% stearic acid (C18:0), and 3% arachidic acid (C20:0). Due to the high palmitic acids compared to other vegetable oils, making it is very useful in the tribological process [18]. To improve the tribological properties as lubricant further research is required. Table 2 shows important physical properties of corn oil.

Table 2: Physical properties of corn oil [18].

Specific gravity	**Density(Kg/m^3)**	**Flash Point(^{0}C)**	**Pour Point(^{0}C)**	**Viscosity @ 40 °C(mm^2/s)**	**Viscosity @ 100 °C(mm^2/s)**	**Viscosity Index**
0.924	920.0	**315**	-38	**34.5**	**9**	**176**

2.2.3 Peanut oil

Peanut oil is a readily available, eco-friendly, and biodegradable vegetable oil which is extracted from peanuts. The major fatty acids of peanut oil acylglycerols are palmitic (C16:0), oleic (C18:1), and linoleic (C18:2) acids, and only a trace amount of linolenic fatty acid (C18:3) is present [19]. Due to the high content of palmitic acid, it can be used as lubricant oil. The smoke point of peanut oil is 232^{o}C which is highly comparable to other vegetable oils. Table 3 shows important physical properties of peanut oil.

Table 3: Physical properties of peanut oil [19].

Specific gravity	Density(Kg/m^3)	Flash Point(^0C)	Pour Point(^0C)	Viscosity @ 40 °C(mm^2/s)	Viscosity @ 100 °C(mm^2/s)	Viscosity Index
0.920	920.0	**271**	**-7**	**34.5**	**9**	**176**

2.3 Nanoparticles as lubricant additives

Nano-lubricants are solid-like particles of nanometer size suspended in a base oil or fully formulated lubricants and exhibit better tribological properties. Nano-lubricants usually consist of lubricant or base oil solvent, the nanoparticles that act as anti-wear or friction modifiers, and the surfactant that inhabits the interface area between the lubricating oil and the particles. Nano-particle additives have a great impact on lubrication because of their nano size and high surface area which enables the nanoparticles to enter the contact area, resulting in a positive lubrication effect [20]. More on, nanoparticles are small enough to pass through lubricant oil filters. Primary purposes of using nanoparticles as lubricant additives are insolubility in base oils, comparatively less reaction capability with other additives in the lubricant, higher probability of lubrication film formation, high durability, and high nonvolatility to withstand high temperatures [21]. The effectiveness of nanoparticles depends on various factors, including their compatibility with a base oil, sizes, and morphologies, as well as their concentrations [22]. Due to its high effectiveness in lubrication, a huge concentration is given to nanoparticles as lubricant additives. Most studies of nanoparticles as lubricant additives have shown better tribological performance by reducing friction and wear compared to its base oil. The shape of nanoparticles has an impact on the tribological performance of nano-lubricants. The most common shape for nanoparticles is spherical, followed by granular, sheet, onion, and nanotube morphologies.

2.3.1 Types of nanoparticles

Nanoparticles are ultrafine particles of diameter ranging from 1nm to 100nm. According to size, morphology, chemical and physical properties nanoparticles are classified in different categories. Most common nanoparticles types are carbon-based nanoparticles, metal nanoparticles, ceramic nanoparticles, semiconductor nanoparticles and lipid-based nanoparticles. Fullerenes and carbon nanotubes are most common carbon-based nanotubes which have high commercial application. Ceramic nanoparticles are usually inorganic solid materials of carbides, carbonates, oxides and phosphates. Ceramic nanoparticles have high heat resistive capacity and chemically inert thus it is a good candidate for lubricant additives. Metal nanoparticles are derived from metal precursors and have applications in tribological research primarily on nano-lubricants. Table 4 shows different types of nanoparticles with their primary categories.

Table 4: Summary of different nanoparticles used as lubricant additives [23].

Types	Nanoparticles
Carbon and its derivatives	Graphene, Diamond, SWCNT, MWNTs
Metals	Sn, Fe, Bi, Cu, Ag, Ti, Ni, Co, Pd, Au
Metal oxides	CuO, ZnO, TiO_2, Al_2O_3, Fe_3O_4, ZrO_2
Sulfides	WS_2, MoS_2, CuS, ZnS
Rare earth compounds	LaF_3, $La(OH)_3$, $CeBO_3$, Y_2O_3
Nanocomposites	Cu/SiO_2, Cu/MoS_2, Al_2O_3/TiO_2, Al_2O_3/SiO_2, Cu/Graphene oxide
Others	$CaCO_3$, $ZnAl_2O_4$, SiO_2, ZrP, Zeolite, PTFE, BN, Serpentine, Hydroxide

In most research, researcher usually used commercially synthesized nanoparticles. Field Emission Scanning Electron Microscopy (FESEM) and High-resolution Transmission Electron Microscopy (HRTEM) usually used to characterize the morphology of nanoparticles. Table 5 shows the various sources and shape of nanoparticles used as lubricant additives.

Table 5: Summary of sources and typical properties of nanoparticles used as lubricant additives [24].

Type	**Nanoparticle**	**Source**	**APS(nm)**	**Shape**	**Morphology analysis technique**
Metal	Cu	Commercial	25	Nearly spherical	TEM
	Ni		20	Nearly spherical	TEM
	Al		65	Spherical	SEM
	Pb	Fabricated	22	Spherical	TEM
Metal oxides	CuO	Fabricated	5	Sphere like	TEM
	ZnO	Fabricated	4,35	Nearly spherical	SEM
		Commercial	11,71	Nearly spherical	SEM
	TiO_2	Commercial	20	Nearly spherical	TEM
Chalcogenides	MoS_2	Fabricated	80	Sphere like	TEM
	WS_2	Commercial	90	Layered lamellar flaky	FESEM
Carbon based	Diamond	Commercial	10	Spherical like	TEM
	Graphite		55	Spherical	TEM
	Carbon nanohorns		80	Dahlia like	SEM
	Graphene	Fabricated	10	Spheroidal	TEM
Nitrides	BN	Commercial	70	Spherical	SEM
			114	Nonspherical	SEM, XRD
Ceramic	Al_2O_3	Fabricated	78	Spherical	SEM
	SiO_2	Commercial	30	Spherical	FESEM, TEM
		Fabricated	362,215, 140,58	Spherical	FESEM
Composites	Al_2O_3/SiO_2	Fabricated	70	Elliptical	TEM
	ZrO_2/SiO_2	Fabricated	50-80	Nearly spherical	TEM
Polymer	PTFE	Commercial	30-50	Spherical	FESEM

2.3.2 Lubrication mechanisms

At present researchers using nanoparticles as a form of anti-wear and friction modifiers. Nanoparticle's small size and high surface area can easily slide between two mating surfaces thus reducing friction. Nanoparticles reduce friction in different ways, these include a rolling, protective film, mending, and polishing effect shown in Figure 1 [25]. In rolling effect friction mechanism nanoparticles roll between two surfaces just like a roller bearing. In the protective film mechanism, nanoparticles from a layer of protection film on one surface of the mating parts and improve tribological behavior. Nanoparticles deposition on interacting surfaces and compensation for mass loss characterize the mending effect, also known as the self-repairing effect. In the mending effect mechanism, the nanoparticles help to fill up the pores or scars present on the surface of mating parts and help to reduce friction. The deposition of nanoparticles on the rubbing surface in the mending effect lubrication mechanism is confirmed by EDX analysis. The polishing effect, also known as the smoothing effect, is assumed to cause when nanoparticle-assisted abrasion lowers the roughness of the lubricating surface. The polishing effect mechanism is another method of friction mechanism where nanoparticles act as a polisher to remove any asperities that is available on the surface of the contact parts.

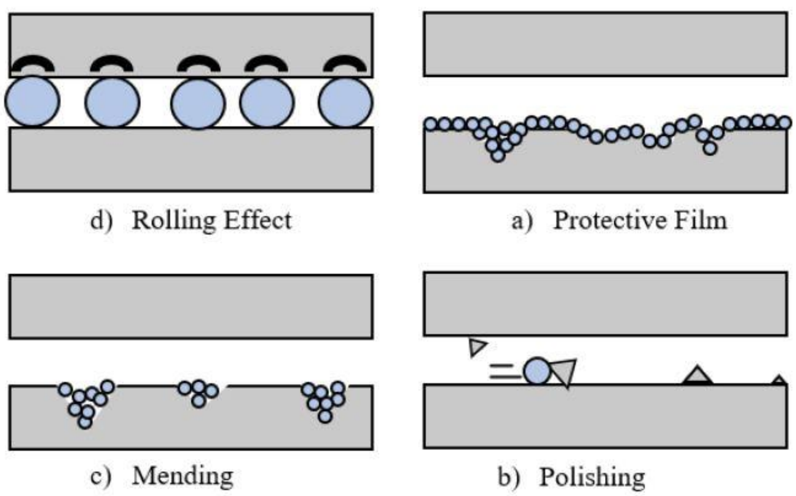


Figure 1: Nanoparticle lubrication mechanism [25].

Table 6: Lubrication mechanisms of nano-lubricant additives [26].

Type	Additives	Lubrication mechanisms
Nanometal-based additive	Cu	Tribofilm formation, rolling bearing effect, mending effect
	Ag	Tribofilm formation, synergistic effect
	Ni	Tribofilm formation, mending effect
	Pd	Tribofilm formation
	CuO	Tribofilm formation, rolling bearing effect, mending effect
	Al_2O_3	Tribofilm formation, rolling bearing effect
	ZnO	Tribofilm formation, mending effect
	TiO_2	Tribofilm formation, rolling bearing effect, mending effect
	MoS_2	Tribofilm formation, mending effect
	WS_2	Tribofilm formation, rolling bearing effect
	LaF_3	Tribofilm formation
	$CaCO_3$	Tribofilm formation
	$CeBO_3$	Tribofilm formation
Nanocarbon-based additive	Graphene	Tribofilm formation, transformation of microstructure
	CNT	Tribofilm formation, transformation of microstructure, rolling baring effect
	Diamond	Rolling bearing effect
	PTFE	Formation of tribofilm
Nanocomposite-based additive	$Cu@SiO_2$	Tribofilm formation, mending effect
	$Al_2O_3@SiO_2$	Synergistic effect
	Cu@GO	Synergistic effect
	Au@GO	Synergistic effect
	$Mn_3O_4@G$	Synergistic effect
	$GNS@MoS_2$	Synergistic effect
	$SOCNTs@MoS_2$	Formation of tribofilm, synergistic effect
	$Co(ReO_4)_2@MoS_2$	Tribofilm formation

2.3.3 Nanoparticles suspension stability

When nanoparticles mixed in lubricant medium, the size of the nanoparticles is small enough to remain dispersed in liquids by Brownian motion due to the random motion of particles. Suspended particles may clump together and create larger agglomerates, which will eventually settle owing to gravity. Agglomeration of nanoparticles results in sedimentation, as well as a reduction in wear resistance and friction reduction capacity. As a result, dispersion stability is essential for consistent lubricating performance. Sedimentation and blockage can occur when dispersion stability is weak [27]. In a reciprocating test setup, Figure 2 illustrates two profiles for IF-MoS_2 dispersion. The loss of friction reduction of MoS_2 nanoparticles is shown in two situations of "stirred" and "not stirred" nano-lubricant samples. A stable suspension is a requirement for a successful nano-lubricant formulation. Different methods of nanoparticles dispersion in lubricating oils are used. Magnetic stirring, Chemical agitation, agitation using ultrasonic shaker, agitation using mechanical ball milling agitation, stirring using ultrasonic probe, agitation by ultrasonic bath are commonly used methods.

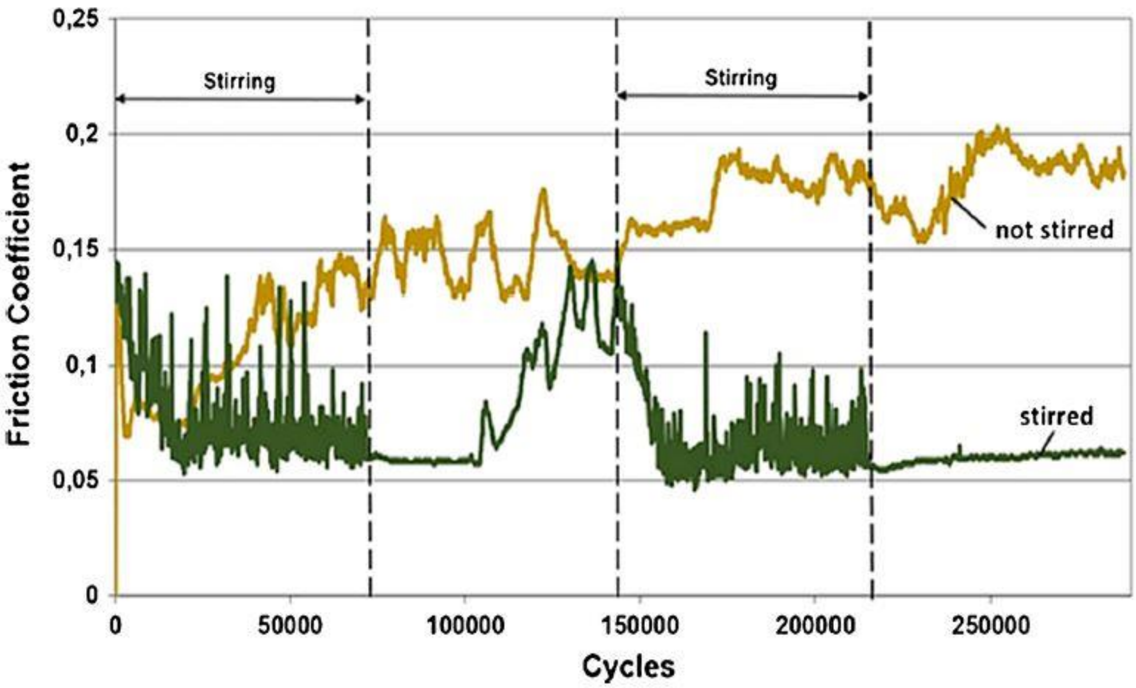


Figure 2: Friction behavior of‘‘stirred’’ and ‘‘not stirred’’lubricants showing effectiveness of stable dispersion for nano MoS_2-enriched lubricant [27].

To be effective as lubricant additives, the distribution of nanoparticles in the basic lubricant must be remain stable over time. The sedimentation method, optical absorbance spectrum/UV–vis spectrophotometer, dynamic light scattering (DLS), zeta potential study, and imaging method have all been developed to assess the stability of nano-lubricants. Table 7 compares the benefits and drawbacks of the various approaches for assessing the stability of suspended nano-lubricants.

Table 7: Comparison of common methods used for evaluation of dispersion stability of nano-lubricants [27].

Stability test	**Advantages**	**Limitations**
Sedimentation	Simplest method, low cost	Time consuming
UV–Vis spectrophotometer	Applicable to all base lubricant	Not applicable for highly concentrated base lubricants
DLS	Short time required	Requires information on sample history, require a larger number of particles compared to imaging method, limited to base lubricant, Expensive
Zeta potential	Ease of measurement	Not applicable for high viscosity base lubricants, not applicable for very low concentrations nanofuids, not applicable for highly conductive nanofluids, Expensive
Imaging method	Ease of measurement	The observation might not be representative of the whole sample
Imaging method (SEM, TEM, FESEM)	Gives detailed shape and morphological information	Time consuming, not sufficient to obtain statistical results because only from tens to hundreds particles are measured among a large number of particles, changes in particle properties during drying and contrasting the sample Not applicable for high viscosity base lubricants

2.3.4 Thermal conductivity of nano-lubricants

The ability of a material to conduct heat is measured by its thermal conductivity. One of the most essential characteristics that determine a lubricant's efficiency is its thermal conductivity. A lubricant with a higher thermal conductivity will transfer heat more quickly and provide better cooling. Brownian motion, radiative heat transfer, liquid layering of oil around nanoparticles, and nanoparticle aggregation are four possible mechanisms for increasing thermal the thermal conductivity of nano-lubricants [28]. Mainly the Brownian motion of nanoparticles in oil controls the thermal conductivity of nano-lubricants. Brownian motion of nanoparticles boosts a lubricant's thermal conductivity in two ways: first, it causes nanoparticle collisions, resulting in a solid-solid conduction heat transfer mode. Second, the convective heat transfer mechanism increases thermal conductivity [28]. Brownian motion of nanoparticles is seen to increase with increasing temperature and decreasing size, implying that high temperatures and small nanoparticles increase Brownian motion, resulting in better thermal conductivity. The thermal conductivity of nano-lubricants is also affected by liquid layering at the interface of base oil and nanoparticles [29]. When liquid molecules come into touch with solid nanoparticles, they tend to build a layered structure around them. Ordered layered structures are linked to better thermal transport, resulting in an improvement in base oil thermal conductivity. Liquid layering, on the other hand, causes the development of interfacial resistance at the solid-liquid contact, resulting in a decrease in thermal conductivity [29]. The aggregation of nanoparticles is the most contentious technique for increasing the thermal conductivity of nanofluids. Aggregation of nanoparticles results in the creation of clusters of nanoparticles, which increase the radius of the particles and create thermally less resistant paths. The thermal conductivity of fluid increase as a result of this. Many studies, on the other hand, have suggested the contrary [30]. The efficiency of nanoparticles in fluids is determined by filler conductivity, interfacial thermal resistance, and cluster form, according to Evans et al. [31]. Furthermore, the author claimed that there is a maximum increase in thermal conductivity at a certain concentration of nanoparticles.

2.3.5 Viscosity of nano-lubricants

Viscosity is an important property of oil lubricants. The frictional force that causes an energy loss in the hydrodynamic lubrication regime reduces as the viscosity of a lubricant lowers. The lubricant's extreme pressure drops with the decrease of viscosity of lubricant, causing the friction surface to be damaged at high loads owing to metal contact, reducing reliability. The addition of nanoparticles to the lubricant as additives can resolve this problem and improve the lubrication properties of the lubricant. The content of fatty acids is a fundamental determinant of the viscosity of vegetable oils. Low viscosity in vegetable oil is observed because of polyunsaturated fatty acids, whereas high viscosity is obtained due to the presence of monosaturated fatty acids. This is because the increase in double bonds affects the packing of fatty acid molecules in oil, making them less rigid and causing oils to behave more fluidic. The percentage of saturated fatty acids in vegetable oil also has a significant impact on its viscosity. The addition of nanoparticles has an impact on the viscosity of base oil as well as nano-lubricants. The viscosity of the base fluid (canola oil) increases as the nanoparticle concentration increases, and the viscosity of the nano-lubricants is higher than that of the base oil [32]. When nanoparticles are added in a particular quantity of base fluid, van der Waals forces tend to attract them to each other in the base fluid. As a result, large clusters of particles form, and the lubricant layers' ability to move with each other is disrupted, resulting in an increase in viscosity. D. F. Rodriguez observed that the addition of 5 and 40 nm nanoparticles in sunflower vegetable oil increased the viscosity of base oil and create shear thinning behavior whereas addition of 18 nm nanoparticles reduced the viscosity of the nano-lubricants as well as changed the properties of the sunflower oil to increase as the shear rate increases causing a shear thickening effect [33].

2.3.6 Halloysite (HNT) clay nanotubes as lubricant additives

Halloysite nanotubes (HNT) are natural aluminosilicate clay minerals ($Al_2Si_2O_2(OH)_2$ nH_2O) similar to kaolinite [34]. "Halloysite-(10 Å)" is the hydrated version of halloysite (where n = 2), which has one layer of water molecules between the multilayers. The “halloysite-(7 Å)” dehydrated structure of halloysite (where n = 0) is formed by the loss of the interlayer water molecules under mild heating and/or a vacuum environment [35]. HNT has a multilayer tubular shape which usually consists of walls include 15-20 layers and an outer diameter of ca. 50 nm and a length ranging from 500 to 1000 nm. HNTs internal surface consists of Al-OH bond and external surface consist Si-O-Si bond because of which it can exhibit different properties [36]. Figure 3 depicts a schematic illustration of Halloysite's structure.

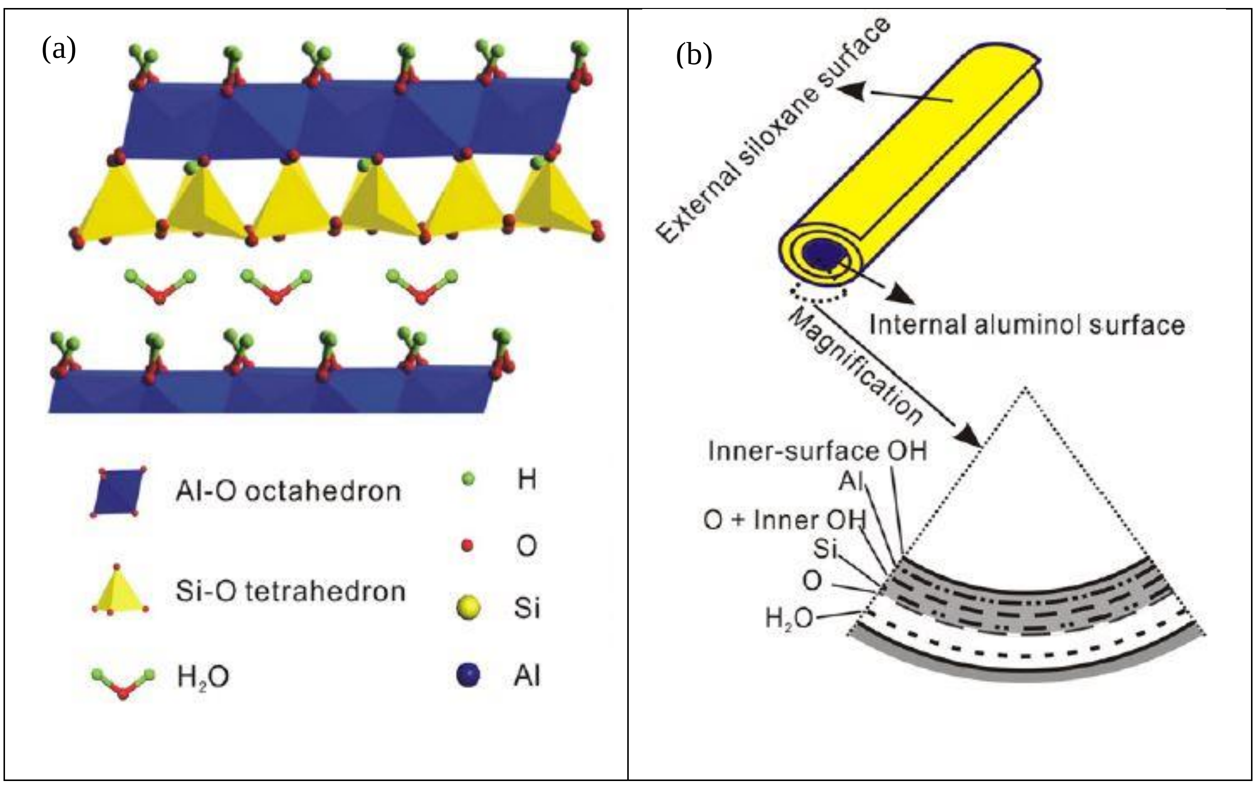


Figure 3: Schematic diagram (a) Crystalline structure of Halloysite Nanotubes (b) Curly morphology of HNT particle [35].

Halloysite nanotubes (HNTs) are good candidates for lubricant additives because they are naturally formed low-cost and non-toxic nanoparticles. A study shows that HNTs dispersed at the varying concentration in polymeric lubricants can increase the load-carrying capacity by about 72 percent and reduce wear volume loss and COF by about 70 percent because of the formation of tribofilm [35]. The addition of HNT as lubricant additives can also lower the cost of lubrication by lowering energy consumption. Further study on HNT as lubricant additives can be a good solution for green lubricants. It is good to use this oil in closed machinery systems. Further research can be done to modify nano-lubricants by adding anti-oxidant agents.

2.4 Applications

The most important parameter of vegetable oil-based nano-lubricants is their biodegradability. So, our current modified nano-lubricants are non-toxic and have renewable properties. More on, flash points of our nano-lubricants are higher than most of the mineral oils. Due to high flash points, it can be used in a higher temperature environment. This oil has high viscosity index, so there is less viscosity variation with temperature. It can be used to better lubricate hard contacts under the boundary lubrication mechanism. Another important area of our nano-lubricants application is in the automotive lubrication system.

CHAPTER III

METHODOLOGY

3.1 Nano-lubricants Formulation

Nano-lubricants were prepared using commercially available sunflower oil, corn oil, and peanut oil with the addition of halloysite nanotube (HNT) as lubricant additive in different concentrations. The halloysite nanotube was supplied by SIGMA-ALDRICH Co. (St. Louis, MO, USA) and dispersed it in vegetable oil with great care to formulate nano-lubricants. The morphology of the HNT nanotubes was verified using Scanning Electron Microscopy (SEM). To measure the weight, a Mettler Toledo XS205DU electronic balance (Mettler-Toledo LLC, Columbus, OH, USA), as shown in Figure 4, with an accuracy of 0.01 mg was used not only for preparing samples but also for measuring blocks before and after each test. For each vegetable oil (sunflower oil, corn oil, peanut oil) six samples were prepared with HNT concentrations of 0.50, 1.00, 1.50, 2.00, 2.50, and 3.0 wt.% in separate vials. To prepare the nano-lubricants, the electronic balance machine is first turned on by using the start button shown in Figure 4 and setting the weight to zero by pressing the button 0. Then, the weight of an empty vial needs to be measured and the weight needs to be calibrated to 0 while the vial is placed on the balance machine. Then HNT was poured in empty vial by using a spatula in different concentrations followed by different vegetable oils. The vegetable oil should be poured into the vial until the total weight of the lubricant become 15gm.

To determine the mass of nanoparticles required to prepare the nano-lubricants at different concentrations, the following equation was used:

$$\text{Mass of nanoparticles} = \text{Weight of nanolubricant} \times \ \% \text{ of nanoparticle} \qquad (1)$$

Figure 4 : Electronic balance (Mettler Toledo XS205DU).

Different concentrations of nano-lubricant were prepared for sunflower, corn, and peanut vegetable oil. Table 8 shows peanut nano-lubricants data.

Table 8: Peanut nano-lubricants preparation data.

Concentration	HNT weight (gm)	Total lubricant weight (gm)
Peanut Control	0	15.009
0.50%	0.0750	15.007
1.0%	0.1500	15.017
1.5%	0.1875	15.000
2.0%	0.3000	15.003
2.5%	0.3750	15.004
3.0%	0.4500	15.024

The next step is to mix the nanotubes with vegetable oils by ultrasonication to get the perfect mixture of our nano-lubricants. The vials are put through ultrasonication for pulse intervals of 3 seconds “on” and 3 seconds “off” for a total of 6 minutes using a 120-Watt FisherbrandTM Model 120 sonic dismembrator (Thermo Fisher Scientific Inc., Waltham, MA, USA), shown in Figure 5. At first, power on the ultrasonic dismembrator by pressing the “on” button. Then, the lubricant vial was fixed on the bench using the orange clamp, as shown in Figure 5. Then press the “start” button to continue the mixing process until it is complete on its own. During ultrasonication, a frequency of 20KHz was used to ensure uniform dispersion and suspension of nanoparticles in the lubricant. Dispersion of halloysite Nanotubes in vegetable oils by ultrasonication reduces agglomerates' size.

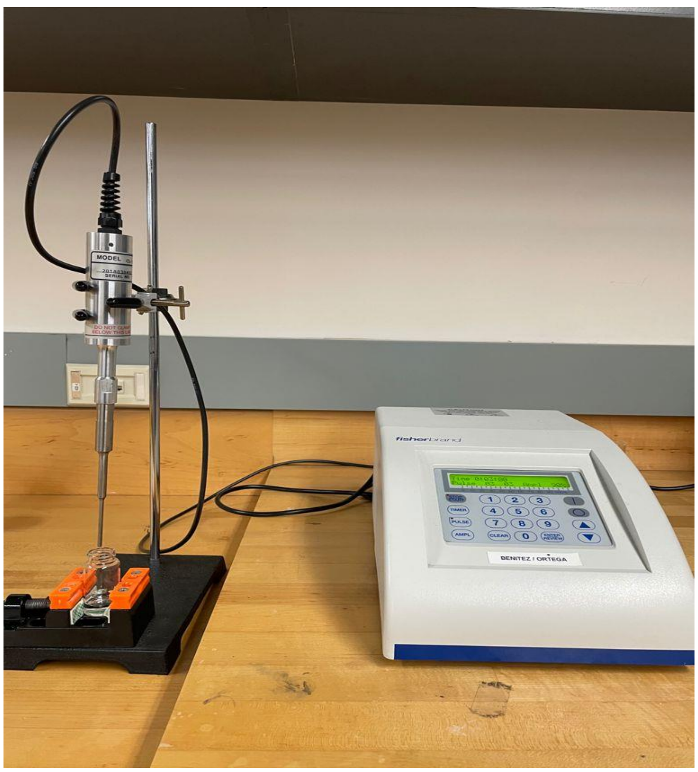


Figure 5: 120-Watt FisherbrandTM Model 120 sonic dismembrator.

3.2 X-Ray Diffraction (XRD)

XRD experiment is used to characterize the halloysite nanotube (HNT) to find out its crystal structure. XRD experiment is based on the principle of Bragg's law ($n\lambda = 2d\sin\theta$), where λ is the wavelength of x-ray, d is the spacing of crystal layers, θ is the incident angle and n is an integer. In this experiment, the X-ray diffractometer D8 Advance was used where CoKα was the source radiation. The sample was examined in the 2θ range, ranging from 10 ° to 70 °, step size 0.01° and count time 2s /step. To examine the phase of the HNT, 10 gm powder sample was used on the sample holder by using a spatula. To perfectly set the sample on the sample holder, HNT powder was flushed with a flat piece of glass with a smooth surface. Then the glass piece was removed with great care to avoid anomaly and introduce the sample holder for exposing the surface X-ray diffractometer. A beam of monochromatic X-rays is allowed to the incident in the sample and the reflected x-rays are detected by a one-dimensional detector. The diffractograms show the intensity of the observed diffraction function of angle of incidence and the intensity is characteristic of each crystalline component present in the sample. To identify crystalline phases, the resulting spectra were compared with spectra patterns available in the global database.

3.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was done to determine the thermal stability of the halloysite nanotube. A thermobalance TA Instruments SDT 2960 Symultaneus was used to perform TGA. The device consists of an electronic balance placed inside an oven; the device is coupled to a control microprocessor and a processing station data. Samples in the form of fine powder are slid and placed inside the analysis equipment for testing; they are then calcined at 800°C temperature range that increases at 10°C per minute. The HNT sample of 1 gm was used to examine the TGA parameters. HNT powder was placed on the sample holder carefully and ensured that 5/6 of the total volume were covered. Then the prepared sample with sample holder is placed into the analysis equipment.

3.4 Tribological Characterization

A block-on-ring tribo-tester, shown in Figure 6, was used to measure the wear depth, frictional force, and temperature with respect to time for the different vegetable oils with and without HNT additives. Volumetric wear and coefficient of friction (COF) were then calculated by using measured experimental data.

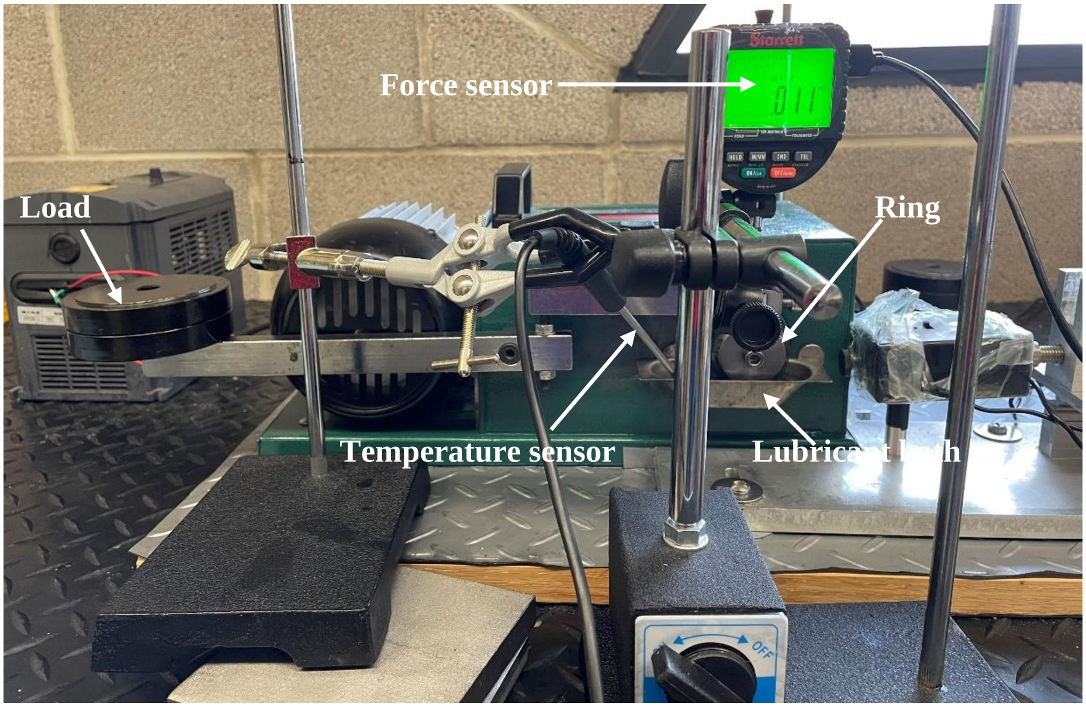


Figure 6: Setup of custom -made block-on-ring tribo-tester.

To carry out the tribological test, first block specimens were prepared by cutting an AISI 304 steel square bar into blocks using a Band Saw. Then, the blocks were sanded to the size of

6.35 x 6.35 x 14 mm by using the NANO 1200T Grinder Polisher (Pace Technologies), shown in Figure 7, to fit perfectly to the arm of the block-on-ring tribo-tester.

Figure 7: Nano 1200T grinder polisher.

The blocks are marked by using an engraver rotary tool to identify, and polished on two sides by using 600-grit sandpaper to gain similar surface textures for each of the block specimens. Then impurities are removed by placing blocks into the ultrasonic bath shown in Figure 8.

Figure 8: Ultrasonic bath.

During the ultrasonic cleaning, the blocks are first placed into a container with acetone for five minutes, then five minutes in a container with methanol. This cleaning process removes metallic dirt as and as grease or other factors that can affect the weight of the block. All the steps were done based on ASTM G-077-17 standard procedure [37]. While the sliding tests are being performed in the block on ring tribotester, the nano-lubricants are placed into an oil bath chamber to allow consistent lubrication; as the test ring is being rotated, it is covered by the lubricant through centrifugal forces. This can be observed in Figure 6.

The tribological tests were performed using a load of 266N, at an environmental temperature varying from 19 ℃ to 23 ℃, at 172 rpm, for about 1200 sec. After testing, the blocks were cleaned again in the ultrasonic bath for 10 minutes (5 minutes in acetone and 5 minutes in a methanol). Then tested blocks were kept enclosed for 24 hours and measured the block mass to determine the volumetric wear by considering block density of 0.008 g/mm^3. Table 9 shows the test specimens characteristics.

Table 9: Characteristics of test specimens.

Specimens	Material	Dimension
Blocks	AISI 304 steel	14 × 6.35 × 6.35 mm
Rings	AISI 52100 steel	*d* = 40 mm

3.5 Surface Characterization

3.5.1 Surface characterization by SEM

Scanning Electron Microscopy (SEM) was used to characterize the morphology of the halloysite Nanotube and the wear scar of the blocks that experienced less wear during the tribological tests. To study the HNT morphology, a small amount of HNT powder is placed on aluminum stubs using conductive tape. Then the sample is mounted on a stage in the vacuum chamber area. The position of the electron beam on the sample is controlled by scan coils situated above the objective lens. These coils allow the beam to be scanned over the surface of the sample. In the case of blocks, same procedure was followed to analyze the wear scars. Figure 9 shows scanning electron microscope used in surface characterization.

Figure 9: Scanning electron microscope.

3.5.2 Surface Characterization by profilometer

A MahrSurf M300 C surface profilometer (Mahr Inc., Providence, RI, USA) was used to measure the surface roughness of the blocks before and after the wear tests. The surface roughness of the blocks used for the best concentration nano-lubricants was analyzed for each vegetable oil. To get a good result each specimen was tested three times. Figure 10 shows the surface profilometer used in measuring the roughness of the blocks.

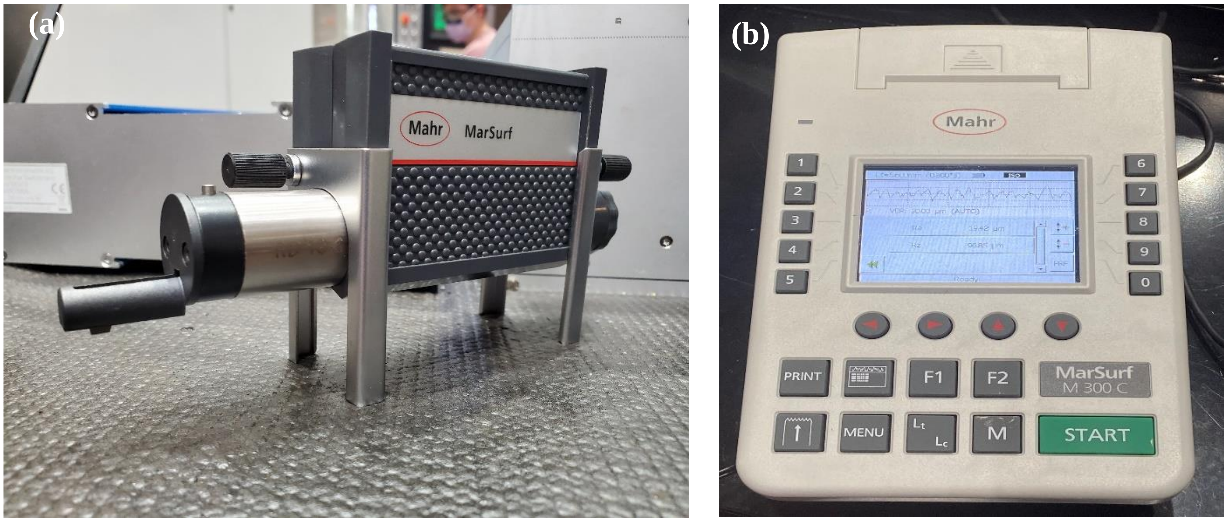


Figure 10: Mahrsurf M300C profilometer (a) Inductive skidded probe (b) Control unit.

Profilometer working procedure:

- The Mahrsurf M300C profilometer must be connected to a power source in order to perform the roughness test.
- Then the surface profilometer needs to be turned on by pressing the “START” button as shown in Figure 10(b).
- The profilometer probe must be calibrated after the machine is turned on.
- After the profilometer has been calibrated, block must be placed under the probe illustrated in Figure 10(a) to determine the roughness. The roughness test was carried out on the blocks that had been lubricated with a base oil as well as the blocks that were the most compatible.
- Roughness was measured three times on the worn part and three times on the untested area for each block. Finally, the perfect result was obtained by averaging three results.

3.6 Tapping Torque Tests

Tapping torque tests were carried out to determine the performance of the best concentration of each vegetable oil-based nano-lubricant in a real-world application. To determine the torque acting on the specimens with different lubricant conditions a tapping torque tester was used following the ASTM D5619-00 standard [38], titled “Standard Test Method for Comparing Metal Removal Fluids Using the Tapping Torque Test Machine”. The quality of the tapping test result depends on tapping material specimen, tool size, working speed, etc. In this work, Aluminum 6061 specimens were used as tapping material, and taps of size M6 x1.00 mm were used as a tapper. To perform the tapping torque tests, a milling machine (Grizzly mill model G0796, Grizzly Industrial Inc., Springfield, MO, USA) was used. The testing speed of the spindle was kept constant at 90 rpm. At first, a hole of 33.02 mm was created in each specimen by using a drill bit. After that, the tap was used to create threads that reached a depth of 31.75 mm into the hole. The taps were completely lubricated with 0.5 mL of the selected lubricants during the tapping torque test. A screw was used to secure the specimens in the specimen holder. The moment arm attached to the specimen holder is be used to determine the force exerted by the tap as it forms threads on the workpiece. Two tapping torque tests were performed for each tapping operation: one for the base oil and another for the highest concentration nano-lubricants in each vegetable oil. Figure 11 shows the tapping torque tests performed in the Grizzly milling machine.

Figure 11 : Tapping torque test in Grizzly milling machine.

During tapping torque test, Logger lite software was used to collect the acting force on the specimen with time. Then final torque is calculated by using the following equation,

$$\tau = F \times d \tag{2}$$

Where τ is the tapping torque, F is the force obtained from the force sensor during tapping, d is the distance of the moment arm attached to the tapping torque specimen holder.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Morphology (HNT SEM analysis)

Halloysite Clay Nanotubes (HNT) are used as lubricant additives to prepare the nano lubricants. Figure 12 shows the morphology of the HNT. The SEM images were taken at a magnification of 15.00KX, 20.00KX, 25.00KX, and 40.00KX. As the manufacturer provides only the particles with mentioning the specific gravity, density, and chemical formula, to analyze the specific shape of the particles it was required to do SEM observations. From Figure 12, it is observed that the shapes of the halloysite nanotubes are hollow tubular. The length and diameter of the tubes vary significantly. The variation of sizes of nanotubes may be due to the harsh processing of nanotubes in industry. No agglomeration was observed from SEM images thus nanotubes were not stuck together. The length and diameter of the nanotubes were measured by using more than sixty data points. The maximum length of the nanotube was 676.871 nm and the minimum length of the nanotube was 124.544 nm. The average length of the HNT nanotubes obtained from the SEM images was 303.267nm. The average diameter of the nanotube was 65.373 nm, where the maximum diameter of the nanotube was 130.435 nm and the minimum diameter was 31.353 nm. From the images, it was clear that the nanotube presents a hollow cylindrical shape

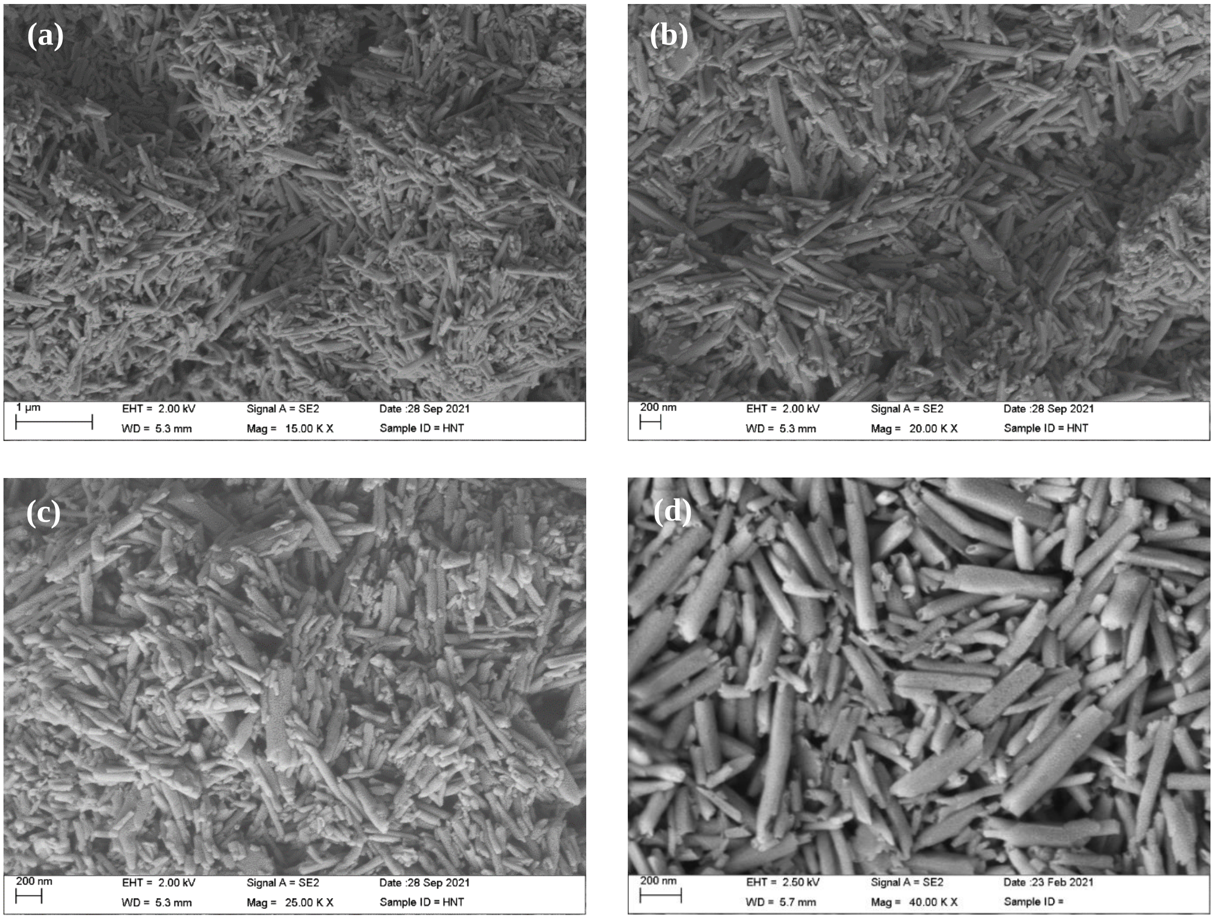


Figure 12 : Morphology of Halloysite Nanotubes at (a) 15.00KX, (b) 20.00KX, (c) 25.00KX, and (d) 40.00KX magnifications.

4.2 X-Ray Diffraction Analysis (XRD)

To analyze crystal phases present in halloysite, XRD analysis was carried out. Figure 13 shows the XRD curve for Halloysite Nanotubes. The location of the characteristics peak of the XRD pattern of HNTs is 13º, which is consistent with the fundamental spacing of the layer space. The diffraction signals at 24.6º, 28.0º, 32.5º, 43.7º, 46.2º are also in accordance with the values described in other documents [39]. The sharp peak at 13º (2θ) indicates a plane of 001 at 15.318Aº, which implies that the halloysite nanotube was in hydrated condition [40].

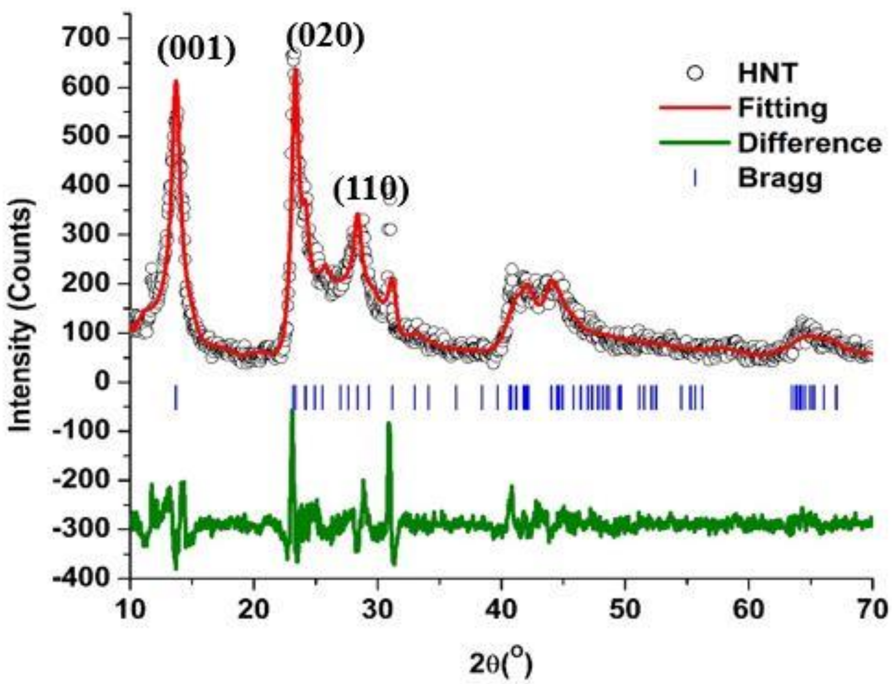


Figure 13: X-Ray analysis of HNT.

Table 10 shows the lattice parameters for HNT nanoparticles. The HNT c lattice parameter is longer than it should be, this parameter is known to expand and contract depending on the amount of water present in the sample. This is due to the c-axis of the crystal contains planes stacked together as water get stuck between the layers the c-axis will expand.

Table 10: Lattice parameters determined for the HNT nanoparticles using the LeBail fitting procedure.

Sample	Space Group	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	χ^2
HNT	C c	8.916(6)	8.916(6)	15.318(6)	90.00	101.89	90.00	2.91

4.3 Thermogravimetric Analysis (TGA)

TGA analysis were performed to evaluate the thermal stability of the halloysite nanotube by using a NETZSCH TG 209F3 analyzer. The samples were heated from room temperature to 1000 ºC within an open ceramic pan at a heating rate of 10k/min under a nitrogen flow of 20ml/min. The TGA curve of HNT is shown in Figure 14. The HNTs lose 16% of their total mass during the heating process in two steps. A slight mass loss of 2.23% from room temperature to 100 ºC was observed from the TGA data which is due to the evaporation of the adsorbed water on the surface of HNTs. Then the mass loss between 100 ºC to 400 ºC was a result of the gradual loss of crystal water in the sheet of HNTs. As condensation reaction of Al-OH groups occurs between 400ºC to 600ºC, a rapid weight loss was observed. Mass loss remained unchanged in the range of temperature of 600ºC to 1000ºC, which implies very negligible loss of mass.

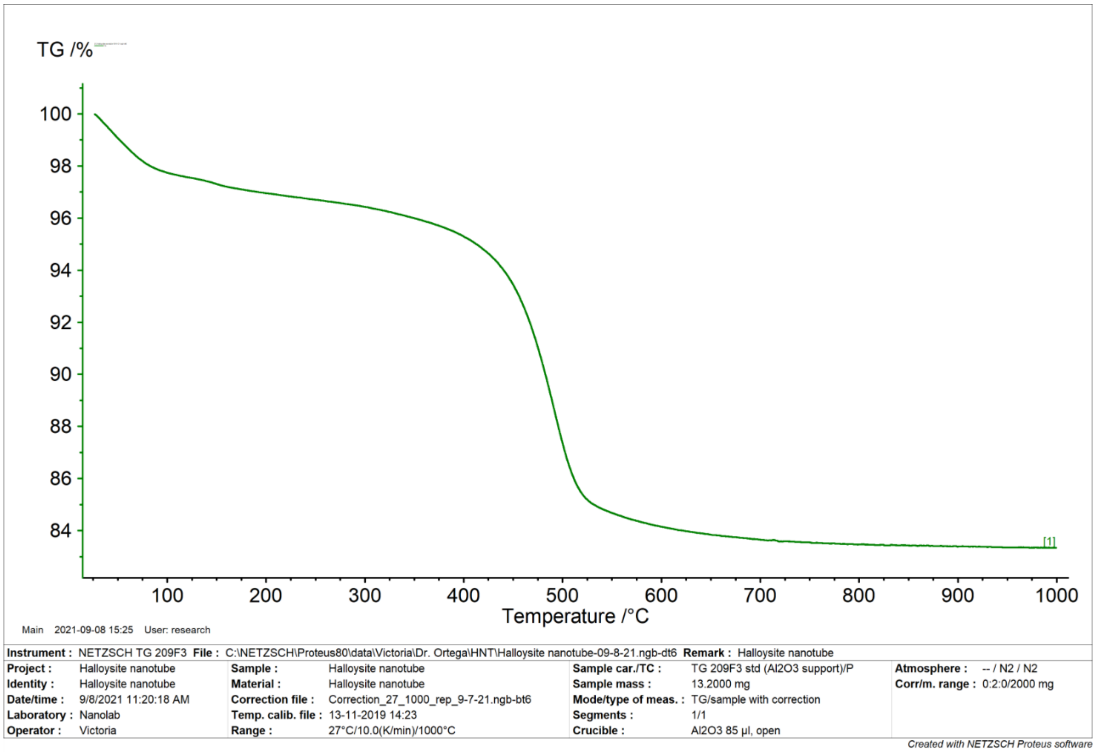


Figure 14: TGA curve of HNT.

4.4 Tribological result

The tribological performance of sunflower, corn, and peanut oil was analyzed with and without the addition of halloysite clay nanotubes at different concentrations. The experimental data was collected from a block-on-ring tribometer experiments under similar test conditions for each sample. For each sample, data of frictional force acting on block specimens, lubrication temperature, and wear depth were gathered. To calculate wear volume equation 3 is used which is shown in below

$$\text{Wear volume}(\text{mm}^3) = \frac{\text{mass of block before test(g)} - \text{mass of block after test(g)}}{\text{block density (g/mm}^3)} \quad (3)$$

Where the block density value 0.008 g/mm^3 corresponding to stainless steel. To find out the coefficient of friction (COF), the average friction force acting on block was collected, and was calculated by using equation 4

$$F_f = \mu \times F_N \tag{4}$$

Where F_f is the friction force acting on the block specimen, μ is the coefficient of friction, and F_N is the normal force acting on the block.

During the test, a constant normal force was applied to the tribometer, so it was easy to calculate the coefficient of friction by using equation (4).

4.4.1 Friction Force

The addition of different concentrations of halloysite nanoclay nanotubes has a great impact on the friction force acting on the block. The friction forces recorded during the experiments for the different nano-lubricants are shown in Figures 15, 16, and 17. Figure 15 shows the friction force recorded during the tribological tests lubricated with sunflower oil-based nano-lubricants. The frictional force of sunflower base oil was initially 35 N whereas, with the addition of HNT nanoclay, the initial friction force was less than 20 N. This could be attributed to the shape of the nanotubes. Since the nanotubes are cylindrical, they act as rollers, reducing the friction between the contact surfaces. In the case of sunflower and its nano-lubricants, 1.5 wt% of HNT experienced less friction force compared to other concentrations.

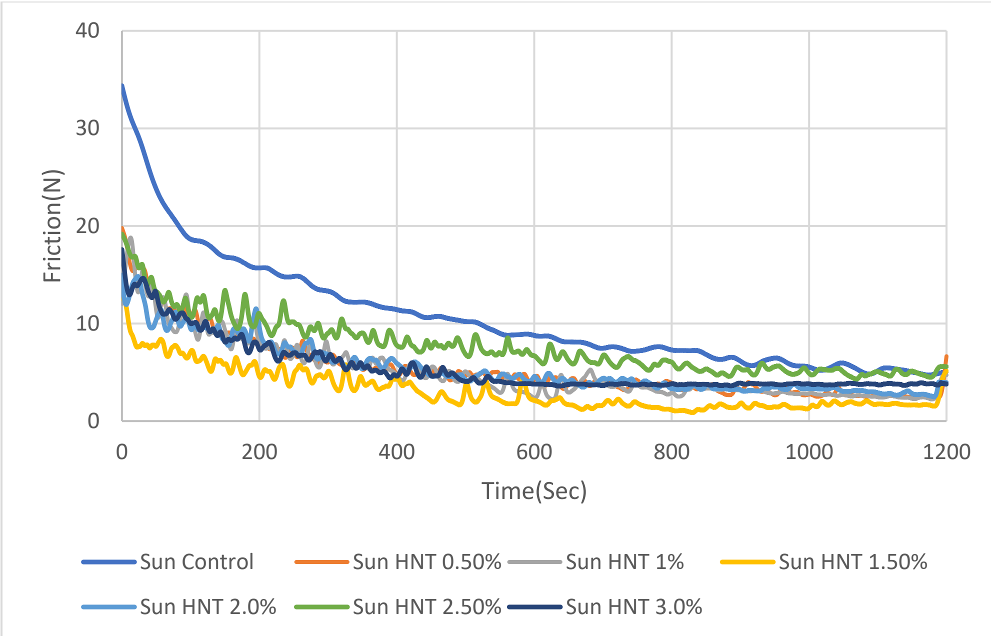


Figure 15: Friction force vs time graph for sunflower oil-based nano-lubricants.

Figure 16 shows the variation of the friction force with respect to time for corn oil with and without HNT additives. For the control corn oil, the maximum friction force was 22 N and the addition of HNT nanotubes reduced the maximum friction force to less than 16 N. With the addition of HNT nanotubes to the corn oil, the friction force was reduced remarkably, and for 1.0 wt% concentration, friction force decreased 54% compared with the base corn oil.

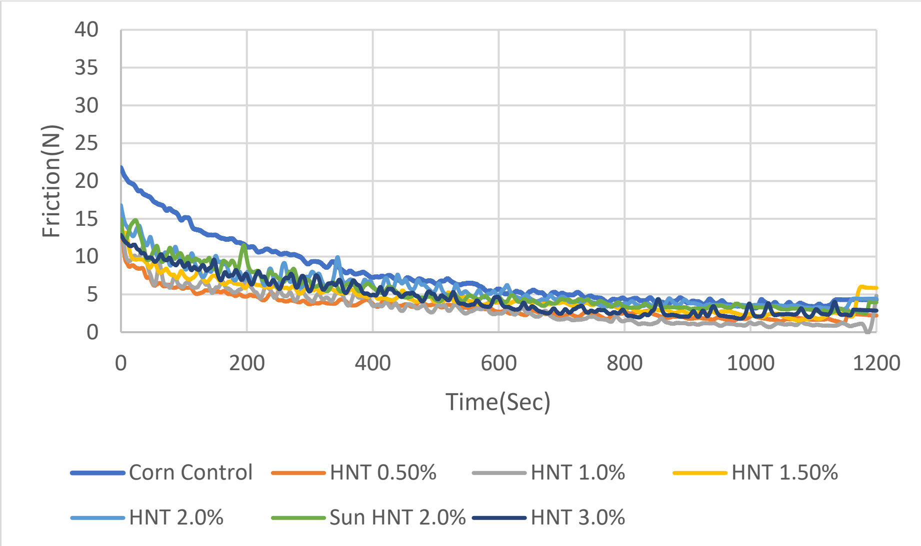


Figure 16: Friction force vs time graph of corn oil-based nano-lubricants.

From Figure 17, the maximum friction force for peanut oil is 35N, and the lowest friction force was observed for 2.0 wt% HNT peanut nano-lubricants. From base peanut oil maximum frictional force for the 2.0 wt% HNT concentration. The friction force gradually decreased for peanut base oil and after a certain point, the frictional force started fluctuating till the end of the experiment. This is maybe due to the low lubrication properties of peanut base oil.

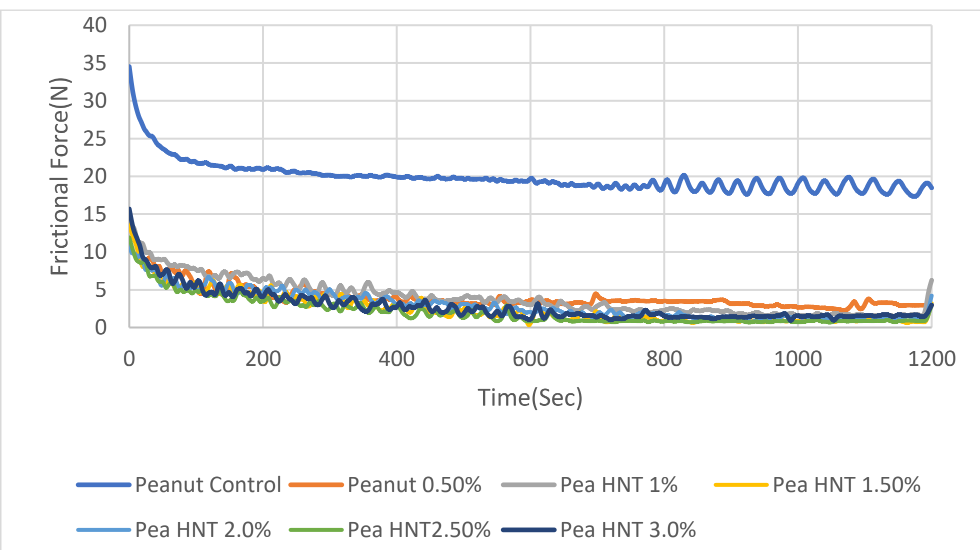


Figure 17: Friction force vs time graph for peanut oil-based nano-lubricants.

With the inclusion of nanoparticles, the friction force was reduced, resulting in thin-film lubrication and a change in friction type from sliding to rolling. This result agreed with that of Pena-Paras et al. [41], who reported that the presence of HNT particles reduced the contact area.

4.4.2 Coefficient of friction

Figure 18 shows the Coefficient of Friction (COF) results for the base vegetable oils modified with different HNT concentrations. Figure 18a shows the COF results for the sunflower oil nano-lubricants. It can be observed that the COF for sunflower base oil was 0.0398 and with addition of HNT at different concentrations, the coefficient of friction was reduced significantly. The lowest COF (0.0118) was obtained with the 1.5 wt% concentration, 70.35% lower than the COF obtained with base sunflower oil. The maximum COF (0.0286) was obtained with the 2.5 wt% HNT concentration among all other sunflower nano-lubricants. In Figure 18b, shows the COF results for corn oil-based nano-lubricants. The lowest coefficient of friction was obtained with the 1.0 wt% HNT concentration which was 55.63% lower than base corn oil. COF for all corn oil-based nano-lubricants with concentrations from 0.5 to 3.0 wt% of HNT were lower than its base oil COF. Coefficient of friction was reduced due to the rolling effect of HNT nanotubes. Figure 18c, shows the COF results for peanut oil-based nano-lubricants. Peanut control showed the maximum COF which was 0.0743, notably higher than corn and sunflower base oils. The lowest COF was obtained at 2.5 wt% HNT concentration which was 0.0093, 89.50% lower than the COF of base peanut oil. The polishing and rolling actions of nanoparticles decreased the coefficient of friction [33].

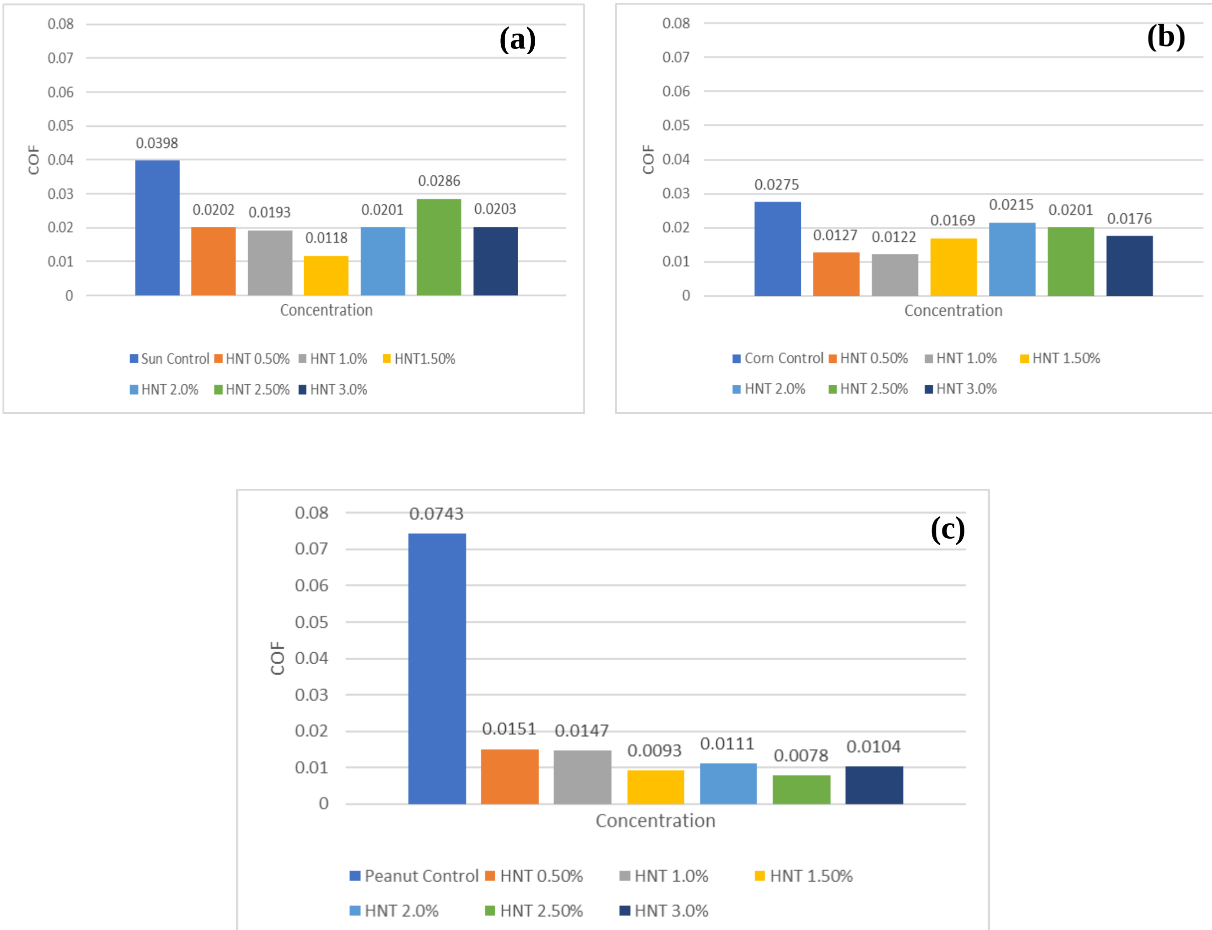


Figure 18: Coefficient of friction results for (a) sunflower (b) corn (c) peanut oils modified with HNT at different concentrations.

4.4.3 Volumetric wear

The volumetric wear of the each blocks was calculated by considering the mass loss before and after the test. The differnces of the initial and final mass of the block of each test was divided by the density of the block to get the wear using equation (3). Each block was prepared for two friction test along two sides of the block faces. So, three weights for each block was recorded to get the data of mass loss. A density value of 0.008 g/mm^3 was used for the stainless steel specimens. The mean volumetric wear for sunflower, corn, and peanut oil are shown in

Figures 19, 20 and 21 respectively. In case of the sunflower oil without nanoparticles, the volumetric wear loss was 9.013 mm^3 and with addition of HNT the volumetric wear was reduced upto 6.425 mm^3 with the 1.5wt% concentration of HNT. Volumetric wear was reduced upto this concentration due to the rolling effect of halloysite nanotubes, which reduce the contact surface area between the mating surfaces. Then, the volumetric wear started to increase from 2.0 to 3.0 wt% of HNT modified sunflower nanolubricant due to aggolomeration of HNT nanoparticles [33].The overall percentage of wear reduction was for the best concentration was approximately 29% compared to the base sunflower oil. After adding HNT percentage more than 1.5wt%, the volumetric wear loss started to increase and exceeded the base sunflower volumetric wear loss.

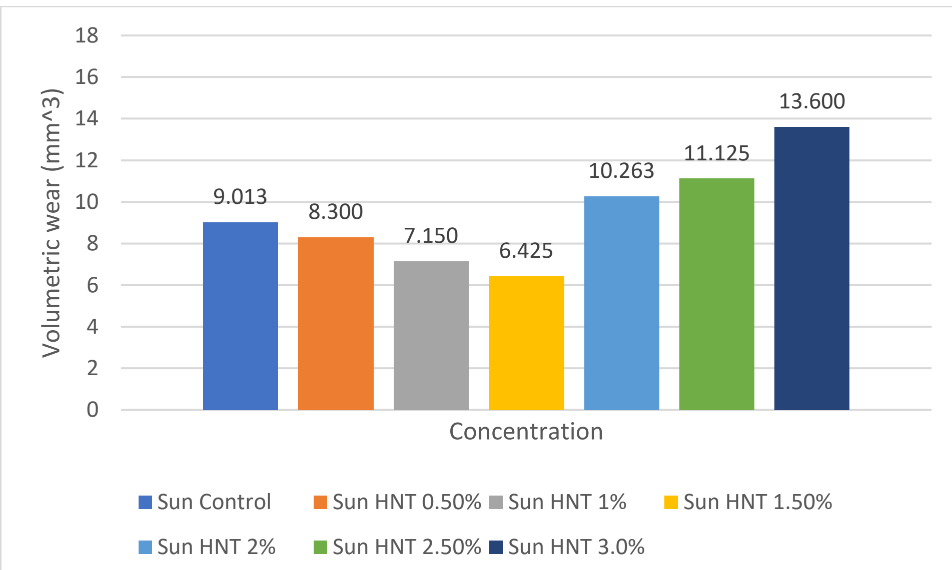


Figure 19: Mean volumetric wear of AISI 304 specimens lubricated with sunflower oil modified with HNT.

Volumetric wear of corn oil modified with HNT at different concentrations is shown in Figure 20. The corn base oil showed a volumetric wear of 16.125 mm^3. Addition of HNT at different concentrations reduced the volumetric wear. The lowest volumetric wear was obtained with 1.5

wt% HNT, which was 77.75% lower than base corn oil. Volumetric wear reduced gradually upto 1.5 wt% of HNT concentration and then it increased again above 2.0 wt% of HNT nanolubricant.

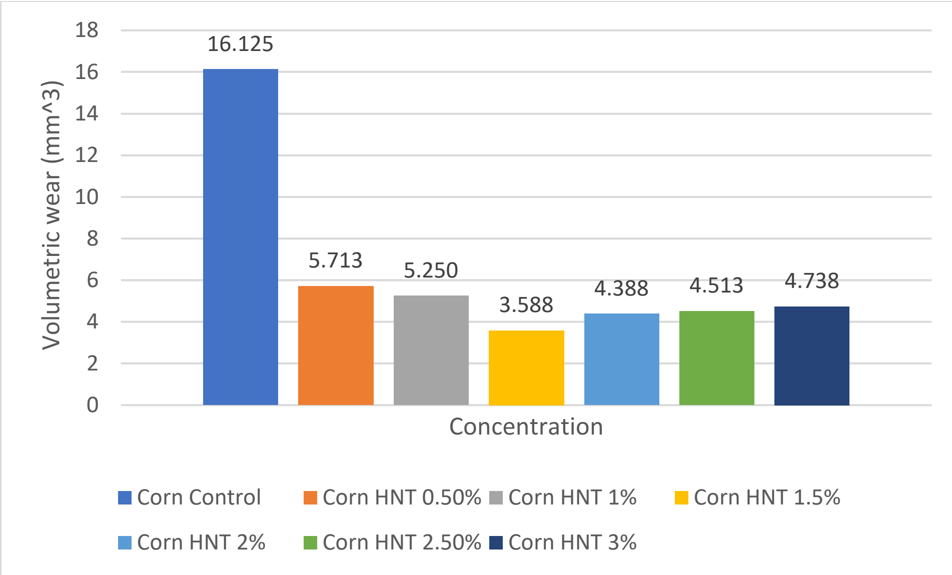


Figure 20: Mean volumetric wear of AISI 304 specimens lubricated with corn oil modified with HNT.

Compared to peanut base oil, its modified lubricants respresents improved tribological performance shown in Figure 21. The 1.5 wt% of HNT peanut nanolubricant showed lowest volumteric wear 5.8 mm^3 which is 66.83% lower than the base peanut oil. Among three base vegetable oils, peanut showed highest volumetric wear, whereas sunflower oil showed the lowest volumetric wear. Volumetric wear is reduced by adding nanoparticles up to a specific concentration, as demonstrated by Cortes and Ortega [42], who found that adding 1.00 wt percent CuO nanoparticles to coconut oil the volumetric wear was reduced by 33.32% compared to the base oil.

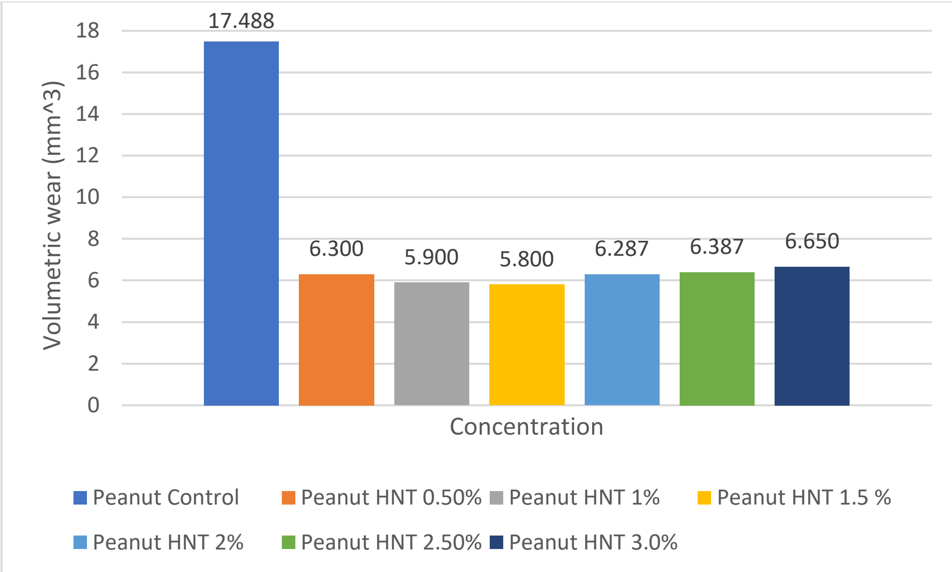


Figure 21: Mean volumetric wear of AISI 304 specimens lubricated with peanut oil modified with HNT.

4.4.4 Lubrication temperature

During the experiments, a temperature sensor was used to monitor the lubricant temperature. From the experimental data, it was observed that for all vegetable oil-based nano-lubricants, the lubrication temperature decreased with addition of halloysite nanotubes. The results of the lubrication temperature analysis are shown in Figures 22, 23 and 24.

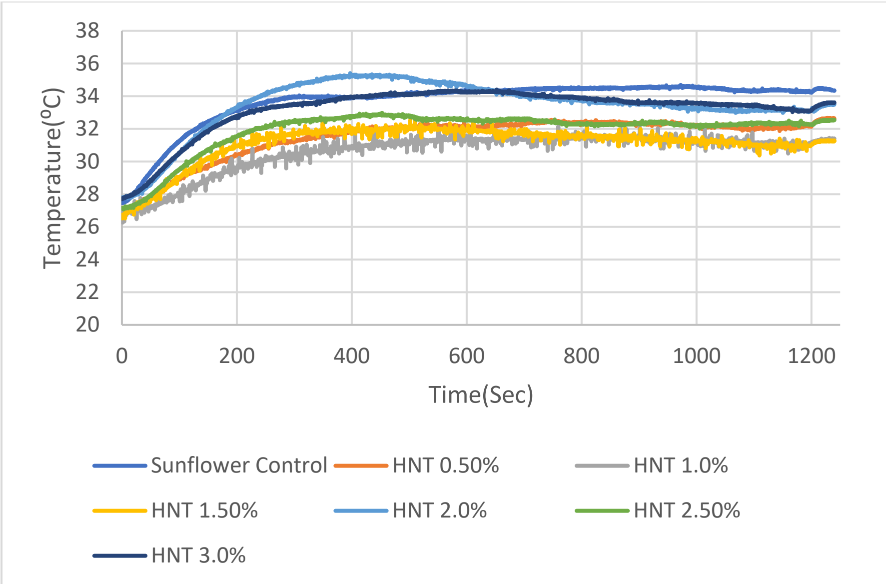


Figure 22: Temperature of sunflower oil-based nano-lubricant during tribological test.

In the case of the sunflower oil, shown in Figure 22, the base oil lubrication temperature was higher compared to HNT modified sunflower nano-lubricants. With the addition of HNT at different concentrations, the lubrication temperature was also reduced. The 1.0 wt% HNT concentration nano-lubricant showed the lowest lubrication temperature which was approximately 20% lower compared to the final temperature of base sunflower lubrication temperature. From the lubrication temperature profile, it is also clear that the lubrication temperature rises initially with time then takes a steady-state condition.

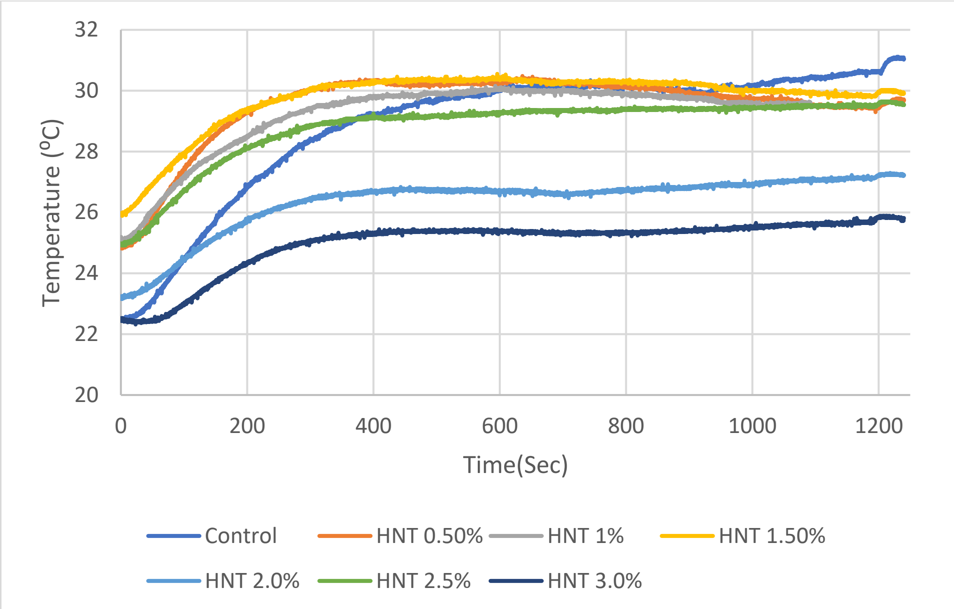


Figure 23: Temperature of corn oil-based nano-lubricants during tribological test.

In Figure 23, the lubrication temperature of corn base oil is higher compared to the temperature of the corn nano-lubricants. The 3.0 wt% concentration exhibits the lowest lubrication temperature. For all concentrations of HNT, the lubrication temperature decreased but it does not follow any linear pattern.

Figure 24 shows the lubrication temperature profile for peanut base oil and HNT modified peanut nano-lubricants at different concentrations. The lubrication temperature of peanut base oil was significantly high, and it showed a significant fluctuation. With the addition of nanotubes, the lubrication temperature was decreased and the 1 wt% of HNT concentration showed the lowest temperature profile of lubrication. Among sunflower, corn, and peanut base oils, the peanut oil showed maximum lubrication temperature and corn oil showed the lowest lubrication temperature.

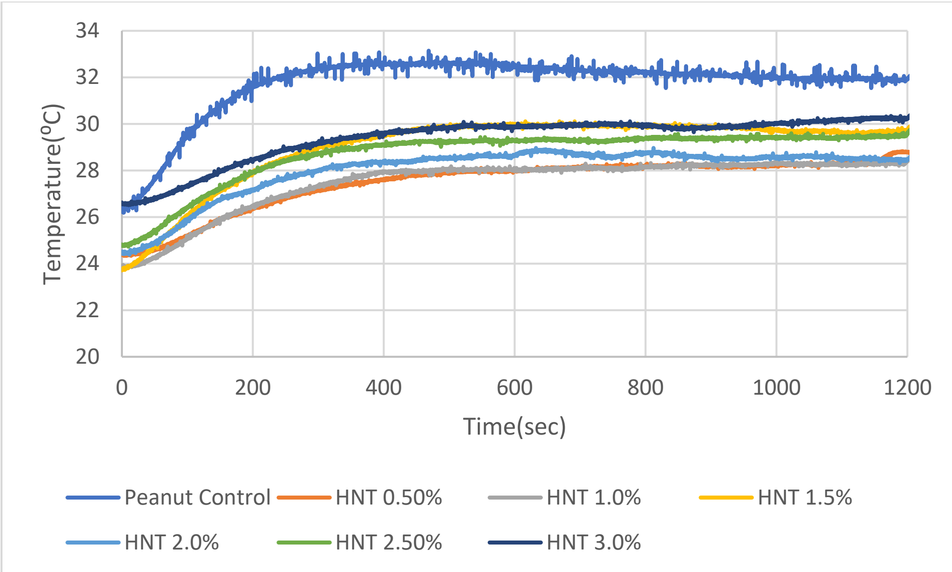


Figure 24: Temperature of peanut oil-based nano-lubricants during tribological test.

4.5 Wear surface characterization

Roughness tests were performed to analyze how the nano-lubricants would affect the surface roughness of the materials being evaluated in order to better understand the wear mechanisms occurring on wear scars. The surface topography of the wear scars was also examined using SEM on the blocks. Roughness test and SEM analyses were performed to examine blocks utilized in base sunflower, corn, and peanut oil, as well as their best concentration nano-lubricants. For sunflower, corn, and peanut oil, 1.5 wt% HNT nano-lubricants produced the best results in terms of volumetric wear and friction.

4.5.1 SEM of wear scars

Figure 25 shows the SEM images of wear scar of base sunflower, corn, and peanut oil. In the case of sunflower, corn, and peanut base it is observable from wear scar that there are a large number burrs and furrows due to the adhesive wear in the absence of tribofilm. These burrs and furrows increase friction between sliding surfaces thus resulting in higher mass loss. Large pits and grooves were also found in the wear surface, which increased friction and wears between the sliding surfaces.

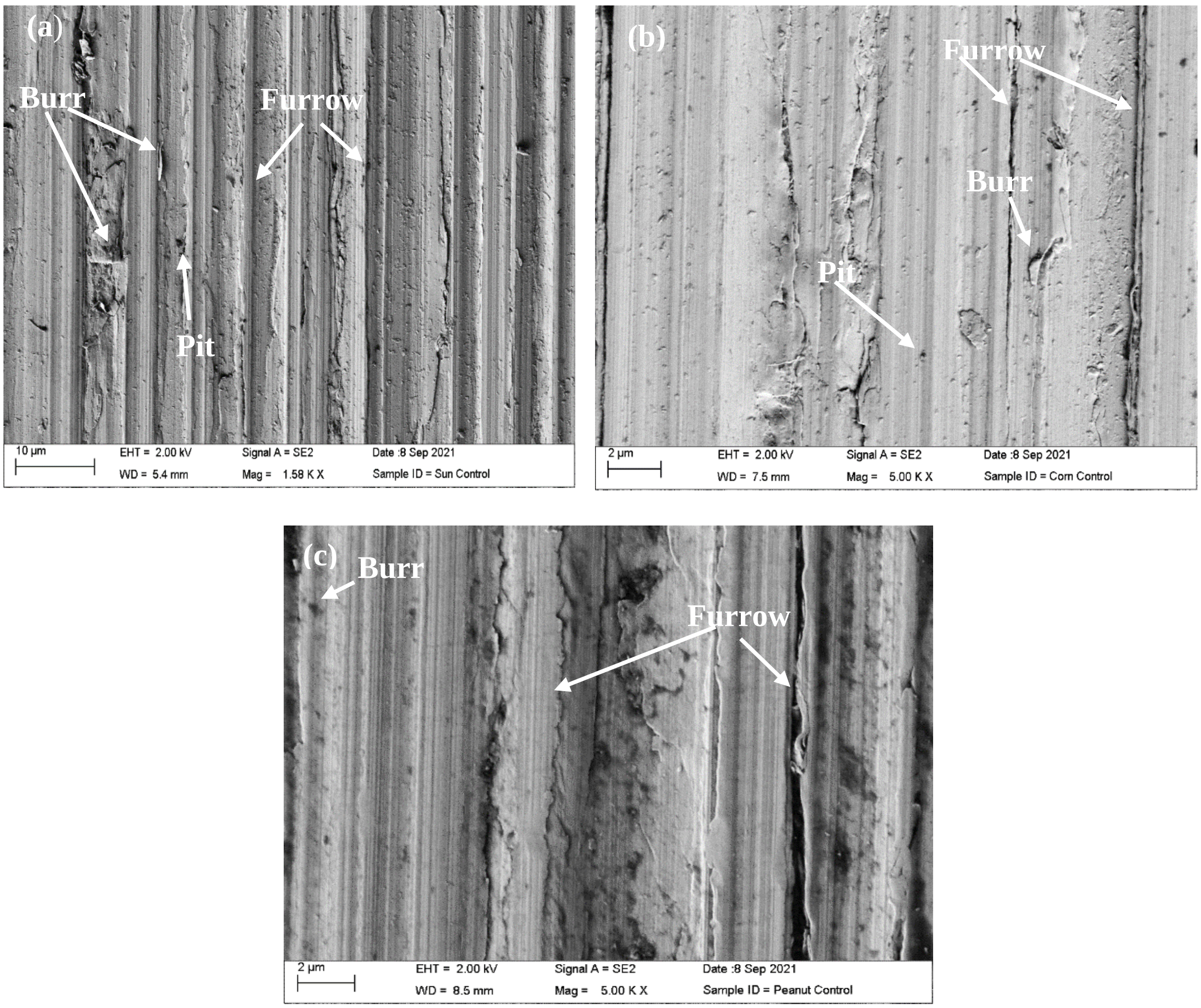


Figure 25: SEM micrographs of worn surfaces in blocks lubricated with base (a) sunflower, (b) corn (c) peanut oils.

Figure 26 shows SEM pictures of wear scars of the blocks used for best concentration HNT modified sunflower, corn, and peanut oil nano-lubricants. The wear scar in 1.5 wt% HNT modified sunflower oil, corn, and peanut oil has a limited number of burrs and furrows, reducing frictional force and resulting in low volumetric wear. More on, the exfoliation that occurs on the surface of the block of the best-modified nano-lubricant also helps to reduce the overall friction during the lubrication. It was also noticed that there were fewer grooves on the surface of used blocks when compared to base oil used blocks. As it acts as a rolling contact bearing, the inclusion of HNT nanotubes has an impact on the sliding surface, reducing contact. This result indicates that halloysite clay nanotubes play an active role in the contact zone [44].

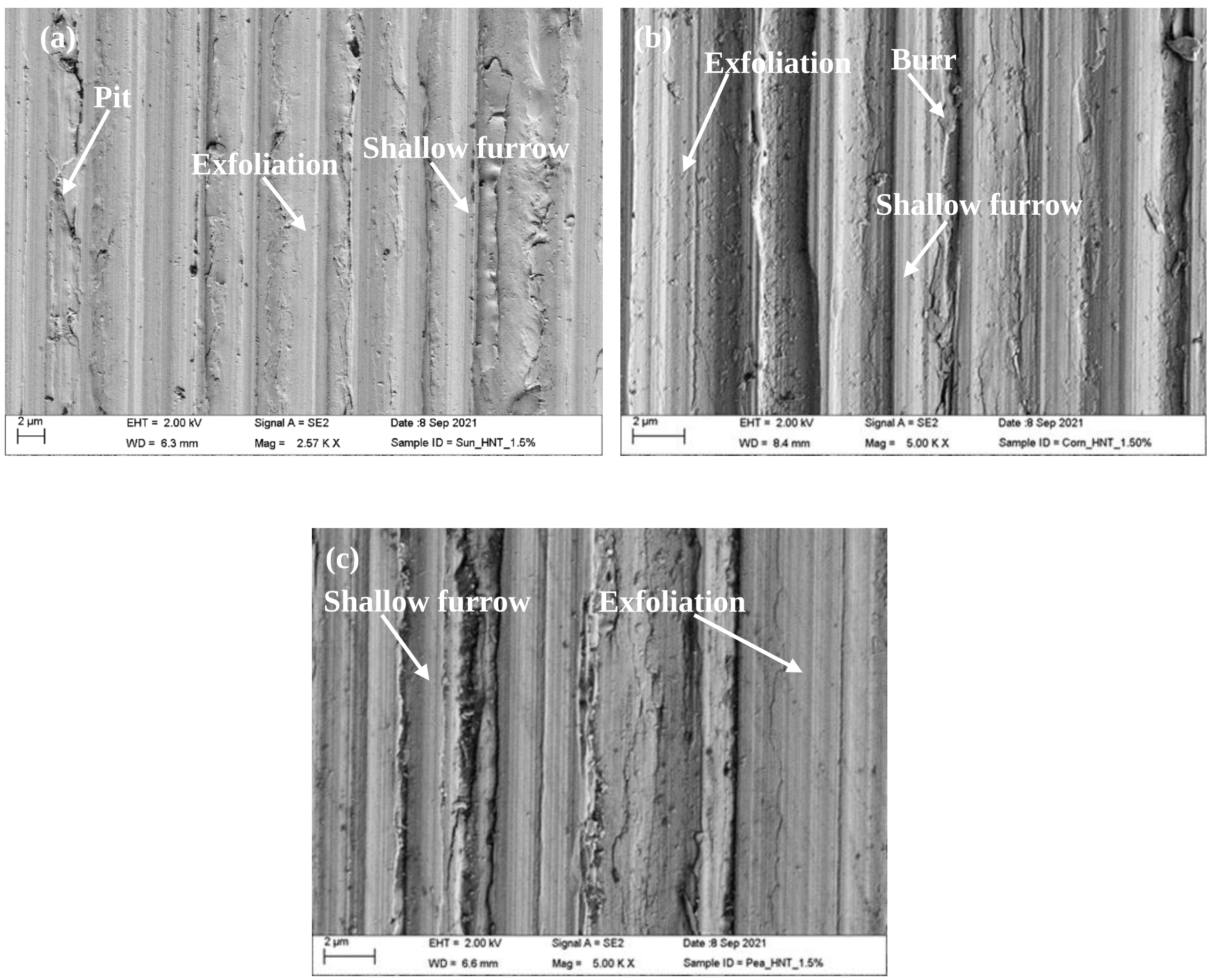
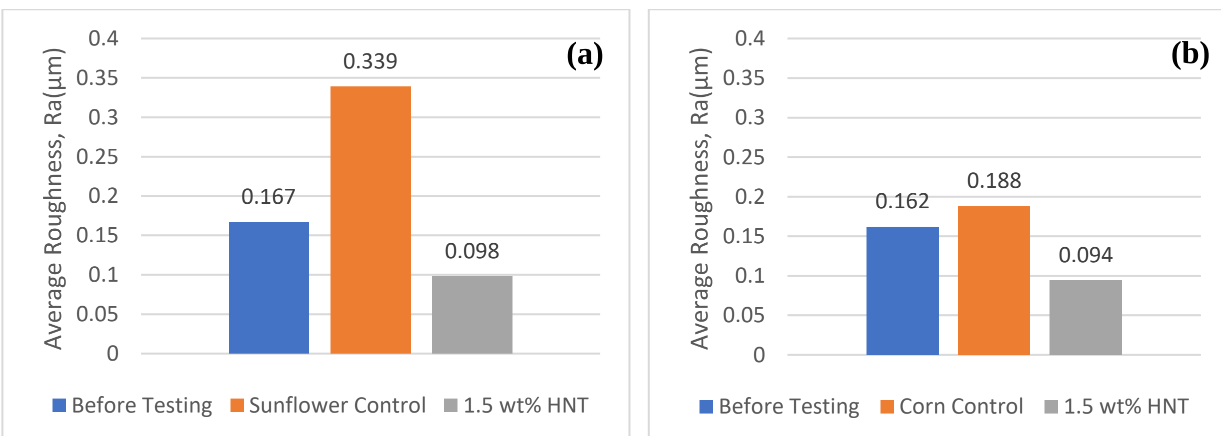


Figure 26: SEM micrographs of worn surfaces in blocks lubricated with (a) sunflower, (b) corn (c) peanut oils modified with HNT at 1.5 wt%.

4.5.2 Roughness

For each vegetable oil, and their best concentration nano-lubricant, the surface roughness of the blocks was measured before and after the test. The average surface roughness Ra values, acquired by the Mahrsurf M300C surface profilometer, are shown in Figure 27. The base sunflower oil had an interesting activity shown in Figure 27a, increasing the average roughness of the block by 102% when compared to the untested control block. This could be related to the low linoleic acid content in sunflower base oil [37]. The lowest average roughness was found in the wear scar of the block lubricated with 1.5 wt% HNT sunflower oil nano-lubricant. It can be observed that the average roughness was decreased by 71%, compared with the block lubricated with base sunflower oil.



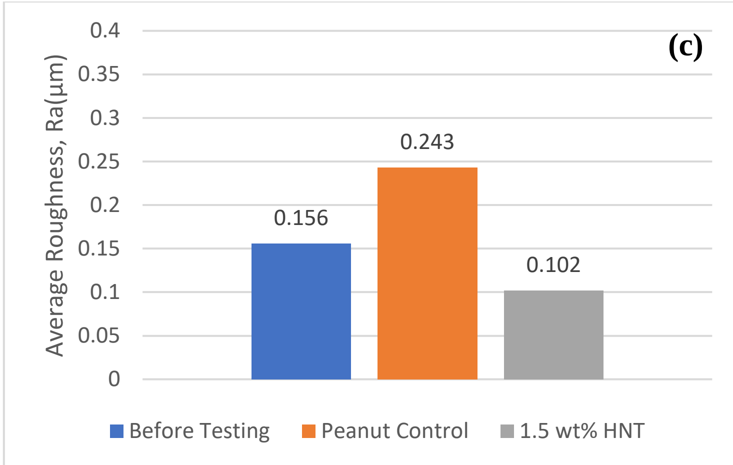


Figure 27: Average surface roughness of AISI 304 blocks lubricated with (a) sunflower oil(b) corn oil (c) peanut oil and modified with the best results of 1.5 wt% HNT nanotubes.

The average roughness of the block used for corn base oil was higher by 16% when compared to the untested specimen as shown in Figure 27b. The lowest average roughness was found in the wear scar of the block lubricated with 1.5 wt% HNT corn oil nano-lubricant. It can be observed that the average roughness was decreased by 50%, compared with the block lubricated with base corn oil. Similarly, peanut oil best HNT nano-lubricant showed the lowest average roughness compared to its base oil average roughness. The average roughness of the 1.5 wt% HNT modified peanut nano-lubricant was reduced by 58% when compared to the base oil. Block lubricated with corn base oil showed the lowest average roughness, 0.188 µm, among all three base vegetable oils used blocks. This is may be due to having higher concentrations of linoleic and palmitic acids, which help with friction and roughness. The block lubricated with corn oil with 1.5 wt% HNT presented the lowest average roughness of 0.094 µm among the three best concentration vegetable oils. Average surface roughness was reduced with addition of 1.5wt% concentration of HNT for each vegetable oil. Pena-Paras et al. [43] found a similar results, in which lower roughness values delayed the loss of the lubricant layer film thickness, explaining anti-wear and friction reduction.

4.6 Tapping torque test

Figure 28 shows the results obtained from tapping torque results conducted in the Grizzly mill following the ASTM D5619 standard. Among all base oils, corn oil showed a maximum tapping torque of 2.237 Nm, whereas for peanut base oil presented the minimum tapping torque of 0.967 Nm. This could be because the corn base oil produced a lower roughness, requiring the milling machine to spend less energy to do the treads. The time required by each test to complete the tapping to the aluminum specimen for different base oil was different. Peanut oil took the longest time to complete the test whereas corn oil took the shortest time. In Figure 28a shows that the tapping torque produced for 1.5 wt% HNT modified sunflower nano-lubricant is lower than the base sunflower oil. The maximum tapping torque was reduced to 32.25% for the best concentration of HNT nano-lubricants. For corn best concentration nano-lubricant in Figure 28b tapping torque is 1.136 Nm which is 49.22% lower than the maxim torque produced by corn base oil. In the case of peanut oil, the best concentration HNT nano-lubricant in Figure 28c shows the lowest tapping torque 0.967 Nm which is 34.92% lower than the base peanut oil torque.

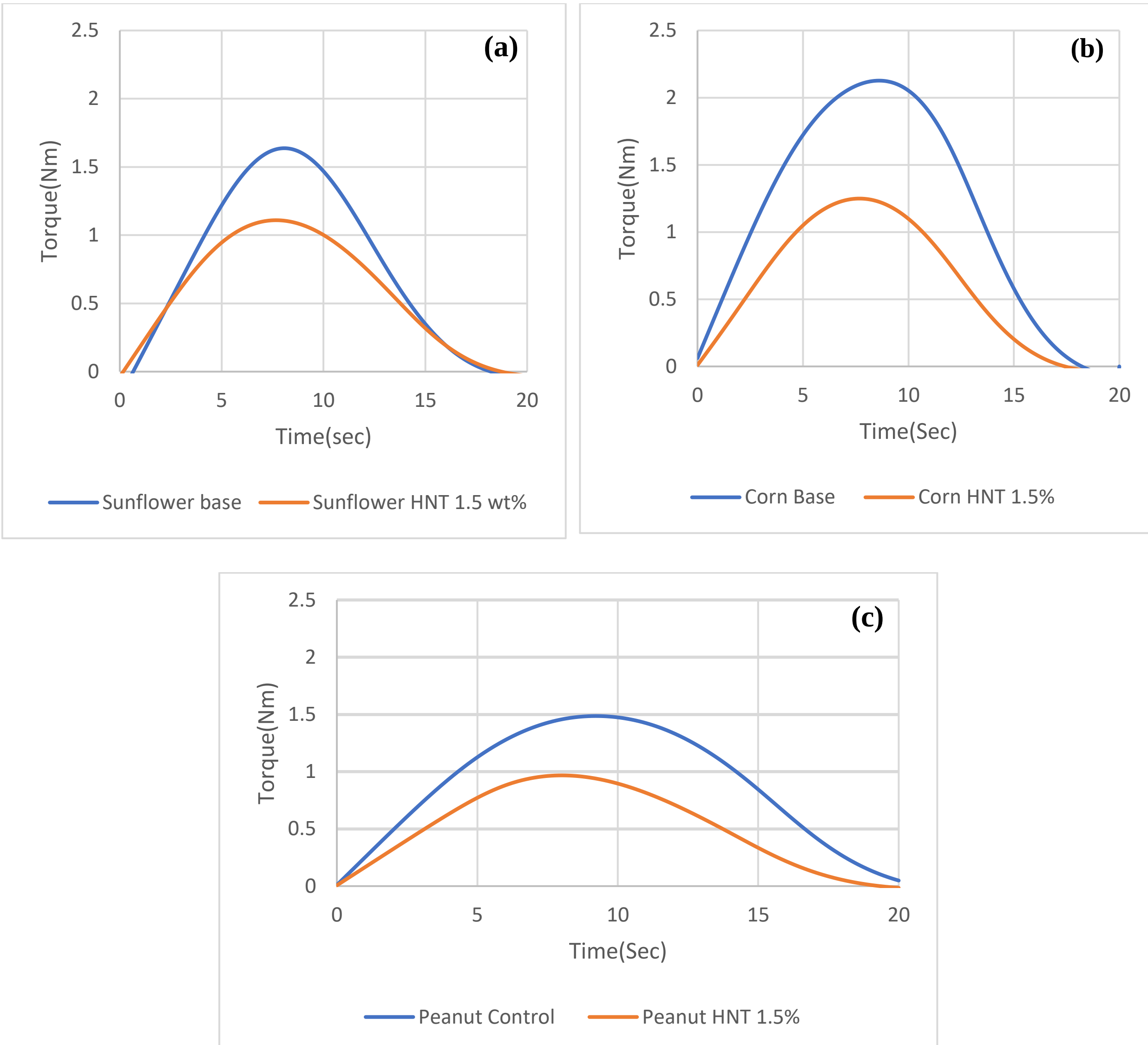


Figure 28: Tapping torque results for base oil and best concentration nano-lubricant for each vegetable oil (a) sunflower (b) corn (c) peanut oils.

Figure 29 shows the average maximum torque for sunflower oil, corn oil, peanut oil, and their corresponding best concentration nano-lubricants. In the case of all three vegetable oils, their modified 1.5 wt% HNT concentration nano-lubricants gave lower average maximum torque, and corn 1.5 wt% HNT nano-lubricant experienced the lowest reduction in maximum average torque.

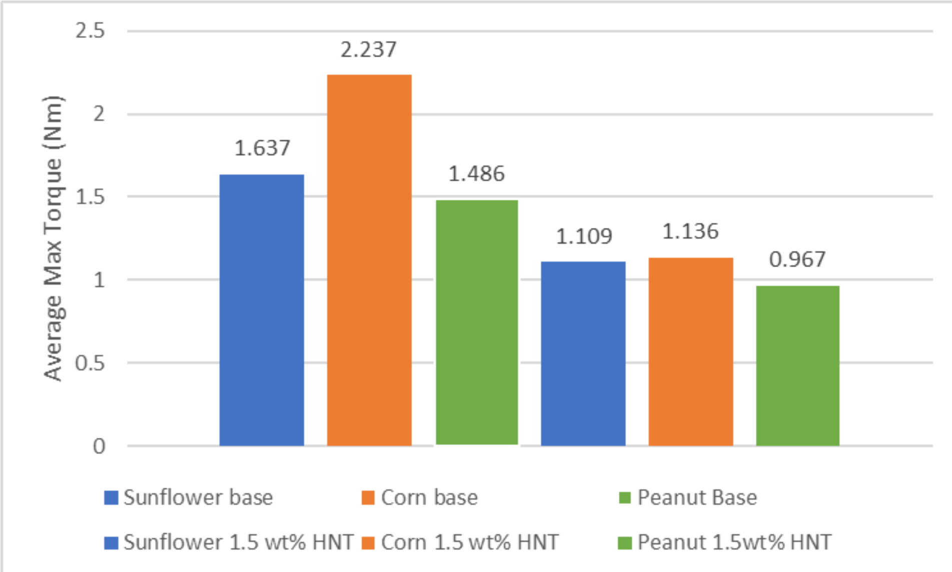


Figure 29: Average maximum torque for (a) sunflower (b) corn (c) peanut oils and their corresponding best concentration nano-lubricants.

Tapping torque reduced with addition of 1.5 wt% concentration of HNT for each vegetable oil. The presence of HNT nanoparticles created a thin lubricating film that allowed the particles to transition from sliding to rolling friction, lowering the force and torque required for tapping, also obtained by Talib et al. [45].

CHAPTER V

CONCLUSION

In this work, the lubrication performance of sunflower, corn, and peanut oils modified with halloysite nanotube additives was discussed broadly. Different concentration of HNT exhibits different tribological performance as well as tapping torque. The results indicated that sunflower, corn, and peanut oils mixed with 1.5 wt% of HNT provided the best tribological behavior. The wear volume loss lowered by 29%, 78%, and 67% for sunflower, corn, and peanut oil with the addition of 1.5 wt% of HNT respectively compared to its base oil. The tapping torque test results also provided high tapping torque efficiency that can prolong tool life in the machining process. The frictional force of each nano-lubricant lowered notably from its base oil which is another indication of improved tribological behavior. The tapping torque of the nanoparticles is quite less than the base oil of each vegetable oil. The overall tapping torque reduced by 32.25%, 49.22%, 34.92% for sunflower, corn, and peanut 1.5 wt% of HNT modified nano-lubricant respectively compared to their base oil. It can be concluded from results that sunflower, peanut, corn oil modified with halloysite clay nanotubes can be a great alternative to mineral and synthetic lubricants. More on, its adverse effect on the environment is negligible compare to an alternative source.

5.1 Future work

The tribological properties of sunflower, corn and peanut vegetable oil and their modified nano-lubricants were analyzed. I hope this work of nano-lubricants lubrication mechanism will set a reference for future groundbreaking work. Lubricants can have a wide range of qualities, necessitating more investigation, such as determining the thermal properties and suspension stability of Halloysite Nanotube Nanoclay (HNT). This is critical because it may be used in conjunction with heat transfer equations to provide more precise data on the friction forces operating on the block specimens.

5.2 Future market

Improved lubricant performance is required in today's global industry to promote energy efficiency, sustainability, and cost reduction. Nano-lubricants, a nanofluid dedicated to lubrication, have shown promise in lowering wear and friction coefficients. Our produced nano-lubricants can play an important role in world industrial and economic development, mainly by reducing friction and wear in mechanical contacts. As our produced nano-lubricants undergo tribological tests and show significant improvement in tribological behavior, they can be a great alternative to petroleum-based lubricants. Modified 1.5wt% HNT concentration sunflower, corn, and peanut oil nano-lubricants have desirable properties of cutting fluids, which can play an important role in conserving the environment by means of sustainability. Tapping test results also showed that the overall reduction of tapping torque for best concentration nano-lubricants. This tapping torque reduction implies that it can be used in different metalworking process like turning, drilling, milling and multiple lathe operations. As our nano-lubricants additives and vegetable oils are really cheap, it can easily take the lubricant market in the near future.

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APPENDIX

APPENDIX

STATE OF THE ART EQUIPMENT AND SOFTWARE

Table 11: State of the art equipment.

Equipment	Purpose	Results
NETZSCH TG 209F3 analyzer	TGA characterization of HNT	To analysis the thermal stability of Halloysite Clay Nanotube
XS205DU Electronic Balance	To measure blocks and nanolubricants	To measure the mass loss as well as volumetric wear
120 Sonic Dismembrator	Mixing the nanolubricants	To mix HNT with vegetable oil to get uniform mixer of lubricants
Nano 1200T grinder polisher	Sanding the blocks to get smooth surface	Surface finished blocks required to get better tribological results
Ultrasonic Bath	Removing dirt, grease from the surface of blocks	Cleaned surface required to reduce friction
Custom-made Tribotester	Measure the tribological performance of sunflower, corn and peanut oil modified with HNT	Frictional force, lubrication temperature, wear of the nanolubricants
Custom-made Tapping Torque Tester	Measure the tapping torque of base vegetable oils and best concentration nanolubricants of each sample	Tapping torque analysis of nanolubricants
Profilometer	Measure the roughness of block before and after test	Average surface roughness of the block before and after the test

Table 12: State of the art software.

Software	Purpose	Results
MATLAB	Simulation and analysis	Frictional data, tapping torque data analysis and removing noise
Excel	Raw data analysis	Plotting graph and comparing results
Logger Lite	Collecting data from sensor	Data collection for tribological analysis and tapping torque

BIOGRAPHICAL SKETCH

Md Abu Sayeed Biswas was born in Jessore, Bangladesh on December 20, 1990. He completed his secondary and higher secondary from Mirpur Bangla High school and Dhaka College respectively with excellence. He is an ordinate lover of science and technology. So, he was motivated to pursue his undergraduate in engineering and completed Bachelor of Science in Mechanical Engineering from Chittagong University of Engineering and Technology(CUET) in 2012. After completion of his undergraduate, he was appointed as faculty of Mechanical Engineering at The Bangladesh University of Textiles, one of the top public engineering universities in Bangladesh. He also worked as a member of the World Bank- Campus networking project at BUTEX.

In December 2021, he obtained his Master's in Mechanical Engineering at the University of Texas Rio Grande Valley. During his graduate study, he worked as a graduate research assistant in the same department and worked on nano lubricants under the supervision of Dr. Javier Ortega. His research interest includes nanotechnology, biomaterials, energy systems, tribology, advanced manufacturing, and biomechanics. He wants to build his carrier as a researcher and academician and serve society. Biswas can be reached by email at sayeedbiswas2012@gmail.com.