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Thermophysical Properties of Molybdenum Disulfide (MoS₂) and Aluminium Oxide (Al₂O₃) in Bio-based Coconut Oil Hybrid Nanolubricant for Cleaner Metalworking Cutting Fluid Applications

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ABSTRACT

Green metalworking fluids have increasingly gained pivotal relevance as environmentally compatible lubricant with equivalent performance since conventional lubricant poses significant threat. This study performs experimental and theoretical discovery on the new approach to metalworking fluid; a bio-based coconut oil nanolubricant with hybrid nanoparticles of Al₂O₃/MoS₂ regarding the thermophysical properties. The colloid was produced by suspending Al₂O₃ and MoS₂ nanoparticles in coconut-based oil at different volumetric ratios of 1:1, 1:2, and 2:1 but equal volumetric concentrations of 0.3 vol%. The thermal conductivity of bio-based lubricants increased up to 4.3% with the addition of hybrid nanoparticles which was ascertained using KD2 Pro thermal analyzer. A contact angle goniometer was used to obtain the water drop profile and the maximum wettability of bio-based hybrid nanolubricant was obtained at 27.76° (Al₂O₃:MoS₂ (1:1)) which indicates that incorporating both nanoparticles into the base system improved lubricant spreadability. The kinematic viscosity was evaluated through the viscometer and hybrid nanofluid possessed a remarkable increase in viscosity index of at least 49.6% (Al₂O₃:MoS₂ (2:1)) among other samples. The stability test revealed that the nanolubricant $(Al_2O_3:MoS_2 (1:1))$ was more stable than others. The experimental outcomes showed that the ratio of hybrid nanoparticles in base fluid has a significant role in enhancing thermophysical properties.

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1. INTRODUCTION

The metalworking fluid industry significantly impacts the physical environment, with approximately 38 million metric tons of

consumption worldwide. Petroleum-based oil, which is also widely known as mineral-based oil, is a non-biodegradable lubricant that dominates the market with over 85 percent of annual production [1]. Two-thirds of toxic and non-

decaying fluids require chemical treatment prior to disposal to prevent hazardous waste from contaminating the ecosystem [2]. Alternatively, bio-based metalworking fluid, which is a more environmentally compatible lubricant with equivalent performance, is now widely preferred due to its organic properties [3]. Previous research findings on bio-based lubricants have shown consistent evident impact in minimizing an imminent threat to humans and the environment [1]. Compared to petroleum-based lubricants, bio-based lubricants are superior in terms of renewability and biodegradability. With respect to its bio-based lubricants have a higher viscosity index and flash point, shear resistance and lubricity. Bio-based oils possess natural lubricity that is independent of any chemical additives as compared to petroleum-based oils, which mainly depend on sulphur and chlorine for lubricity. Current research selected coconut oil as the bio-based lubricant due to its outstanding physicochemical properties, especially it's high viscosity and low coefficient of friction at metallic interfaces. Furthermore, the high flash point of coconut oil produces less smoke, which prevents it as an ignition source [4].

For a higher energy conservation, the industry is now demanding lubricants with improved tribological properties such as wear resistance and friction. Nanolubricant, which is a lubricant infused with nanoscale particles, has been shown to have great potential to improve tribological properties and contribute as a solution to energy conservation [5]. Nanolubricant can be characterized in several different categories such as thermal conductivity [3], contact angle [5], lubricant properties [6] as well as homogenization and stability of the lubricants [7]. The thermal conductivity of a substance is a measure of how well it transmits heat [8]. The thermal conductivity of a lubricant is essential to identify the effectiveness of a lubricant to remove heat from the working equipment and workpiece. Meanwhile, contact angles are a traditional way to describe liquid adherent to a solid [9]. It is vital to identify the contact angle of a lubricant, as it provides information regarding the frictional characteristic of the lubricant. An effective lubricant adheres to a solid surface less tightly and cause less friction. In order to identify a more efficient nanolubricant in practices, it is necessary to thoroughly investigate the properties of the lubricant such as heat conductivity, viscosity, flash point, and pour point as the knowledge of these

properties is critical for meeting the demands of heat transfer and overcoming loss of system pressure [10]. Information regarding the stability of a lubricant is also vital to alleviate sedimentation as it may have an opposite impact which produces harm rather than benefits to the working equipment and workpiece [11].

There are mainly two types of nanolubricants, which cover conventional or mono nanolubricant and composite or hybrid nanolubricant. Mono nanolubricant is the dispersion of a single type of nanoparticles in a base fluid while a hybrid nanolubricant is the dispersion of two or more types of nanoparticles in a base fluid [12]. Earlier studies claimed that mono nanolubricant can sufficiently augment thermal conductivity. As the mean particle size decreases, the total surface area of the solid increases geometrically causing a large fraction of their surface to be exposed to the surrounding environment [13,14]. The diameter of nanoparticles contributes to the enhancement of convective heat transfer, which is the transfer of heat through a fluid due to the fluid motion itself. The rate of heat transfer increases due to vortices or eddies those nanoparticles created when dispersed in a lubricant. Aggregation and stronger Brownian motion occur in nanoparticles due to their smaller diameter, thus increasing the thermal conductivity of nanolubricants [15]. However, the utilization of only a single type of nanoparticles limits the heat transfer ability of a lubricant to a certain extent. Nanoparticles from compounds such ceramic oxides have lower thermal as conductivities compared to compounds of metals and carbon. The combination of two or more nanoparticles allows the synergetic effect between particles to take place, which produces a hybrid nanolubricant with superior thermal conductivity and stability [16,17]. However, as can be seen from the literature knowledge most studies on hybrid nanolubricants increase/decrease the volumetric concentration of the additives and there is insufficient information regarding the hybrid bio-based characterization of these nanolubricants for proper utilization in industries. Based on these grounds, the purpose of this study was to test all applicable as well as potential compositions with a disparate twist of having an equal volumetric weightage but dissimilar hybrid proportions of the chosen nanoadditives taking physical, mechanical, and their geometric properties into consideration. The present study hybridized two different nanoparticles which are

aluminium oxide which also known as alumina (Al_2O_3) and molybdenum disulfide (MoS₂). Due to the repair mechanism in mending material friction and wear, availability as well as cost-effective factors, alumina has easily become one of the most extensively used metal oxides in producing nanolubricants [18]. Previous studies utilized alumina to enhance machinability performance, namely, cutting force, tool wear, lubricity and coefficient of friction [20-22]. Molybdenum disulfides possess a low value of coefficient of friction, superior thermal and chemical stability [22,23]. These are fundamental properties in selecting nanoparticles for metal-working fluid. Hence, molybdenum disulfide nanoparticles are possibly an excellent choice to be hybridized with alumina to achieve a new composite nanostructure with prominent features.

Ample information regarding these characteristics is necessary to select the best-performing hybrid bio-based nanolubricant to aid the machining process without deterring the quality and performance of the workpiece and the equipment used. It is anticipated that a designated hybrid biobased nanolubricant effectively removes heat with minimal friction without affecting the environment if it possesses the right combination of excellent characteristics. In this study, the thermophysical properties of the prepared bio-based hybrid nanolubricants has been investigated and their results were discussed. Aluminium oxide (Al_2O_3) and molybdenum disulfide (MoS₂) nanoparticles were used as hybrid nanolubricant additives in biobased oil, and their performances, particularly thermophysical properties elucidated in constant volumetric concentration (0.3%) with various volumetric ratios (1:1, 1:2 and 2:1).

2. EXPERIMENTAL DETAIL

2.1. Nanolubricants preparation

The performance of cermet cutting tools under prepared mono/hybrid nanofluids has been investigated and also compared with those of under dry and base-MQL conditions while turning AISI 420 hardened stainless steel.

Two different types of nanoparticles, namely Al_2O_3 and MoS_2 , were utilized as nanoadditives in the preparation of bio-based lubricants. These nanoparticles were manufactured by Sigma Aldrich and acquired from AR Alatan Sains Sdn. Bhd. Table 1 outlines the nanoparticles details of the physical properties as indicated by the manufacturer.

Table 1. Features of the nanoparticles Al2O3 and MoS2.

Characteristic	Aluminium oxide	Molybdenum disulfide	
Abbreviation	Al ₂ O ₃	MoS ₂	
Purity	Null	99%	
Form	Nanopowder	Nanopowder	
Colour	White	Gray	
Shape	Spherical	Layered	
Average size(nm)	50 (TEM)	90 (APS)	
Thermal conductivity (W/mK)	18.0	34.5	

Of all types of vegetable oil that are currently being delved into, coconut oil exhibits unique properties. In addition to being non-toxic and biodegradable [24], coconut oil demonstrates good thermal stability and viscosity index, making it able to withstand high temperatures without oxidation, which is crucial in machining applications to prevent heat generated from friction [25]. Coconut oil is also a safer option as it possessed a high flash point in comparison to other oils, which means it will vaporize and ignite at a high temperature between 290°C to 300°C [4].

Table 2. Description of nanolubricants andnanoparticles ratios.

No.	Type of lubricants	Description of lubricants	Nanoparticles additives amounts	
1	Coconut oil	Straight oil	-	
2	Bio-based oil	Water-in-oil emulsion	-	
3	Al ₂ O ₃ :MoS ₂ (1:1)	Bio-based oil + equally proportional hybrid nanoparticles	Al ₂ O ₃ (0.15 vol%) + MoS ₂ (0.15 vol%)	
4	Al ₂ O ₃ :MoS ₂ (1:2)	Bio-based emulsion + different proportional hybrid nanoparticles	Al ₂ O ₃ (0.1 vol%) + MoS ₂ (0.2 vol%)	
5	Al ₂ O ₃ :MoS ₂ (2:1)	Bio-based emulsion + different proportional hybrid nanoparticles	Al ₂ O ₃ (0.2 vol%) + MoS ₂ (0.1 vol%)	

Based on these properties, coconut oil was selected as the base oil. The base system is made up of 45% distilled water and 55% of oilemulsion. A 4:1:1 mixing proportion was employed to prepare the base system; a biobased emulsion comprised of four portions of coconut oil as base oil and one portion of each surfactant (base oil: surfactant I: surfactant II). These surfactants are cocamidropropyl betaine (CAPB) and sodium dodecylbenzene sulfonate (SDBS). CAPB acted as an emulsifier and bacterial inhibitor, whereas SDBS served as a thickening agent. Each hybrid nanolubricant was made up of equal volumetric concentration an of nanoparticles (0.3 vol%) but different volumetric ratios (1:1, 1:2, and 2:1). The nanopowder was weighted separately according to the designated volumetric ratios and a mechanical stirrer was used to mix the quantified nanoadditives in the bio-based emulsion before being homogenously suspended using a sonicator as shown in Table 2.

2.2. Thermal conductivity measurement setup

The thermal conductivity of the composite nanolubricant was determined in accordance with the ASTM D53334 standard using KD2 Pro thermal property analyzer. KD2 Pro is a thermal property employed to determine the ability of the heat transfer rate of the lubricant. The experimental procedure utilized a single needle sensor, called TR-1, as shown in Fig. 1 which can compute the thermal conductivity of liquids.



Fig. 1. Setup of thermal conductivity measurements.

Prior to any measurement, the device was calibrated with the provided glycerine in order to ensure accurate and reliable readings. The thermal conductivity was measured by immersing the sensor in the tested lubricants for 60 seconds to allow it to acclimatize to the ambient temperature. Each sample measurement was repeated ten times to obtain an average value.

The considered temperatures for the transient hotwire (THW) based method ranged from 30°C to 70°C in order to perceive the disparity of temperature in thermal conductivity. At room temperature, the readings of thermal conductivity between samples varied by insignificantly small Hence, the considered values. minimum temperature was set to be slightly higher, at 30°C to augment the values. The mixture was made up of a large amount of water due to the 45% of water to oil-emulsion proportion and also from the used surfactant. Cocamidropropyl betaine (CAPB) is an aqueous fluid with a total of 38% active ingredients. Since water possesses a boiling point of 100°C [26], the tested lubricant was boiled over into the water bath while taking measurements at high temperatures. Due to this, the maximum temperature was set at 70°C.

2.3. Wettability test measurement setup

The encapsulation of wettability is a valuable characteristic for a lubricant as it describes its tendency to cover a solid surface [27]. The literature reported that enhancing wettability helps prevent the friction pair from coming into direct contact, as it promotes the formation of a protective film [28,29]. Fig. 2 illustrates the schematic diagram of contact angle. The degree of angle between the surface and fluid is evaluated to denote the wettability of the lubricant, with a smaller angle indicating better wettability [30].



Fig. 2. Contact angle.

The contact angle test was performed on cylindrical nickel-titanium alloy, simulating the turning surface of the workpiece used during machining. The sessile drop method, as specified in ASTM D7334, was used to obtain the water drop profile, which was measured using a contact angle goniometer, Lauda LSA200, equipped with an optical subsystem. Disposable syringes were used to draw the lubricant, a total of 5μ m was then dropped onto the cylindrical workpiece for immediate measurement. The dispersion of the lubricant microdroplet on the surface of the roll material was detected as an enhanced profile projection, which was followed by an angulation via affiliated image analysis software to determine the contact angle. Five-point samplings were taken for each lubricant to achieve a mean contact angle.

2.4. Measurement of physiochemical properties (define and justify each property)

The physiochemical properties are imperative to understand and influence lubrication performance. In this study, the physiochemical properties of the fully formulated lubricants, including density, viscosity index, kinematic viscosity and flashpoint were measured. To attain consistent and precise results, the nanolubricants were delivered to Bio-Synergy Laboratories Sdn. Bhd to measure these properties as listed below:

• Density

The density of each tested lubricant was measured as specified by ASTM standard D4052, to identify the mass per unit volume, which impacts its ability to deliver lubrication and dissipate the heat [31]. A pycnometer was used to calculate the ratio of weight-to-volume at 15°C to obtain the density data.

• Kinematic viscosity

The measurement of kinematic viscosity of the tested lubricants was performed using a viscometer with temperatures ranging between 40 ° C and 100°C which fulfills ASTM standard D445 to identify the resistance of the fluids to flow and shear due to gravity. This is a critical parameter that affects the lubricant's ability to flow which determines its performance. In general, thinner oil will flow faster than thicker oil due to relative flow rates governed by the oil's kinematic viscosity [33].

• Viscosity index

The viscosity index was determined based on kinematic viscosity values as per ASTM standard D2270. Viscosity index is a dimensionless

number that indicate the temperature dependence of the tested lubricants kinematic viscosity. Lubricants with high viscosity index indicates a relatively small swing in viscosity as temperature changes [32].

• Flashpoint

The Pensky-Martens Closed Cup Test was used to find the flashpoint in the interim in accordance with ASTM standard D93 which is the minimum temperature where the lubricant vapor is exposed to the air followed by ignition and immediately turns off [33]. Hence, a lubricant with a higher flash point is better suited for metal cutting application at high-temperature conditions [34]. This parameter is crucial for determining the safety and potential fire hazards in metal-cutting applications.

2.5. Measurement of stability test

A stability test using a visual observation test via photo-capturing method was performed to monitor the eventual sedimentation process within the colloids. Each test tube containing 20 ml of nanolubricant that was enclosed with a stopper was mounted on plain plastic cardboard and was fastened with a cable tie. The photos were taken via flashlight-emitting diode (LED) to show a visible profile of the separation and sedimentation that occurred in the nanofluids.

3. RESULTS AND DISCUSSION

3.1. The effect of hybrid nanoparticles on thermal conductivity

As mentioned earlier, each sample was made with different mass fraction ratios of nanoparticles. As shown in Fig. 3 the thermal conductivities of hybrid nanolubricants were observed to increase more substantially as the temperature rose from 30° C to 70° C with Al₂O₃:MoS₂ (2:1) as the highest, followed by Al_2O_3 : MoS₂ (1:2) and Al_2O_3 : MoS₂ (1:1) hybrid nanolubricants. Meanwhile, the heat transfer ability of coconut oil declined marginally with the temperature increase. However, the degree of accretion of bio-based oil was slightly slower compared to bio-based lubricant with nanoadditives. At 30°C, the thermal conductivity of bio-based oil and bio-based hybrid nanolubricant nearly doubled the value of base oil.



Fig. 3. Thermal conductivity of different hybrid nanolubricant ratios.

The increasing trend of thermal conductivity between bio-based oil and hvbrid nanolubricants was more noticeable at 50 ° C and 70°C according to their initial readings. In comparison to the bio-based oil, the suspended bio-based oil with Al₂O₃ and MoS₂ nanoparticles had a slight increase in thermal conductivity. Thermal conductivity increased by 4.3%, 3.6%, and 2.6% with the use of hybrid nanolubricants $(2:1), Al_2O_3:MoS_2$ Al₂O₃:MoS₂ (1:2)and $Al_2O_3:MoS_2$ (1: 1) compared to the bio-based oil. The outcome showed that the thermal conductivity value increased when adding into nanoparticles the base fluid as nanoparticles higher have а thermal conductivity than the base fluid [35]. As these nanoparticles are dispersed in the lubricant, they can act as efficient heat conductors which transfer heat away A significant increase in the thermal conductivity of the hybrid nanolubricant observed was with the proportion of Al_2O_3 : MoS₂ (2:1). An effective heat transfer capability is attainable through hybridizing the exact number of nanoparticles with different kinds, sizes and shapes at low particle concentration [36–38]. Although Al_2O_3 nanoparticles possess relatively low thermal conductivity, they have excellent chemical inertness and stability. MoS₂ nanoparticles have a higher thermal conductivity compared to Al_2O_3 nanoparticles. Thus, hybridizing these two different kinds of nanoparticles improvised the thermophysical properties respectively. Overall, Al₂O₃:MoS₂ (2:1) hybrid nanolubricant showed the best synergistic effect with 4.3% increment to the base fluid respectively.

3.2. The effect of hybrid nanoparticle on contact angle analysis

Fig. 4 shows the result of the contact angle values recorded on NiTi surface using different lubricants. The average contact angles of water, Al₂O₃:MoS₂ (2:1), Al₂O₃:MoS₂ (1:2), Al₂O₃:MoS₂ (1:1) and bio-based lubricants on the NiTi samples were 45.60°, 31.24°, 32.26°, 27.76° and 30.60°, respectively. The contact angle of the bio-based lubricant was slightly lower than Al_2O_3 : MoS₂ (2:1) and Al_2O_3 :MoS₂ (1:2) and higher than $Al_2O_3:MoS_2$ (1:1). However, the value was distinctly lower than water on the NiTi surface. Consequently, the findings of previous research noticed that the addition of nanoparticles to conventional fluids attributed to an increase in the contact diameter of the droplet that implies uniform spreading [39]. The nanolubricant with proportional hybrid of $Al_2O_3:MoS_2$ (1:1) acquired the lowest contact angle among all lubricants, thus providing the maximum wetting area per unit liquid volume. As a result, a different hybrid proportion of Al₂O₃ and MoS₂ nanoparticles increased the wettability of nanofluids, as well as their capacity for heat extraction and lubrication. These results were quite consistent with earlier findings [40,41].



Fig. 4. Contact angle values recorded on NiTi surface using different lubricants.

3.3. The physiochemical properties of the tested lubricants

depicts a total of four different thermophysical properties for each lubricant sample, namely density, viscosity index, and kinematic viscosity.

Type of lubricants	Density (g/cm³)	Viscosity index, VI	Flashpoint	Kinematic viscosity @ 40°C (mm ² /s)	Kinematic viscosity @ 70°C (mm²/s)	Kinematic viscosity @ 100°C (mm ² /s)
Coconut oil	0.913	130	190	24.9	N/A	5.12
Bio-based oil	0.972	270	>300	22.22	14.54	6.40
Bio-based oil + Al ₂ O ₃ :MoS ₂ (1:1)	0.968	757	>300	18.68	15.89	14.27
Bio-based oil + Al ₂ O ₃ :MoS ₂ (1:2)	0.971	685	>300	10.28	6.01	5.77
Bio-based oil + Al ₂ O ₃ :MoS ₂ (2:1)	0.969	404	>300	16.10	8.91	6.21

Table 3. Physiochemical properties of different lubricant types.

The tested lubricants were coconut oil, biobased lubricant, and bio-based nanolubricant with different proportional hybrid of nanoparticles, namely Al₂O₃ and MoS₂. It is wellestablished that the addition of nanoparticles to base lubricants alter the thermophysical properties of the resulting colloids [42]. As shown in Table 1 it was observed that the density, viscosity index (VI) and kinematic viscosity experienced augmentation in value when nanoparticles were added to the base lubricant compared to the bio-based lubricant and coconut oil. The values of the viscosity index increased from Al₂O₃:MoS₂(2:1), Al₂O₃:MoS₂ (1:2) to Al_2O_3 :MoS₂ (1:1), with corresponding values of 404, 685 and 757. This indicates that the hybrid nanofluid intensified the VI by at least 49.6% compared to the base fluid. The increased VI was due to the weak Van der Waals and Brownian random force of the colloid [43]. Overall, the combination of Al_2O_3 and MoS_2 nanoparticles with varying volumetric ratios and equal concentration in bio-based lubricants directly affects the viscosity. The addition of nanoparticles increases the concentration of bio-based lubricants, causing the viscosity to increase [37].

3.3 Observation of the sedimentation of various hybrid nanolubricant

Fig. 5, Fig. 6 and Fig. 7 show the sedimentation observation of various hybrid concentrations after 72 hours. It could be noticed that most of the tested lubricants were stable up to 36 hours. Thereafter, agglomeration and sedimentation of the hybrid nanoparticles took place within the suspension. The nanoparticles tended to clump together over time, resulting in a higher amount of sedimentation particles at the bottom of the tube, as shown in Fig. 7 and Fig. 8.



Fig. 5. Sedimentation observation at 0 hours.



Fig. 6. Sedimentation observation at 36 hours.



Fig. 7. Sedimentation observation at 72 hours.

Based on the sedimentation level of the nanolubricants in Fig. 7, very small precipitation observed on the $Al_2O_3:MoS_2$ (2:1) was nanolubricant after 36 hours. As shown in Fig. 8, the Al₂O₃:MoS₂ (2:1) nanolubricant had the highest precipitation, followed by Al₂O₃: MoS₂ (1:2) and Al₂O₃: MoS₂ (1:1) nanolubricants. The visual inspection further demonstrated that the aggregation of the nanoparticles reduced the stability of the hybrid nanolubricant as the storage time increased. When the Van der Wall attraction forces and Brownian motion of the nanoparticles were stronger than the repelling forces, aggregates of the nanoparticles tend to form [40]. By efficiently controlling the surface free energy of the agglomerate, the dispersion stability of the nanoparticles could be modified.

4. CONCLUSION

The present study reported an experimental study on the characterization and physical properties of Al₂O₃/ MoS₂ bio-based coconut oil hybrid nanolubricant. A bio-based hybrid nanolubricant with enhanced thermal and physical properties was developed by suspending Al_2O_3 and MoS_2 nanoparticles in different volumetric ratios (1:1, 1:2, and 2:1) but with the same volumetric concentration (0.3 vol%). The thermal conductivity of bio-based lubricants was increased up to 4.3% with the addition of hybrid nanoparticles. The maximum wettability of the bio-based hybrid nanolubricant was recorded at 27.76° (Al₂O₃: MoS₂ (1:1)), suggesting that blending both nanoparticles into the base system spreadability. improved The hybrid nanolubricant increased the viscosity index by at least 49.6% with the hybrid nanolubricant compared to the base fluid. After 36 hours of preparation, stability testing via agglomeration observation revealed that Al_2O_3 : MoS_2 (1:1) exhibited nanolubricant superior stability compared to others. Thus far, researchers have concentrated on lubricants with monotype nanoparticles. This study discovered that hybridizing Al₂O₃ and MoS₂ nanoparticles with different volumetric proportions, but equal volumetric concentration leads to improved thermal and physical properties. Future research in optimizing nanoparticle volume fraction, shape and size may aid in the development of nanolubricants with improved thermal and physical behaviors for machining purposes.

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