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# Rheological and tribological behaviors of bio-grease based on palm ester thickened with calcium complex thickener

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KEYWORDS

Bio-grease
Palm oil
Viscoelastic behavior
Friction coefficient
Wear

ABSTRACT

This study investigated the rheological and tribological behavior of a newly developed palm ester-based bio-grease formulated with a composition of 15 to 21 wt% of calcium complex soap thickener. Specifically, the effect of thickener concentration on viscous flow curve and thixotropy characteristics, viscoelastic behavior, as well as friction and wear properties were evaluated. The formulated palm bio-grease exhibited viscoelastic trend, which viscosity decreased gradually with shear strain, indicating shear thinning or pseudoplastic behavior equivalent to that of common commercial grease. Among the samples, the 17 and 19 wt% thickener compositions displayed the most stable structure that maintained higher viscosity and shear stress with temperature changes. Moreover, it also showed promising tribological performance regarding wear preventive characteristics. The sample with 19 wt% of thickener yielded the optimum performance that recorded less than 12% difference in friction coefficient and up to 30% reduction of wear scar diameter compared to available reference grease on the market.

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## 1.0 INTRODUCTION

In mechanical contact where the lubricant needs to be placed without draining or leaking under gravity or centrifugal action, grease is useful for lubrication operations. Grease is basically a multi-phase semi-fluid lubricant consisting of two main components: base oil as continuous phase, and solid thickening agent. In numerous applications, additives are also employed to impart certain properties. Grease is manufactured by dispersing a thickening agent which then forms an entanglement network and physically or chemically entraps the oil and yields the appropriate rheological and tribological properties of the grease (Martín-Alfonso, Martín-Alfonso, Valencia, & Cuberes, 2021; Wang, Xia, & Liu, 2015). The base oil portion is the key determinant of grease performance at various temperatures. It influences most of the main lubrication properties, including pumping and flow abilities as well as susceptibility to oxidation and thermal degradation. Meanwhile, the thickener confers the appropriate rheological behaviour of the lubricating grease (Nagendramma & Kumar, 2015). It not only imparts consistency or rigidity to the base oil but also alters properties in terms of water and corrosion resistance, shear stability, and high-temperature stability. The oil-thickener interaction gives viscoelastic characteristic to the grease, of which the thickener gives elastic response to deformation while the oil gives viscous response when mechanical stress is applied to the grease (Salomonsson et al., 2007).

The grease manufacturing procedures though varies, it depends on the type of thickener whether it is soap or non-soap based, and even the different base oils demand different procedures (Khatavkar et al., 2017). Selection of ingredient type and composition also has a significant influence on the grease properties and performance. According to Abdulbari et al. (2015), the grease manufacturing process is complex and sensitive, which involves various thermo-mechanical properties that may affect the quality of the final grease product. For instance, the thickener type and composition as well as the base oil type and viscosity, temperature profile, mixing conditions, and subsequent process conditions are the "manufacturing parameters" that vary the properties of grease (Suetsugu et al., 2013).

Nowadays, the ever-growing industrialization and development has elevated the demand for lubricants including oils and greases, with the largest demand being the Asia-Pacific region (Garside, 2019). Since the crude oil that dominates the world’s lubricant market is a finite resource, the rapid depletion that has caused fluctuation and uncertainty in the base oil market has aroused a global widespread concern. In addition, concerns over the detrimental impacts of crude oil on the environment due to the toxicity and disposal issues have led to a critical need to look towards easily available, environmental friendly and sustainability of renewable resources of lubricants, . Although mineral oil-based has wide industrial applications, its harmful content such as nitrogen, metals, and sulphuric compounds (Abdulbari et al., 2015) may lead to indirect environment pollution. Therefore, the development of bio-based lubricants has become a growing interest among researchers and industrial players nowadays attributable to the need for seeking environmentally friendly alternative materials as a substitute for crude mineral oil.

Moreover, the concept of green tribology that has been introduced recently as the key strategy to overcome energy, environment and resource problems related to lubrication activities (Minh, Kuzharov et al., 2021) is a great motivation for researchers. In the concept, biodegradable lubrication is stated as one of the 12 principles of green tribology, for which vegetable oils and animal fats are suggested to be used as natural sources. Apart from the environmental and sustainable benefits, the so-called bio-lubricants and bio-greases also have great potential for encouraging national economy by utilizing their own plants for renewable source of base oils. The massive potential of vegetable oils as alternative base stock has been proven in much published research, particularly in terms of having high viscosity index, flash point, and lubricity, in addition to possessing good anti-wear and anti-friction properties (Quinchia et al., 2014; Rao et al., 2018; Talib et al., 2017). Despite those advantages, vegetable oils are also prone to limitations, especially in terms of low oxidative stability and thermal stability which can be overcome by improving the oil structure through chemical modifications including hydrogenation, epoxidation, and transesterification (Zainal et al., 2018). Palm oil also displays prospective bio-lubricants in modified and unmodified forms (Hamdan et al., 2018; Razak et al., 2018; Zulhanafi et al., 2020).

Over the years, more researchers have contributed in the development of the eco-friendly greases utilizing vegetable oils. The applicability of the dedicated vegetable oils was explored through the grease synthesis process parameters (Adhvaryu et al., 2004; Vodounon et al., 2019), formulation of different types of thickener (Buczek & Zajezierska, 2015; Padgurskas et al., 2015), formulation of biogenic thickeners (García-Zapateiro et al., 2014; Acar et al., 2018; Cortés-Triviño et al., 2019), optimum composition of thickener (Martín-Alfonso et al., 2021; Liu et al., 2018) as well as the additive type and concentration to improve the grease performance (Dai et al., 2018; Saxena et al., 2021). Among vegetable oils, palm oil is also occasionally used as a base oil for biogrease lubricant development as it has major fatty acid content of palmitic acid (C16:0), oleic acid (C18:1), and stearic acid (C18:0) which generate strong interaction with the lubricated surfaces (Dandan & Samion, 2017). It also can form a strong, thick film between the metal contacts. In terms of rheological behaviour, Vodounon et al., (2019) found that palm oil based greases are superior with apparent viscosity of 1.2 to 2.6 times higher than corn oil-based greases at the same soap concentration and testing temperature. In other studies, conducted by Sukirno et al. (2009) and Sukirno et al. (2010), the modified Refined Bleach Deodorized Palm Oil (RBDPO) was utilized in the formulation of palm-grease with calcium and lithium thickeners. The base fluid was prepared by three step processes of transesterification, epoxidation and ring-opening. The studies reported better surface protection and anti-wear properties of palm-grease that were comparable to the commercial food-grade grease.

The semi-solid characteristic of grease is mainly attributed to the thickener agent that remains in the grease during operation and acts as a seal. With 5 to 25% of total grease composition, the thickener forms fibre structure that holds the base oils and provides viscosity to the grease, where the grease hardness or consistency is determined by the fiber length and density (Khatavkar et al., 2017). The thickener in lubricating greases not only give consistency or rigidity properties to liquid lubricants but also alter their properties of water resistance, corrosion resistance, shear stability and high temperature stability. Thickener can basically be metallic soaps and non-soap such as phyllosilicates and polyurea compounds. Metallic hydroxide or alkali is the most widely used thickener in industries and is categorized into simple and complex soaps. Simple soap greases typically have dropping points below 210°C (Sniderman, 2016). Lugt (2016) stated that in the 2012 NLGI survey, lithium thickened soap was the most used grease, accounting for 70% of the total grease volume.

Complex technology of soap thickener provides better option to the conventional soap thickener. The complex soap is produced by combining simple soap with a complexing agent – a short-chain organic or inorganic acid, usually azelaic acid or benzoic acid - creating a more robust structures that offer different properties. Reaction of two dissimilar organic acid compounds – long-chain fatty acid and short-chain complexing acid – gives the grease a wider temperature application range, with dropping point above 210°C (Sniderman, 2016). In addition, the rust protection, water resistance, load-carrying capacity and worked stability are also improved (Sander and McDaniel, 2007). One of the regularly employed complexing agents is benzoic acid, which is an aromatic carboxylic acid and acts as a heat resistance component. According to Watanabe and Tanaka (2016), calcium complex soap consisting of aromatic carboxylic acid and hydroxide will produce high heat resistance grease due to the benzene ring of benzoic acid with a decomposition point at a temperature from 390-410°C. Apart from low cost, availability in large quantities, and easy handling, calcium grease also has good water resistance, corrosion resistance, and shear stability. It also has a high level of biodegradation under the CEC-L-33-T-82 test standard (Dicken, 1994). This thus being the core motivation for this study to choose this type of thickener in formulating a bio-grease.

Although the tribological capability of palm oil has been discussed well in past literature, the rheological capacity and optimum formulation for grease has still unexplored. In this paper, the applicability of palm-ester as an alternative base fluid for bio-grease formulation was examined. The palm-ester grease was formulated with different compositions of calcium complex soap thickeners. The rheological and tribological characteristics were explored and compared with equivalent commercial greases as benchmark. The purpose was to investigate the lubricating ability of palm-ester grease, and to examine how the composition of calcium complex soap thickener influenced the grease consistency and performance. This is in order to determine an optimum thickener composition that will yielding an effective bio-grease.

## 2.0 MATERIALS AND METHOD

### 2.1 Materials

Palmester 2090 trimethylolpropane trioleate as a base oil with properties as listed in Table 1 was supplied by KLK OLEO (Petaling Jaya Malaysia). The oil contains C18-unsaturated, mixed esters with oleic acid and trimethylolpropane (TMP). Calcium hydroxide ($Ca(OH)_2$) from R&M Chemicals, and stearic acid ($C_{18}H_{36}O_2$) and benzoic acid ($C_6H_5COOH$) from HmbG Chemicals were used to form the calcium complex thickener via saponification reaction. Both stearic and benzoic acids are high and low molecular acids with 18 and 6 carbon chains, respectively. The benzoic acid is an aromatic carboxylic acid and acts as a heat resistance component. A commercial grease was used for benchmarking (NLGI 0). The grease is a synthetic ester-based with solid lubricant content, particularly $MoS_2$ and/or graphite.

Table 1: Physical characteristics of the palm-ester.

| Characterization | Test Method | Palm-ester 2090 |
|---|---|---|
| Colour | | Light yellow |
| Kinematic Viscosity @40°C ($mm^2/s$) | ASTM D445 | 76.6 |
| Kinematic Viscosity @100°C ($mm^2/s$) | ASTM D445 | 14.95 |
| Viscosity Index | ASTM D2270 | 149.8 |
| Density at 15°C ($g/cm^3$) | ASTM D1298 | 0.921+ |
| Pour point (°C) | ASTM D97 | -48 |
| Cloud point (°C) | ASTM D2500 | -24 |
| Flash point (°C) | ASTM D92 | 326 |
| Acid value (mg KOH/g) | ASTM D1980 | 1 |
| Saponification value (mg KOH/g) | ASTM D5558 | 197 |

## 2.2 Synthesis of the Calcium Complex Grease

The bio-based grease formulated in this study comprised palm-ester as the base fluid, and calcium complex soap as the thickener. The complex calcium thickener was formed through the reaction of two acids and calcium hydroxide, and the acids were the mixture of high and low molecular acids: stearic acid and benzoic acid, respectively. The grease samples were produced on a laboratory scale in a glass beaker with hot-plate and overhead rotary paddle apparatus. The grease was obtained from the reaction of calcium hydroxide with stearic and benzoic acids in a composition ratio of 0.8:1:1 into the palm ester, as identified in the previous findings (Razak & Ahmad, 2022). Five samples in proportions from 15 to 21 wt% of thickener were prepared.

For the synthesis process of palm grease, about 80% of the total weight of the base oil was pre-heated by an electric laboratory hot plate to 80-90°C before stearic acid was added. The mixture was stirred gently by an overhead rotary paddle stirrer for uniform heating. After complete dissolution for about 5 min, benzoic acid was added and stirred for 15 min until it completely dissolved. At 80-90°C, a water slurry of $Ca(OH)_2$ pre-heated to about 70°C was added dropwise. Heating and stirring were continued for about 40 min to ensure the completion of saponification reaction. The formation of homogenous thickened mass of the stirred mixture could be observed before the temperature gradually increased. After the completion of free-water rejection, the temperature was then raised very slowly up to 145-150°C which took about 2 hours to maintain and reach the maximum temperature. This heat treatment process was to completely expel the water (dehydration), which was the byproduct of the saponification reaction (McGuire, 2017), and melts the soap. Higher than 150°C temperature however need to be avoided since it may cause polymerization to the thickener, which separation between base oil and thickener could occur (based on the earlier trial experimentation). Water, in fact, is an unwanted content in a grease mixture since it can influence to the rheological and chemical properties, and may lead to accelerating equipment failure through corrosion and oxidation (Gurt & Khonsari, 2020). In the finishing stage, the heating was terminated and the remaining 10% base oil at room temperature was added to quench cool. When the mixture cooled, the soaps crystallized into a network of fibrils, which in turn thickened the grease. The remaining 10% base oil was slowly added during finishing, and the grease was homogenized for about 30 min. The thickened grease was formed after cooling.

## 2.3 Characterization Tests

In this study, grease consistency, or stiffness, was analyzed using the SKF Grease Test Kit TKGT 1, according to a scale developed by the National Lubricating Grease Institute (NLGI) Standard. In this test, a small amount of grease sample was placed in the center of the NLGI measuring scale sheet and weighed for 15 sec. By spreading the grease along the scale, the grease hardness was determined according to the NLGI number. Larger spread will extend to smaller NLGI number, which indicates softer grease.

The rheological characterizations of the formulated palm greases were conducted with Anton-Paar MCR 302 Rheometer, with parallel-plate configuration (50 mm diameter) separated by 0.5 mm (Figure 1). Two measurements were conducted: (i) flow behaviour under rotational shear, and (ii) linear viscoelastic behaviour under oscillatory shear. For flow behaviour, steady-state viscous flow and shear stress – shear rate relationship in the shear rate range of 0.1 to 100 $s^{-1}$ over the temperature range of 25-100°C were performed. For linear viscoelastic behaviour, small- amplitude oscillatory shear test was conducted in the shear rate range of 0.1 to 10 $s^{-1}$, or between 0.1 to 100% shear strain corresponding to a constant angular frequency of 6.28 rad/s obtained at 25°C.

Tribological test was conducted using four-ball wear tester (Koehler Instrument Company, Inc.), under wear preventive test according to ASTM D2266. In the test operation, three steel balls in a pot containing grease sample was pressed upward with 40 kg force against the top ball rotated at 1200 rpm speed for 60 min. The friction coefficient due to the friction between the steel balls were recorded, and the wear scars due to the friction actions were observed using Alicona Surface Metrology System. Meanwhile, the extreme pressure behavior of the formulated palm greases was evaluated according to ASTM D2596. Under the applied stepwise load, the load-carrying ability of the grease was determined based on the last non-seizure load, in which the last load was applied before the four balls were welded to each other.

Figure 1: The MCR 302 rotational rheometer.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Physical Properties

The palm greases in this study were formulated with 0.8:1:1 ratio of metallic base (calcium hydroxide) to fatty acid (stearic acid) to complexing agent (benzoic acid) as the optimum calcium complex soap composition (Razak & Ahmad, 2022). The excess of stearic acid in the formulation contributes to good consistency yield (Doi et al., 2021) due to the long carbon chain length (C18) that creates stronger interlocking fiber in metal soap, thus resulting in a stable grease matrix (Sharma et al., 2006). Five samples of palm-ester greases were formulated with thickener composition between 15-21 wt%. The NLGI grade of the greases is exhibited in Table 2, where the calcium complex thickener concentration yielded palm grease consistency between NLGI 00 (semi-fluid) to NLGI 0 (very soft) – same as the reference grease that set as benchmark grease in this study. This consistency level is preferred for spray grease type, which improves the pump-ability. More than the 21 wt% thickener composition, based on the earlier trial experiment, yielded the harder structure, or NLGI 1 (soft), which was not taken into account in this study.

Table 1: Variation of thickener concentration and NLGI grade.

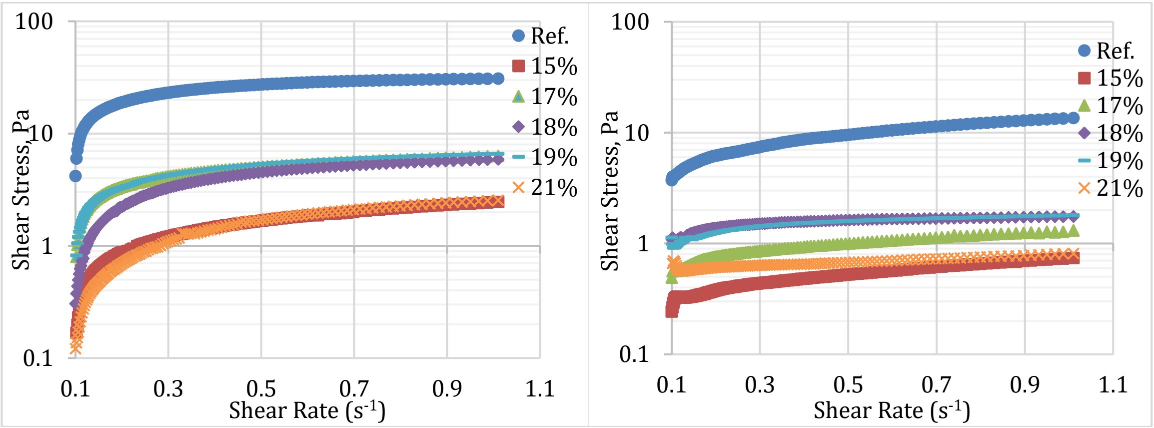
| Palm-ester grease samples | Concentration of palm ester (wt%) | Concentration of calcium complex thickener (wt%) | NLGI | Grease structure |
|---|---|---|---|---|
| PG15% | 85 | 15 | 00 | Semi-fluid |
| PG17% | 83 | 17 | 0 | Very soft |
| PG18% | 82 | 18 | 0 | Very soft |
| PG19% | 81 | 19 | 0 | Very soft |
| PG21% | 79 | 21 | 0 | Very soft |

## 3.2 Rheological Properties

### 3.2.1 Flow Curves and Thixotropic Behavior

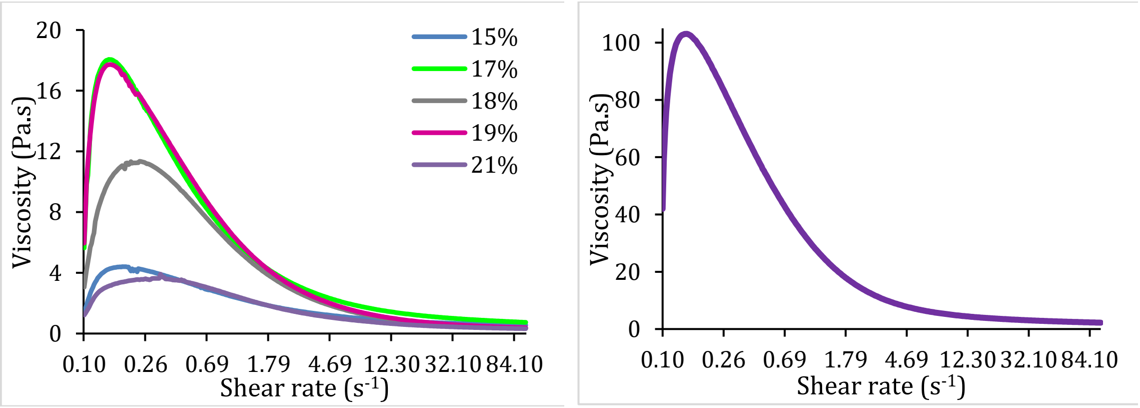
Rheological behaviour of a lubricating grease is related to the flow and deformation of the grease under applied deformation forces or stress. Grease is basically classified as a viscoelastic material, which thickener type and concentration determine the flow properties (Salomonsson et al., 2007). According to García-Zapateiro et al. (2014), the rheological response of a lubricating grease is dependent on oil viscosity, polar interactions as well as chemical reaction between the base stock and thickener compound. Figure 2(a) depicts the shear stresses for palm grease samples with different thickener concentrations under room temperature (25°C), which displayed pseudoplastic behaviour with yield stress similar to the reference grease (referred to as Ref.). According to the results obtained, about 0.12 to 0.60 Pa shear stress or yield stress is required to initiate the flow of the formulated palm greases. During the rest condition, grease forms intermolecular network structure that gives it predominantly the solid-like characteristics associated with elasticity. The external stress applied through rotational shear changes the intermolecular network structure, and when exceeding the yield stress, the grease deforms elastically, and it begins to flow. The shear stress then constantly increases with higher shear rates, displaying typical shear-thinning behaviour of a lubricating grease system (Saxena et al., 2021).

In addition, with increasing thickener concentration, moderate fluctuations in the values of yield point were observed. For instance, the palm grease sample with 21 wt% of thickener concentration with the lowest yield point demonstrated instability of the suspension, possibly due to external factors during formulation. However, for the palm grease sample with 15 wt% thickener concentration, the thickener was insufficient for the grease to properly bind the grease and resulted in low shear stress under low shear rates. Figure 2(b) shows the stress behavior of the grease samples at high working temperature of 100°C. The palm greases were able to maintain the pseudoplastic behaviour with lower yield point, except for the palm grease sample with 15 wt% thickener concentration. The sample displayed Bingham plastic behaviour, where the structure was changed to Newtonian behaviour after yielding.



(a) (b)

Figure 2: Shear stress of the grease samples with different thickener concentration at (a) 25°C and (b) 100°C operating temperature.

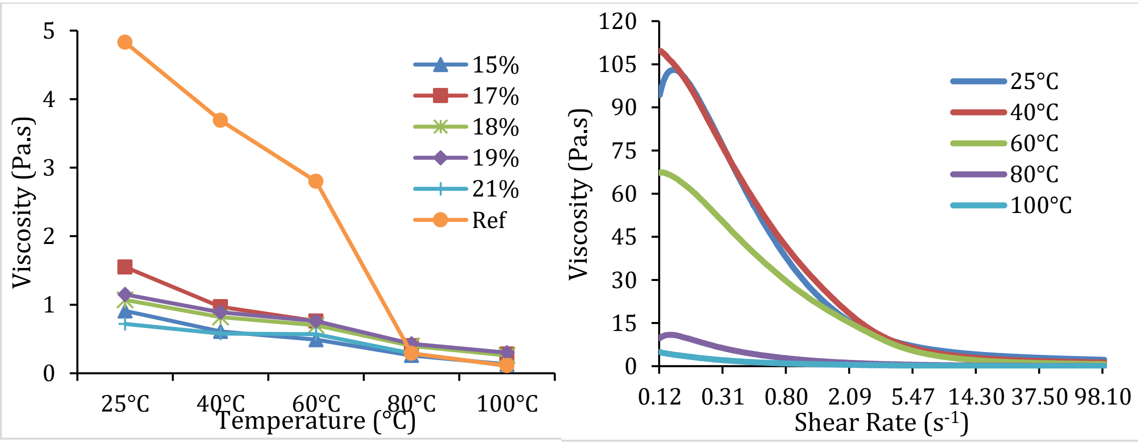


(a) (b)

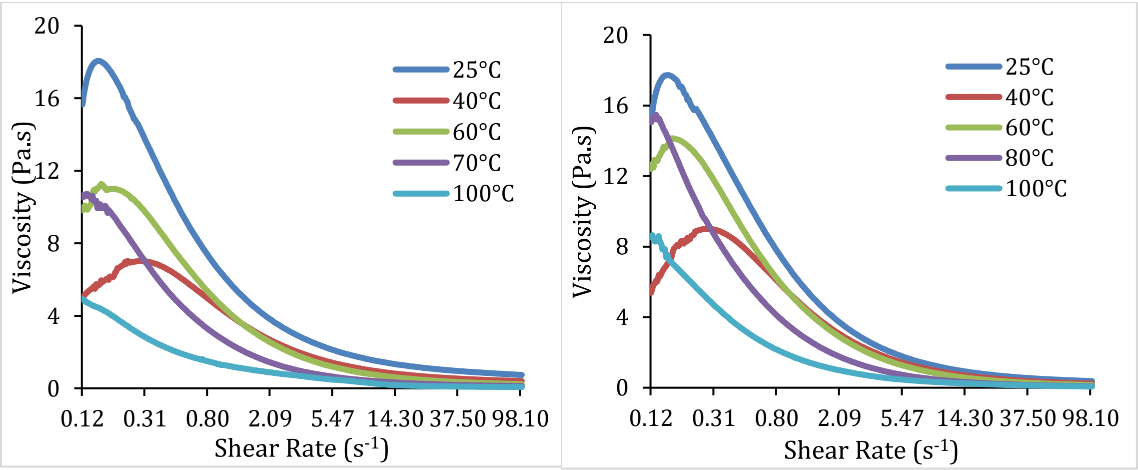
Figure 3: Viscous flow curves of the grease samples at 25°C for (a) palm bio-grease with different thickener concentrations and (b) reference commercial grease.

Figure 3(a) and (b) display the apparent viscous flow curves of the formulated palm greases containing different thickener concentrations and the reference grease, respectively, at room temperature of 25°C. Viscosity peak was observed for both palm and reference grease samples, of which the greases underwent elastic deformation or stretching. The peak represented the yield point of the grease, at which the elastic structure broke down and the grease began to flow. Overall, the viscosity decreased gradually with increasing shear rate and exhibited a shear thinning response or pseudoplastic flow with limiting viscosity in the high shear rate region, which was similar to the commercial reference grease (Figure 3(b)). Shear thinning is, in fact, the result of micro-structural rearrangements occurring in the plane of applied shear.

According to the result obtained at working temperature of 25°C, palm bio-grease with thickener compositions of 17 wt% and 19 wt% displayed the most viscosity among the palm bio-grease samples, with viscosity values of 18.02 Pa.s and 17.7 Pa.s, respectively, at shear rate of 0.14 $s^{-1}$. The viscosity values then dropped to 0.88 Pa.s and 0.48 Pa.s at a shear rate of 50.0 s-1, which was about 95% and 97% decrease, respectively. The reference grease, as comparison, recorded about 97% viscosity drop, or changed from 103.06 Pa.s to 2.67 Pa.s in the same shear rate range. This showed equivalent flow behaviour of the formulated palm bio-greases with the commercial grease. The viscosity of palm grease sample with low thickener concentration, particularly 15 wt% was very low and subtle shear thinning was observed. This was due to the semi-solid structure of the grease sample which was close to Newtonian fluid. Similar conditions were also observed for the sample with 21 wt% thickener. Despite having a high thickener concentration, the grease sample becomes low viscous due to the unstable suspension during the formulation, that also recorded low yield point (Figure 2).



(a) all (b) Ref.



(c) 17% (d) 19%

Figure 4: Temperature dependence of viscosity (a) for all the grease samples; also viscosity at increasing shear rate for (b) reference grease, (c) grease samples with 17 wt% thickener concentration, and (d) grease samples with 19 wt% thickener concentration.

The effects of temperature on the viscosity of the formulated greases are shown in Figure 4. The gradual decrease in the viscosity of the greases is exhibited in Figure 4(a) when the experimental temperature increased from 25°C to 100°C. However, for the reference grease, the viscosity was abruptly decreased at temperature from 60°C to 80°C, which at high working temperatures, the viscosity was equivalent to the palm grease samples with thickener concentration of 17 wt% and 19 wt%. In actual practice, the reference grease in the application needs to be heated to 75°C before being applied by spraying method. In this temperature, referring to Figure 4(b), the recorded grease temperature was below 11 Pa.s. The viscous structure at room temperature is for storage purpose to facilitate material handling, especially for export. The equivalent viscosity of the formulated palm greases even at lower temperatures may therefore exclude heating step prior to use. The detailed temperature dependence of the viscosity change is shown in Figure 4(b-d) for reference grease and palm grease with17 wt% and 19 wt% thickener concentrations. Temperature stability can be observed for the 19 wt% palm grease sample which showed the least change in viscosity at higher working temperatures.

### 3.2.2 Linear Viscoelastic Behavior

The viscoelastic behaviour of the grease demonstrated both viscosity and elasticity during the shearing process and allowed it to remain in place despite repeated tribological stresses. The solid-elastic and viscous-liquid behaviours of grease were characterized by the storage modulus (G’) and loss modulus (G’’), respectively. The amplitude sweep curve at 25°C, as illustrated in Figure 5, exhibited typical viscoelastic behaviour of the formulated palm greases, which closely resembles the rheological response of the commercial grease and other lubricating greases (Saxena et al., 2021; Wang et al., 2015). Linear viscoelastic region appeared in the lower shear strain, where the grease samples were still in elastic behaviour (G’>G”). Until a certain intercepting point was reached, where G' was equal to G'', or tanδ = 1 (tanδ=G”/G’), the grease started to flow which its viscous behaviour took place (G”>G’). The palm grease with 19 wt% thickener recorded the highest flow point, or intercepting point of G’ and G’’ at 3.57% shear strain, indicating elastic behaviour up to the maximum shear stress. This resulted in a strong microstructural network of the grease sample which may contribute to the viscous properties compared to other samples. The sample with 17 wt% thickener displayed lower viscoelastic behaviour with lower intercepting point but better than the other palm grease samples. However, the samples with 18 wt% and 21 wt% thickener concentrations displayed even lower viscoelastic behaviour that started to flow at very low shear stress, implying weak microstructural network of the greases. For the palm grease with 15 wt% thickener concentration, the G’ pattern over shear stress was very low in terms of energy storage capability (Wang et al., 2015). The pattern showed that the sample did not behave like an oleo gel, where the insufficient thickener concentration allowed the microstructure to move easily and became the least viscous among the compositions.

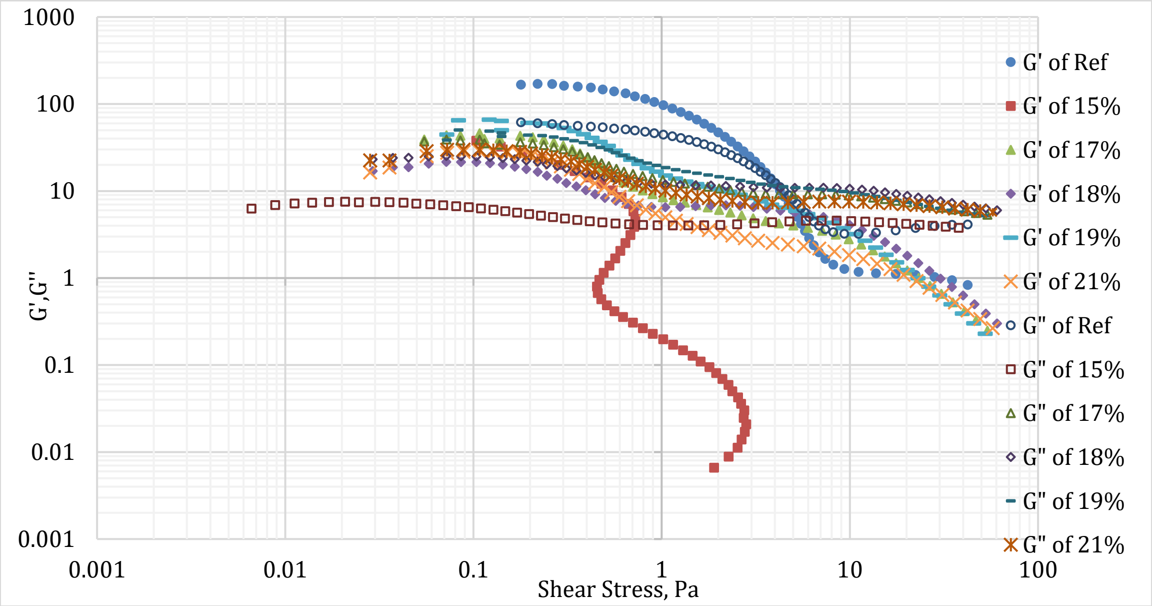


Figure 5: Amplitude dependence of storage and loss modulus.

## 3.2 Tribological Properties

### 3.3.1 Wear Preventive (WP) Properties

The applicability of the formulated palm greases was studied through the tribological test of steel/steel contact. Figure 6 displays the friction curves of contacts lubricated with palm greases with different concentrations of calcium complex thickener as well as the reference commercial grease. During the initial run, a sharp spike in the friction coefficient value was observed for all measured grease samples in the run-in period, probably due to the least lubricating film between the contact surfaces (Mujtaba et al., 2021). The friction coefficient values then fluctuated for about 10 min before becoming stable as a result of the formation of protective lubrication film. However, fluctuations in the friction coefficient were observed for the palm bio-grease samples with thickener compositions of 15, 18 and 21 wt%. This trend may also reflect fluctuations in friction force due to the deformation and fracture of the tribofilm, which occurred to low viscosity samples (refer Figure 3(a)) with nearly semi-fluid structure, where a stable boundary film was not properly formed.

From the WP test, Figures 7(a) and 7(b) exhibit the readings of friction coefficient and wear scar diameter, respectively, for five different calcium complex soap compositions of palm bio-greases. The average friction coefficient recorded was between 0.073 and 0.087, which was close to the range of reference commercial grease. This may be due to the triacylglycerol structure in vegetable oil, particularly the palm-based oil, which contains long, polar fatty acid chains, which contribute to the formation of a thick and effective lubricating layer between the contact surfaces (Sukirno et al., 2009). It was also observed that the palm bio-grease sample with 21 wt% thickener composition demonstrated the lowest friction coefficient which was 7.6% lower than the reference grease even without any performance additives, and it also has low viscosity that induced strong lubricating capacity. The high thickener composition of this palm bio-grease sample formed a dense fiber matrix that effectively held the oil-thickener structure, resulting in better lubricating film. Therefore, it can be inferred that the amount of thickener composition significantly affects the grease friction performance. However, the friction coefficient values did not increase proportionally with the increase in thickener composition. It may be due to very small differences in composition, aside from other factors during the preparation procedure or testing conditions. A significant friction reduction, however, was observed between the palm bio-grease samples composed of 15 wt% and 21 wt% calcium complex thickener, which recorded an increase of about 16%.

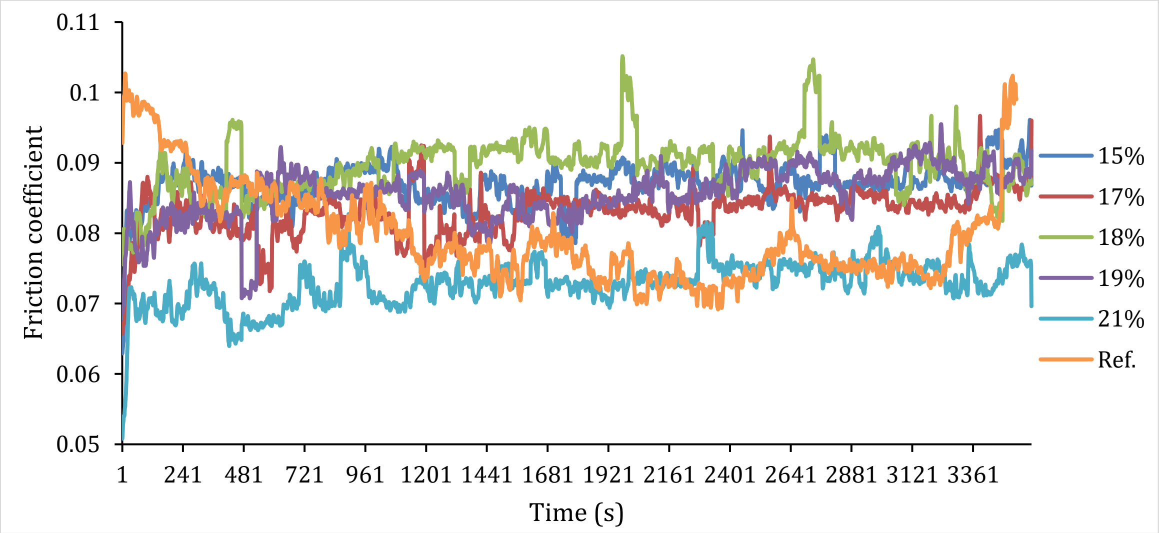


Figure 6: Variation of the friction coefficient with time of the palm greases with different thickener concentration.

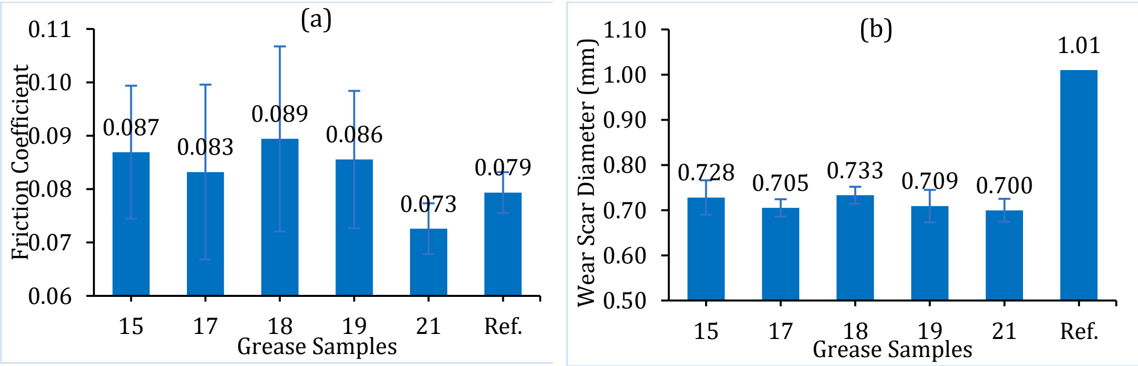


Figure 7: Effect of the calcium complex soap compositions on the (a) The friction coefficient and (b) Wear scar diameter of the formulated greases.

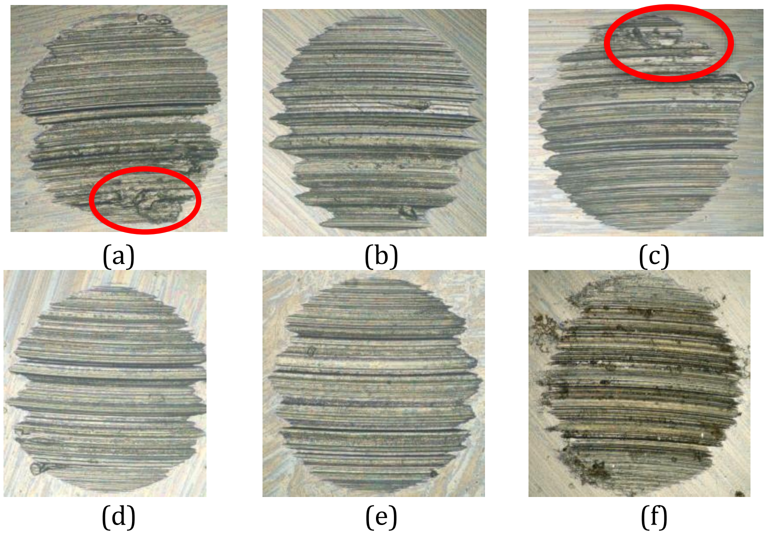

(a) (b) (c)
(d) (e) (f)

Figure 8: The wear scar image from optical micrograph for the palm bio-grease with (a) 15 wt%, (b) 17 wt%, (c) 18 wt%, (d) 19 wt%, (e) 21 wt% and (f) reference grease.

The surface analysis showed that the wear scar diameter values for the palm bio-grease, as in Figure 7(b), were significantly low, which in range of 0.700-0.733 mm, or about 4.6% difference only. In overall, the palm grease samples that having lower friction coefficient producing smaller wear scar, yet in very slight difference. This trend of variation was similar with findings by He et al. (2018). However, the significantly high wear scar diameter for the reference grease was evidence even having low friction coefficient. This probably due to the high concentration of solid additive particles contains in that commercial grease, leading to the formation of abrasive wear and rubbing actions between the contact surfaces. Wear and friction, according to Kato (2000), are responses of a tribo-system that are affected differently by a variety of elements. These factors include surface roughness, ductility, oxide film, reaction layer, and material transfer, all of which have an impact on how the contacting surface reacts.

Referring to Figure 8, the grease samples with 19 wt% and more thickener composition produced better scar surfaces compared to the rough surfaces observed for lower compositions, indicating the significant contribution of the calcium complex soap thickener on the surface quality. In addition, a small amount of transferred material was observed on the scar surfaces of the grease samples with 15 wt% and 17 wt% thickener (Figure 8 (a) and (c)). Basically, it occurred when the lubricating film was broken down and minimized the gap between the contact surfaces, which eventually may cause adhesive wear on the surface (Talib et al., 2017). According to Gulzar et al. (2015), this condition can be overcome with the utilization of anti-wear additives including solid additives to promote protective tribo-films formation between the contact surfaces.

### 3.3 Extreme Pressure (EP) Properties

Extreme pressure (EP) test was conducted to determine the last non-seizure load and weld point of greases applied under specified conditions. In the test, when the grease reached the initial seizure condition, the thickness of the lubricating film became thinner, and severe adhesive wear occurred between the rubbing surfaces. As the applied load increased, the friction between the rubbing surfaces increased sharply. Consequently, the lubricating film was completely broken down and plastic deformation occurred, causing the ball material surfaces to attach and become welded. The last non-seizure loads recorded for the formulated palm bio-greases are shown in Table 2. The result implied that there was no significant change in the load-carrying capacity for the palm bio-greases with calcium complex thickener compositions of 15-21 wt%, which could only retain the tribo-film strength up to 120 kg load before breaking down and seizing at 160 kg. In this case, the tribo-film of a very soft grease – with NLGI 0 - was mainly contributed by the base oil itself, where the presence of polar molecules in the palm ester, such as the carboxyl group of fatty acids forms a thin layer of lubricant that separates the contacting surfaces (Zahid et al., 2017). Referring to the EP properties of the commercial reference grease in Table 2, high weld loads of up to 500 kg were recorded.

The high load-carrying capacity was attributed to extreme pressure additives in the form of solid particles. Despite its very soft properties, it has a good ability to retain the properties under high loads without breaking down the lubricating film. Thus, for the further development of the palm bio-greases, it is recommended to incorporate effective EP additives to enhance the load-carrying capacity.

Table 2: The grease extreme properties.

| Grease compositions (wt%) | Last non-seizure loads (kg) | Weld loads (kg) |
|---|---|---|
| 15 | 120 | 160 |
| 17 | 120 | 160 |
| 18 | 120 | 160 |
| 19 | 120 | 160 |
| 21 | 120 | 160 |
| Ref. | 400 | 500 |

## CONCLUSIONS

In this study, palm ester bio-greases were formulated with different compositions of calcium complex soap thickener. Their characteristics were assessed through NLGI consistency test, rheological analysis, as well as wear preventive and extreme pressure analyses. The test result showed that the palm ester bio-greases with 17 to 21 wt% calcium complex thickener compositions were adequately competent to yield the NLGI 0 palm bio-grease, which was structurally equivalent to the reference grease. The developed palm bio-grease displayed a viscoelastic tendency, in which the viscosity was gradual decreases with shear strain, exhibiting shear thinning or pseudoplastic behavior that equivalent to that of regular common commercial grease. This thus supports commercial use of the produced grease on an industrial scale. It was also suggested that calcium complex thickener composition higher than 17 wt% is required to obtain friction and wear performance compatible with commercial grease, even without the presence of performance additive. In addition, the palm ester bio-grease formulated with 17 and 19 wt% thickeners also yielded the most viscous structure, which the 19 wt% thickener composition exhibited the most stable structure that maintained higher viscosity and shear stress with changes of temperature. Good viscoelastic behavior was also exhibited by that composition based on the elastic behavior up to maximum shear stress. In addition, the sample with 19 wt% of thickener shows tribological performance that recorded less than 12% difference in friction coefficient and up to 30% reduction of wear scar diameter compared to available reference grease on the market. Taking into account the rheological and tribological properties of the formulated palm ester bio-grease, 19 wt% calcium complex was considered the optimum thickener composition, which maximized the base oil content for better lubricity, and at the same time maintained the viscoelastic structure. Appropriate AW and EP additives are also required to be selected for further development of palm ester bio-grease.

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