Anti-wear properties of bio-grease from modified palm oil and calcium soap thickener

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Abstract: An environmental friendly palm-grease has already been formulated using modified palm oil as base oil and calcium 12-hydroxy-stearate as thickener. Such palm-grease is dedicated for bearing and gear applications in industrial equipment that requires food-grade lubricant, such as in food processing and pharmaceutical machineries. The grease was manufactured via four steps of processes: saponification in a pressurized reactor, soap dilution by heating, crystallization by cooling, and homogenization. Additive-free palm-grease using modified RBDPO (Refined Bleached Deodorized Palm Oil) and epoxy RBDPO as the base oil and calcium soap as thickener gave dropping point of 130℃ and consistency NLGI Grade 3. In the test using 4-ball wear-test, it showed an anti-wear performance that was comparable to that of the commercial food-grade grease, using mineral oil as base oil. The ability of the palm-grease to provide an anti-wear property was probably due to the presence of epoxy ring -COC-, ester groups -COOC- and hydroxides –OH.

Keywords: Bio-grease, modified RBDPO, consistency, dropping point, anti-wear property

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1 Introduction

Semi solid lubricant or grease is widely used in many lubrication systems, because it can provide a simple lubrication system for bearing and gear. Grease is more adhesive than liquid lubricant so it is easier to retain in the bearing. It has lower friction coefficients, improves sealing and provides better protection against corrosion to the surfaces (Dresel, 1994). Lubricating grease is manufactured by the dispersion of a thickening agent in a liquid lubricant and it may also contain additives that impart special properties. Typical grease contains base oil 75%–95%, thickener 5%–20%, and additives 0–20%. The most common additives found in grease are anti-oxidants to prolong the life of grease, anti-corrosion agents to protect metal against attack from water or corrosive elements, anti-wear agent and extreme pressure to guard against excessive wear due to metal to metal contact.

A fundamental difference between a grease and liquid lubricant is the presence in of the thickening agent. The thickeners are usually metallic soaps, such as lithium, sodium and calcium salts of long chain fatty acids. Lithium soap based lubricating greases have been numerous due to the very good properties of these greases, i.e., a smooth appearance, and a high dropping point, but for formulating food-grade grease, calcium soap is favourable (Dresel, 1994). For more environmentally acceptable thickener, oleo-gels that can be prepared by dispersing sorbitan mono-stearate (SMS) in castor can be used as a substitute for the metallic soap (Sánchez et al., 2008).

The thickener gives grease its characteristic rigidity or consistency which is a measure of resistance to deformation by an applied force. The structure will flow under an applied stress, the magnitude of which will depend on the rigidity of the soap fiber network which is governed by the forces holding the fibers together. Soap

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thickeners not only provide consistency to grease, but also affect desired properties such as water and heat resistance and pump-ability (Yousif, 1982). It can also lower the coefficient of friction over that of the base oil alone (Silver & Stanley, 1974).

Fluid lubricants used to formulate grease which are normally petroleum or synthetic oils. With growing environmental awareness and stringent regulations regarding the use of petroleum products, the manufacture and the use of environment friendly lubricant to replace petroleum oils is becoming more and more popular. Vegetable oil can offer significant environmental advantages such as renewable resources, nontoxic or biodegradability, adequate performance in a variety of applications. Sunflower oil has been used to develop bio-grease by European researcher, with polymer thickener for grease application lubrication in earth moving equipment (Barriga & Aranzabe, 2006). Soybean oil has been used by American researchers for manufacturing soy-grease for lubricating heavy duty truck.

The notable challenges in formulating grease using vegetable oils are oxidative stabilities, hydrolytic stabilities, low temperature properties that are innate characteristics of the triglyceride molecule. Oxidation stability of vegetable oils decreasing with their number of double bonds, and their poor low-temperature properties, getting worse with a decreasing number of double bonds (Dresel, 1994). Vegetable oil suitable for lubricant is high oleic oils with mono-saturated fatty acid content >80%, low poly-saturated fatty acid and saturated fatty acid (Dharma, 2002) to provide both high oxidation stability and reasonable low temperature flow properties. Palm oil with mono-saturated fatty acid content (40%) and high saturated fatty acid content is often considered unsuitable for lubricant because it is poor in low temperature properties (0–15℃). However, high content of saturated fatty acid in palm oils may be considered as the advantage point when one uses palm oil for formulating lubricant for tropical region application, because it contributes better oxidative stability meanwhile the limitation in low temperature properties may be neglected.

In our unpublished research, we have successfully prepared a modified RBDPO via trans-esterification and epoxidation reaction to enhance its oxidation stability. By avoiding the involvement of toxic catalysts in the process modification, the product is considered to be biodegradable, superior in its friction reducing and anti-wear properties due to since its active functional group. In this research, the modified RBDPO is used as base oil for manufacturing palm-grease. The purpose of this research is to prepare palm-grease using environment friendly base oil and calcium soap thickener that can lubricate bearing and gear found in agriculture, forestry, and also food pharmaceutical industries. In this study, no additive is used, in the bio-grease formulation. Epoxy RBDPO was mixed to the base oil (modified RBDPO) to get higher base oil viscosity and to allow its active functional group epoxy ring “act” in bio-grease formulation.

2 Materials and methods

2.1 Materials

2.1.1 Base oil

The base fluid used was modified RBDPO and epoxy RBDPO. The modified RBDPO was prepared via esterification, epoxidation and ring opening reactions. The RBDPO has a typical fatty acid composition in percentage: C12:0 (Lauric) = 0.2%; C14:0 (Myristic) = 1.1%; C16:0 (Palmitic) = 44.0%; C18:0 (Stearic) = 4.5%; C18:1(Oleic) = 39.2%; and C18:2 (Linoleic) = 10.1%. Table 1 shows selective properties of the modified RBDPO along with RBDPO which listed together with mineral oil HVI 160S for comparison.

Table 1 Base oil characteristics

Characterization	Test method	Modified RBDPO	RBDPO	HVI 160S
Appearance		light yellow	light yellow	light brown
Specific gravity [-]	ASTM D-1289	0.91	0.85	0.8
Viscosity @40℃ [cSt]	ASTM D-445	35	38.9	96
Viscosity @100℃ [cSt]	ASTM D-446	6.9	8--9	11
Viscosity Index [-]	ASTM D-2270	>100	>100	100
Pour point [℃]	ASTM D-97	0-5	15	-9
Oxidation stability				
Viscosity @40℃ increase [%]	Bulk oxidation	5.6	21.5	7.8
Amount of deposit [g]	Micro oxidation	0.0199	0.0497	0.0329

The modified RBDPO has better oxidation stability than both RBDPO and HVS 160S in micro-oxidation test and bulk oxidation test. The epoxy RBDPO was prepared via epoxidation reaction with hydrogen peroxide and formic acid as catalyst. Epoxy RBDPO has lighter color, but it has higher viscosity than RBDPO. The kinematic viscosity was 55 cSt at 40℃. Two base oils were prepared. Base oil 1 was 100% modified RBDPO. Base oil 2 was a mixture of 50% modified RBDPO and epoxy RBDPO. Epoxy RBDPO was added to increase viscosity and polarity of the base oil.

2.1.2 Thickener

Calcium soap was obtained from the reaction of fatty acid 12-hydroxystearate (melting point 77.5℃) and calcium hydroxide (CaOH).

2.2 Preparation of palm-grease

Grease can be manufactured via well known four stages of grease making processes, referred as saponification, soap dissolution, re-crystallization and homogenization (Jones, 1968). In this experiment, the saponification process was conducted in a pressurized reactor, followed by dilution in the same vessel. Re-crystallization process was carried out in a vessel with cooling jacket. The homogenizing process was conducted by high speed stirring. Composition of the thickener was varied 10%–20% of the total product.

A mixture of 12-hydroxystearate (taken in 1:1.10 to calcium hydroxide) and the base oil (approximately 90% of total base oil) were uniformly mixed with a mechanical stirrer at 90℃ in a pressurized reactor or autoclave (l liter), equipped with a pressure indicator, oil heater, thermometer, as shown in Figure 1. The calcium hydroxide was added slowly until the solution.

Samples of the palm-grease were tested with penetrometer (ASTM D-217) and dropping point test (ASTM D-566) of soap occurred. The temperature was then slowly raised to 130℃ and maintained for 3 h with stirring. Heating was continued until the soap melted (160℃), and the mixture was immediately cooled to 90℃. The remaining amount of base oil (10% of total base oil) was added. The final mixture was allowed to cool to room temperature to obtain the grease. The palm-grease product was then homogenized using high speed stirring until it was soft and thoroughly homogenous for its structure stabilization. The final product had a smooth, paste-like texture. Similar procedure was used to prepare the other greases with varying composition of thickener.

Figure 1 Pressurized reactor (autoclave)

2.3 Lubrication performance test

Lubrication performance of the palm-grease was tested using the 4-ball wear tester and gear wear tester as shown in Figure 2 and Figure 3. Both lubrication testers are non standard test equipments. They are simplified equipments that can be used to asses lubrication performance based on a comparison of amount of wear data. The 4-ball wear test method is used to measure anti-wear properties of the palm grease in simulated ball bearing. The tests are performed with 8 mm steel balls. Testing conditions were selected to simulate boundary lubrication: low speeds (146 r/min; 0.2 m/s), loads 30 kg (3.34 GPa maximum hertzian pressure), two hours of testing period.

Gear wear test method was used to assess anti-wear characteristics in a gear. In this test, a pair of gear was run under load as shown in Figure 3. Each test was carried out at an ambient temperature, and run at 25 rev/s for 10 hours and the applied load of 10 kg. The wear particle was measured by AAS.

Figure 2 Modified 4-ball tester

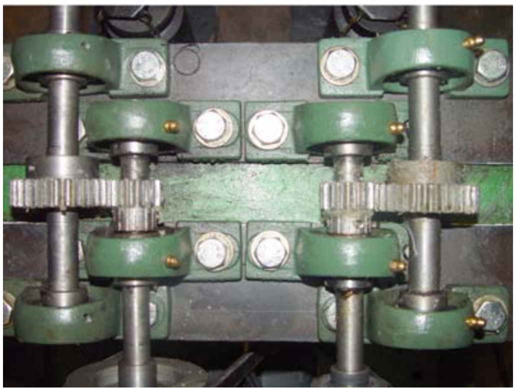

Figure 3 Gear wear tester

3 Results and discussion

3.1 Palm-grease rigidity and appearance

Figure 4 shows the calcium palm-grease, as taken by ordinary camera. Its color was creamy white. The rigidity of the calcium grease at various thickener compositions was determined by measuring its depth of penetration with penetrometer method (ASTM D 217).

Figure 4 Appearance of calcium palm grease

The calcium palm greases were too soft, when the base oil was 100% modified RBDPO (base oil 2). At calcium soap composition 10% to 20% the depth of penetration was 424-317, which was softer than grease NLGI Grade 2 (depth of penetration 265-295). The calcium palm-greases got higher rigidity, as the base oil was the mixture of 50% modified RBDPO and 50% epoxy RBDPO (base oil 1). At calcium composition 10% to 20% their depth of penetration was 276–229. With base oil 2, as can be seen from Figure 5, a palm-grease NLGI Grade 2 (depth of penetration 265-295) can be manufactured using less than 15% calcium soap thickener.

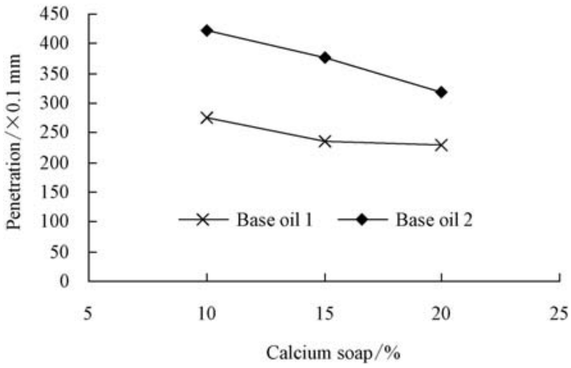

Figure 5 Penetration of the palm-grease at various soap composition

3.2 Palm-grease dropping point

Dropping point is an indicator of the heat resistance of grease. As grease temperature rises, the grease gets softer, until liquefies and its rigidity or consistency is lost. Dropping point is the temperature at which grease becomes fluid enough to drip. The dropping point indicates the upper temperature limit at which grease retains its structure, not the maximum temperature at which grease may be used. The dropping point measurement of the calcium palm-grease at various calcium soap compositions is shown in Figure 6.

As the thickener composition increases, the dropping point increases. At calcium soap composition 10% to 20%, the dropping point of the calcium palm-greases using base oil 1 (100% modified RBDPO) were 114–124℃. The dropping point of the calcium palm-greases became higher when using base oil 2 (mixture 50% modified RBDPO and 50% epoxy

RBDPO). At calcium soap composition 10% the dropping point of the palm-grease could reach 130℃. Thus, grease with higher rigidity (low penetration) shows higher dropping point.

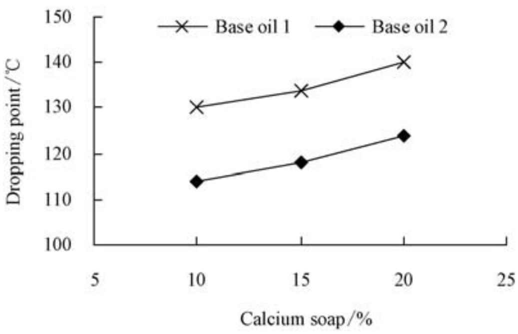

Figure 6 Dropping point of the palm-grease at various soap composition

3.3 Suggested reason for rigidity difference of palm-grease

Rigidity of grease is determined by fibrous formation by the thickener. From Figure 5 and 6, it can be seen that both rigidity and dropping point of the calcium palm-grease using base oil 1 (mixture 50% modified RBDPO and 50% epoxy RBDPO) were higher than that using base oil 2 (100% modified RBDPO), at the same composition of calcium soap thickeners. Indeed, the viscosity of base oil 1 is higher than that of base oil 2, but it must not be the main reason for the rigidity and the dropping point different. The lubricating power of the greases was affected by their chemical/physical interaction between the thickener and the working surfaces of the metal (Silver & Stanley, 1974). Therefore, the chemical and or physical interaction of the functional group containing in the calcium soap and the base oil is considered to be the stronger cause for that difference. Organic compound containing functional group such as ester -COOC-, hydroxide -OH, ether -COC, unsaturated C=C was existed in both base oil, but the base oil 1 was rich in epoxy RBDPO which contained more active group epoxy ring -COC-.

3.4 Anti-wear property from 4-ball wear test and gear wear-test

Lubrication performance of the palm-grease was assessed using 4-ball test, to observe its lubricating ability in ball bearing equipment. In this method the ability of the palm-grease to give surface protection was determined by measuring amount of wear produced during the test where four balls were rotated under boundary lubrication conditions. The smaller the amount of wears generated during the test, the better the performance of the grease sample. Figure.7 shows the amount of wear plotted against thickener composition, obtained from 4-ball wear test of the calcium.

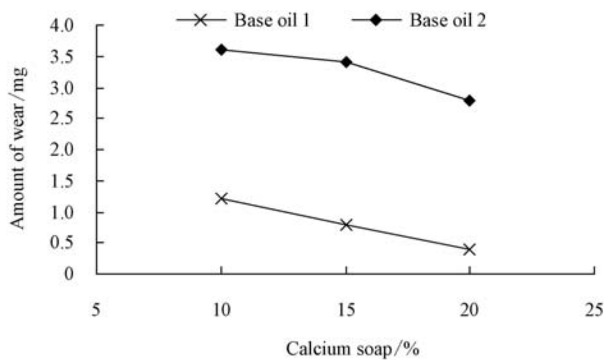

Figure 7 Amount of wear using 4-ball wear test

The figure shows that, the amount of wears produced in the test with calcium palm-greases using base oil 1 (mixture of 50% modified RBDPO and 50% epoxy RBDPO) was less than with calcium palm grease using base oil 1 (100% modified RBDPO). The palm grease using base oil 1 gave better lubrication performance, probably because of the presence of the epoxy ring. In this case, as the rigidity of the palm grease increases, the amount of wear decreases. However, in other case, as the grease getting stiffer the lubrication became worse because it became difficult to flow into the rubbing surface.

For comparison, two fully formulated, high performance food-grade greases (commercial) which use mineral oil as their base oil were also tested, as presented in Table 2.

The results of both the 4-ball wear test and gear wear test showed that the palm greases using base oil 2 were clearly failed to surpass the food-grade grease (commercial) in their anti-wear performance. However, the palm grease using base oil 1 (with composition 15%–20% calcium soap) showed about the same anti-wear performance as the high performance food-grade grease (commercial) did. Though the palm-grease was not formulated with additives yet, it was able to give quite good anti-wear property. This higher ability of the palm-grease using base oil 1 can be related to the existence of the active group epoxy ring. Although some polar functional groups such as ester -COOC-, hydroxides –OH played a role in protecting surface, the epoxy ring was considered to contribute more.

Table 2 Summary of lubrication performance of the palm-grease

	Grease produced in this research						Commercial grease	
Base oil	Modified RBDPO+ Epoxy RBDPO (Base oil 1)			Modified RBDPO (Base oil 2)			Mineral oil Food-grade	
Thickener type	Calcium soap						Calcium soap	
Thickener composition	10%	15%	20%	10%	15%	20%	-	-
Additives	No	No	No	No	No	No	Yes	Yes
Penetration [×0.1 mm]	276	237	229	424	377	317	-	-
NLGI number	2	3	3	0	0	1	-	-
Dropping point [^{0}C]	130	134	140	114	118	124	140	140
Anti wear properties								
Amount of wear from 4-ball test [mg]	1.2	0.8	0.4	3.6	3.4	2.8	0.6	0.6
Amount of wear from Gear test [ppm]	100-200	50-200	50-200	100-200	100-200	100-200	50-100	50-100

4 Conclusions

A palm-grease based on modified RBDPO and calcium thickener has been made, and selective lubrication performance tests have been carried out. From this study several conclusions can be summarized as follows:

1) Additive-free palm-grease can be manufactured using a mixture of modified RBDPO and epoxy RBDPO using 15%–20% thickener, to get dropping point more than 130 ^{o}C, and an appropriate anti-wear performance.

2) The high anti-wear performance of the additive-free calcium palm-grease is attributed to the contribution of the active functional group (epoxy ring) in protecting the surface from rubbing and also other polar groups such as ester (-COOC-) and hydroxide (–OH).

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