Formulation and Performance of Palm-grease Using Calcium Soap

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ABSTRACT

An environmental friendly palm-grease as a bio-grease has already been formulated using modified RBDPO (Refined Bleached Deodorized Palm Oil) mixed with epoxy RBDPO as base oil and calcium 12-hydroxy-stearate as thickener. Such palm-grease is dedicated for lubrication of bearing and gear in food processing and pharmaceutical machineries that require food-grade lubricant. The palm-grease was manufactured via 4 steps of processes, firstly saponification process using pressurized reactor, soap dilution by heating process, crystallization by cooling process and homogenization by high speed mixing. The free-additives palm-grease had dropping point of 130°C and consistency NLGI Grade 3. Lubrication performance of the palm-grease was evaluated using a 4-ball wear and gear wear tester, and the results showed that its anti-wear performance was comparable to that of mineral based food-grade grease.

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

1. INTRODUCTION

Semi solid lubricant or grease is widely used in many lubrication systems, because it can provide simple lubrication system for bearing and gear. Greases are used where a mechanism can only be lubricated infrequently and where a lubricating oil would not stay in position. It is able to lower friction coefficients, to improve sealing and to provide 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 specific 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 grease and liquid lubricant is the presence of the thickening agent. The thickeners are usually metallic soaps, such as lithium, sodium and calcium salts of long chain fatty acids. 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 thickeners not only provide consistency to grease, and they also affect desired properties such as water and heat resistance and pump-ability (Yousif, 1982). Thickener can also lower the coefficient of friction over that of the base oil alone (Silver & Stanley, 1974). Among lubricating greases, the lithium soap based lubricating grease has been numerous due to the very good properties of these greases, i.e., a smooth appearance, and a high dropping point. However, calcium soap is more favorable for formulating food-grade grease (Dresel, 1994). Calcium is not toxic and it is common in all living systems and is essential to life. In addition, calcium thickener has also high resistance to water wash-out.

Base oils used to formulate grease are normally petroleum or synthetic oils. With growing environmental awareness and stringent regulations regarding the use of petroleum products, the use of eco-friendly lubricant from vegetable oils is becoming more popular. Vegetable oils can give adequate performance in a variety of applications and offer significant environmental advantages such as renewable resources, non-toxic or biodegradability. Sunflower based bio-grease using polymer thickener has been developed by European researchers, for lubrication in earth moving equipment (Barriga & Aranzabe, 2006). Soybean based bio-grease has been developed by American researchers to meet both food-grade and non food-grade lubricating grease requirements (Adhvaryu, 2002).

The notable challenges in formulating grease using vegetable oils are oxidative stability, hydrolytic stabilities, low temperature properties that are innate characteristics of the triglyceride molecules. Oxidative stability of vegetable oils are decreasing with their number of double bonds, and their poor low-temperature property is getting worse with decreasing number of double bonds (Dresel, 1994). Therefore, vegetable oil suitable for lubricant is high oleic oils with mono-unsaturated fatty acid content >80%, low poly-unsaturated fatty acid and saturated fatty acid to provide both high oxidation stability and reasonable low temperature flow properties (Dharma, 2002). Palm oil with mono-unsaturated fatty acid content (40%) and high saturated fatty acid content is often considered not suitable for lubricant because it has poor low temperature fluidity. However, when one uses palm oil in formulating bio-grease for tropical region application, its poor low temperature fluidity (pour point 15°C) is no longer critical factor, and thus the high content of saturated may be considered as advantage because it increases oxidative stability. Further improvement of lubrication properties of palm oil may be obtained through carbonyl groups modification, such as esterification, transesterification, or carbon-carbon double bond modification, such as partial hydrogenation, epoxidation, addition or epoxy-ring opening reactions to obtain high performance bio-lubricants (Wagner, 2001).

In our unpublished research, we have successfully prepared a modified RBDPO via trans-esterification, epoxidation and ring opening reaction using non toxic catalyst to produce non toxic foodgrade products. The transesterification is intended to remove β-hydrogen of triglyceride, while the epoxidation and ring opening reaction is intended to modify carbon-carbon double bond of fatty acid chain which are susceptible to oxidation. The obtained bio-lubricant has better friction reducing property, anti-wear property, and oxidation stability than RBDPO. In this research, the modified RBDPO is used as base oil for preparing eco-friendly palm-grease that will be dedicated for bearing and gear of machinery in agriculture, forestry, and also food pharmaceutical industries using calcium soap thickener. This paper also reports anti-wear performance of the palm-grease, when no additives added in its formulation and the base oil was mixed with epoxy RBDPO to allow active epoxy groups "working" as surface protecting agent.

2. MATERIALS AND METHODS

2.1 Base Oil

Two mixtures of base oils were prepared. Base oil 1 was a mixture of 50% v/v modified RBDPO and 50% v/v epoxy RBDPO. Base oil 2 was 100% modified RBDPO. The modified RBDPO was prepared via esterification, epoxidation and ring opening reactions, and it has better oxidation stability than both RBDPO and mineral oil HVS 160S, as shown by micro-oxidation test and bulk oxidation test results in Table 1. Selective properties of the modified RBDPO are also listed along with those of RBDPO and mineral oil HVI 160S, for comparison. The RBDPO has 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%; C18:2 (linoleic)= 10.1%.

Table 1. Selective properties of base oils

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 @40ºC [cSt]	ASTM D-445	35	38.9	96
Viscosity @100ºC [cSt]	ASTM D-446	6.9	8--9	11
Viscosity Index [-]	ASTM D-2270	>100	>100	100
Pour point [ºC]	ASTM D-97	0-5	15	-9
Oxidation stability				
Viscosity @40ºC increase [%]	Bulk oxidation	5.6	21.5	7.8
Amount of deposit [g]	Micro oxidation	0.0199	0.0497	0.0329

The epoxy RBDPO was prepared via epoxidation reaction using hydrogen peroxide and formic acid as catalyst. Epoxy RBDPO has higher viscosity than RBDPO, with kinematic viscosity of 55 cSt at 40^{o}C. The viscosity of the base oil 1 (ca 45 cSt) is higher than that of the base oil 2. Epoxy RBDPO contains epoxides or oxirane groups, are cyclic ethers with three-membered ring. The strained three-membered ring of epoxides makes them active or highly susceptible to ring-opening reactions which can be initiated by either electrophiles or nucleophiles.

2.2 Thickener

Calcium soap was obtained from the reaction between fatty acid 12-hydroxystearate (its melting point is 77.5°C) and calcium hydroxide (CaOH).

2.3 Preparation of Palm-grease

Palm-grease was prepared via well known 4 stages of grease making processes, referred as saponification, soap dissolution, re-crystallization and homogenization (Jones, 1968). In this research, the saponification process was conducted in a pressurized reactor, followed by soap dilution in the same vessel. The re-crystallization process was carried out in a vessel with cooling jacket. The homogenation process was conducted by high speed stirring.

A mixture of 12-hydroxystearate (taken in 1:1.1 to calcium hydroxide) and the base oil (approximately 90% of total base oil) were uniformly mixed with a mechanical stirrer at 90 ºC in a pressurized reactor or autoclave (l liter), equipped with a pressure indicator, oil heater, thermometer, as shown in Figure 1.

Figure1. Pressurized reactor (autoclave)

The calcium hydroxide was added slowly until the solution of soap occurred. The temperature was then slowly raised to 130ºC and maintained for 3 hours with stirring. Heating was continued until the soap melted (160ºC). Then the mixture was immediately cooled to 90^{o}C, and 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 palm-grease. The palm-grease product was then homogenized for structure stabilization, using high speed stirring until it was soft and thoroughly homogenous. The final product had a smooth, paste-like texture. Similar procedure was used to prepare the other greases with varying composition of thickener (10%-20% weight of the total).

The depth of penetration and dropping point of the palm-grease were determined using penetrometer (ASTM D-217) and dropping point tester (ASTM D-566)

2.4 Lubrication Performance Test

Lubrication performance of the palm-grease was tested using 4-ball wear tester and gear wear tester as shown in Figure 2 and Figure 3. The 4-ball wear test method was intended to measure anti-wear property of the palm-grease in a simulated ball bearing. This test used 8 mm steel balls as wear specimens, and it was run at speed 146 rpm and at load 30 kg (3.34 GPa maximum hertzian pressure), the duration of test was 2 hours. The difference in weight before and after the test was quantified as the amount of wear.

Gear wear test method was intended to assess anti-wear property of the palm-grease in a gear system. In this test, a pair of gear was rotated under load. The wear test was carried out at speed 25 rev/s, applied load 10 kg, and running time 10 hours. After the test, the used palm-grease was collected, and its wear particle content was measured by AAS (Atomic Absorption Spectroscopy, ASTM D4628).

Figure 2. Modified 4-ball tester

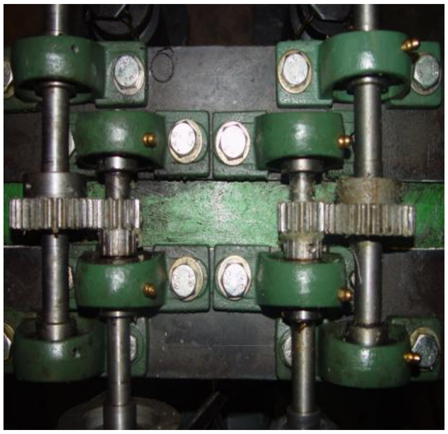

Figure 3. Gear wear tester

3. RESULTS AND DISCUSSION

3.1 Palm-grease Rigidity and Appearance

Figure 4 shows the calcium palm-grease with the color of creamy white and its texture was soft. The rigidity of the calcium palm-grease was determined by measuring its depth of penetration with penetrometer method (ASTM D217).

Figure 4. Appearance of calcium palm-grease

When the base oil was 100% modified RBDPO (base oil 2), and the calcium soap content was varied from 10% to 20%, the palm-grease gave depth of penetration 317-424 which was relatively low of rigidity. NLGI Grade is a widely used classification for lubricating greases based on their consistency and it was established by the National Lubricating Grease Institute

(NLGI). The palm-grease using base oil 2 was softer than multipurpose grease NLGI Grade 2 which has depth of penetration 265-295. When the base oil 1 (50% modified RBDPO + 50% epoxy RBDPO) was used, the rigidity of the calcium palm-grease increased. Figure 5 shows the relationship between the use of calcium soap and penetration. At the range of calcium soap content from 10% to 20%, the palm-grease using base oil 1 gave depth of penetration 229-276. Thus, to prepare a palm-grease using base oil 1 with NLGI Grade 2, one only needs calcium soap less than 15%, as shown in Figure 5.

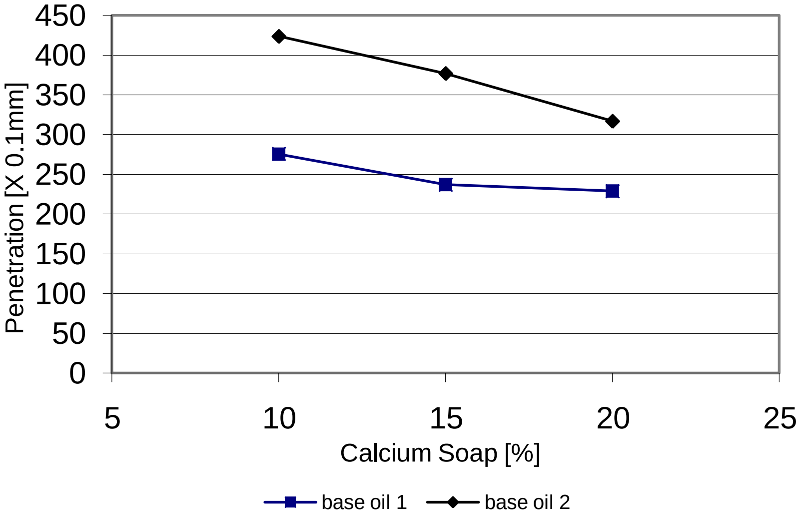

Figure 5. Penetration of the palm-grease at various soap compositions

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 it 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 results of dropping point measurement of the calcium palm-grease at various calcium soap compositions are shown in Figure 6.

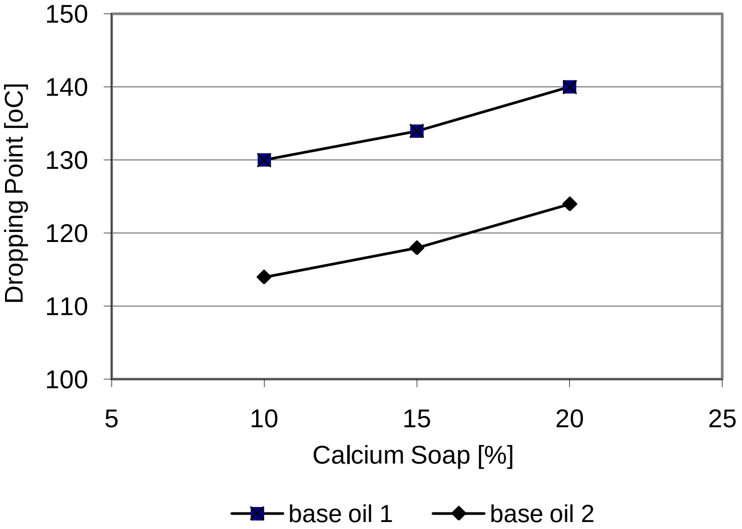

Figure 6. Dropping point of the palm-grease at various soap compositions

The dropping point of the palm-grease increases, as the calcium soap composition increases at a range of 0% to 20%. The dropping point of the palm-grease ranges from 114 to124 °C when using base oil 2 (100% modified RBDPO), and ranges from 130 to 140 °C when using base oil 1 (mixture 50% modified RBDPO and 50% epoxy RBDPO). These results show that increase of soap composition caused increase both dropping point and the rigidity of the palm-grease.

The experiment results in Fig. 5 and Fig. 6 show that at the same composition of calcium soap, both rigidity and dropping point of the palm-grease using base oil 1 were higher than that of using base oil 2. Although the viscosity of the base oil 1 was higher than that of the base oil 2, this viscosity difference must not the main cause for the rigidity and the dropping point difference, because the chemical interaction between the calcium soap and the base oils was considered to have stronger effect than the physical property difference. Both base oil 1 and base oil 2 were organic compounds that contained many functional groups such as ester –COOC–, hydroxide –OH, ether –COC, unsaturated C=C. However, the base oil 1 was rich with active epoxy ring group. –COC– which is considered to be responsible for the rigidity and dropping point difference.

According to report from other researcher, the rigidity of grease is determined by fibrous formation by the thickener (Yousif, 1982), and the fibrous formation is affected by chemical/physical interaction between the base oil and the thickener. In addition, chemical/physical interactions between the thickener and the working surfaces of the metal affect the lubricating power of the greases (Silver & Stanley, 1974).

3.3 Anti-wear Property from 4-ball Wear Test and Gear Wear-test

The ability of the palm-grease to protect surface was assessed using 4-ball test. In this method, the amount of wear was determined by measuring the lost of weight of the lubricated ball specimens. The smaller the amount of wear is the better the performance of the palm-grease.

Figure 7 shows the amount of the wear, plotted against calcium soap composition, resulted from the 4-balls tests.

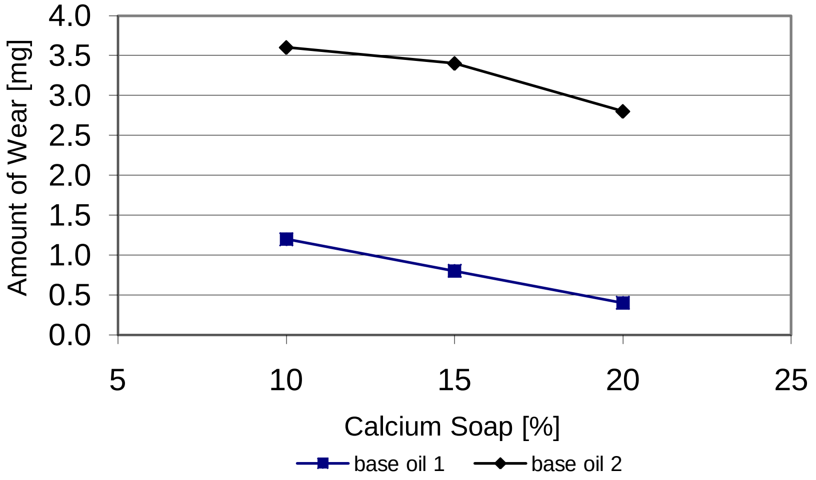

Figure 7. Amount of wear using two different base oils

The amount of wear decreases as the soap composition increases at the range 10% to 20%. The amount of wear with calcium palm-grease using base oil 1 was less than that with calcium palm grease using base oil 2. The palm-grease using base oil 1 gave better lubrication performance. In this case, as the rigidity of the palm grease increases, the amount of wear decreases, but in other case the opposite result may occur. Other researcher reported that as the grease getting stiffer the lubrication became worse because it became difficult to flow on the rubbing surface (Yousif, 1982).

For comparison, the lubrication performance of the palm-grease and commercial food-grade grease were tested and the results were presented in Table 2. The results of both the 4-ball wear test and gear wear test show that the palm greases using base oil 2 were clearly fail to surpass the commercial food-grade grease in their anti-wear performance. The palm grease using base oil 1 (with composition 15-20% calcium soap) showed about the same anti-wear performance as the commercial food-grade grease did. Though the palm-grease was not formulated with additives yet, it was able to give quite good anti-wear property. The ability of palm oil derivatives was also reported by other researcher (Maleque, 2002) who considered that oleic acid and palmitic acid of POME (Palm Oil Methyl Ester) may react with iron oxides and form a soap film which in turn reduces wear and friction**.** 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, but the contribution of epoxy ring could be much more significant.

Table 2. Summary of lubrication performance of the palm-grease

	Palm-grease produced in this research		Commercial grease
Base oil	Modified RBDPO+ Epoxy RBDPO	Modified RBDPO (Base oil 2)	Mineral oil food-grade

	(Base oil 1)							
Thickener type	Calcium soap						Calcium soap	
Thickener composition	10%	15%	20%	10%	15%	20%	-	-
Additives	No	No	No	No	No	No	Yes	Yes
Penetration [X 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 [mg/kg]	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 follow:

a. Additive-free palm-grease can be manufactured using mixture of modified RBDPO and epoxy RBDPO using 15%-20% thickener, to get dropping point of more than 130^{o}C, and an appropriate anti-wear performance.
b. The high anti-wear performance of the additive-free calcium palm-grease is attributed to the contribution of active functional groups such as epoxy ring, ester and hydroxide in protecting the surface from rubbing.

5. ACKNOWLEDMENTS

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