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Biogrease Based on Palm Oil and Lithium Soap Thickener: Evaluation of Antiwear Property

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Abstract: An environmental friendly palm-grease has already been formulated from modified RBDPO (Refined Bleach Deodorized Palm Oil) as base oil and lithium soap as thickener. Such palm-grease is dedicated for general application and or equipment working in areas where biodegradability is required such as in agriculture, forestry and coastal marine, recreation areas. The grease was manufactured via 4 steps of processes: saponification in pressurized reactor, soap dilution by heating, re-crystallization by cooling and homogenization. The result of lubrication performance tests using 4-ball wear-test showed that the amount of wear on ball specimen was smaller in test with the palm- grease than the test with mineral (HVI 160S) grease. This ability of the palm-grease to provide better surface protection or antiwear property was considered as the existence of relatively polar groups in base oil such as ester -COOC-, hydroxides –OH and oxirane ring (epoxy) -COC-.

Key words: Palm-grease · Modified RBDPO · Lithium soap · Dropping Point · Antiwear Property · 4-ball wear-test · Gear-wear-test

INTRODUCTION

Lubricating grease is obtained by dispersion of a thickening agent, usually soap in a liquid lubricant and may also contain additives that upgrade some special properties. Typical grease contains base oil 75-95%, thickener 5-20% and additives 0-20%. The thickeners are usually soaps, such as lithium, sodium and calcium salts of long chain fatty acids. 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, antiwear agent and extreme pressure to guard against excessive wear due to metal to metal contact.

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. The soap thickener gives grease its characteristic rigidity or consistency which is a measure of resistance to deformation by an applied force. Based on present theories, the grease structure can be better visualized as a three-dimensional network of soap fibers, randomly oriented fibres, which is at least partially crystalline. The structure will flow under an applied stress, the magnitude of which will depend on the rigidity of the soap fibre network which is governed by the forces holding the fibres together [1]. Soap thickeners not only provide rigidity to grease and they also affect desired properties such as water and heat resistance and pumpability [2]. It can also lower the coefficient of friction over that of the base oil alone [3].

Base oils used to formulate grease are normally petroleum or synthetic mineral oils. Due to growing environmental awareness and stringent regulations on the petroleum products uses, the manufacture and the use of eco-friendly grease has begun to gain importance. Since biodegradable synthetic ester lubricant are higher in cost, vegetable oils are drawing attention as biodegradable alternates for synthetic esters because of their economical. Vegetable oil may offer significant environmental advantages with respect to resource renew ability, nontoxic and or biodegradability, adequate performance in a variety of applications. For example, sunflower oil has been used to develop biogrease by European researcher, with polymer thickener for grease application lubrication in earth moving equipment [4]. The biogrease was reported to have better properties (especially effective lubrication, wear protection,

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corrosion resistance, friction reduction, heat removal, etc.) than mineral oil base grease [5]. Soybean oil has also been used by American researchers for manufacturing soy grease for lubrication heavy duty truck. Unfortunately, research and or manufacturing of such a biogrease from palm oil is rarely reported.

Formulating or tailoring specific products for lubrication using vegetable oils present many challenges. The notable challenges are oxidation stability, hydrolytic stability, low temperature properties that are innate characteristics of the triglyceride molecule. Oxidation stability of vegetable oils is decreasing with their number of double bonds, but their poor low-temperature behavior is getting worse with a decreasing number of double bonds [6]. To be suitable for lubricant, vegetable oils should have higher oleic oils with mono-unsaturated fatty acid content >80%, low poly-unsaturated fatty acid and saturated fatty acid [7] to provide both high oxidative stability and reasonable low-temperature flow properties. Palm oil with high content of saturated fatty acid is often considered not suitable for lubricant because of its poor low-temperature flow properties (pour point 8-15°C). But, when the palm oil is used for formulating lubricant for tropical region application, the high content of saturated fatty acid in palm oils may be considered as advantage because it contributes better oxidative stability. In the other hand, the limitation in low temperature properties may be ignored.

In previous research, we have successfully prepared a modified RBDPO via 3 step processes of transesterification, epoxidation and ring-opening to enhance oxidation stability. The results of characterization shows that the products has better oxidation stability, superior in friction reducing and antiwear properties. In this trial, the modified RBDPO is used as base oil for manufacturing greases with lithium soap as thickener.

The purpose of this research is to prepare an eco-friendly palm-grease, for use in bearings, gear and other mechanical systems requiring grease lubrication in environmentally sensitive areas, such as equipment used in the construction, forestry and farming industries. In this study, the performance of the palm-grease was compared to that of mineral oil base lithium grease.

MATERIALS AND METHODS

Materials Used

Base Oil: The base fluid used in experiment were modified RBDPO, epoxy RBDPO, mineral oil HVI 160S (produced by Pertamina). The modified RBDPO was prepared via process of esterification, epoxidation and ring opening from RBDPO which 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 shows selective properties of the modified RBDPO presented together with RBDPO and the mineral oil as comparison. The modified RBDPO had been tested using micro-oxidation and bulk-oxidation methods and it shows better oxidation stability than both RBDPO and HVI 160S, indicated by the smaller change in its viscosity and deposit formed after tests. The epoxy RBDPO was prepared via epoxydation reaction of RBDPO with hydrogen peroxide and formic acid as catalyst. The epoxy RBDPO has lighter color and higher viscosity than RBDPO and its kinematics viscosity was 55 cSt @ 40°C.

In this experiment, at first trial the modified RBDPO was used as the based oil 1. This base oil was mixed with non polar mineral oil (HVI 160S) at various composition, to observe grease properties resulted from the base oil with different concentration of polar compound.. At second trial, mixture of modified RBDPO and epoxy RBDPO at ratio 4:1 was used as the base oil 2. This base oil was also mixed with HVI 160S) at various composition. This trial was intended to observe the contribution of epoxy RBDPO which has higher viscosity and rich of epoxy functional groups, for improving lubrication performance epoxy RBDPO.

Thickener: Thickener lithium soap was obtained from the reaction of fatty acid 12-hydroxystearate (mp. 77.5 °C) and lithium hydroxides monohydrate ($LiOH.H_2O$, 98%).

Preparation of Palm-grease: Grease is manufactured via well known 4 stages of grease making processes, referred as saponification, soap dissolution, re-crystallization and homogenization [8]. A palm-grease is made using lithium soap thickener 15% and base oil 85% of total product. A mixture of 12-hydroxystearate (taken in 1:1.10 to lithium hydroxide) and the modified RBDPO (approximately 75% of total product) were uniformly mixed with a mechanical stirrer at 90°C in a 2 L flanged flask or autoclave, equipped with a pressure indicator, oil heater, thermometer, as shown in Figure 1. The lithium hydroxide was added slowly until solution of the soap occurred, the temperature was then slowly raised to 165°C and maintained for 3 h with stirring. Heating was continued until the soap melted (200°C) and the mixture was immediately cooled to 120°C. Additional amounts of modified RBDPO (10% of total product) were added. The

Table 1: Lubricating properties of modified palm oil

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
Viscocity @40ºC [cSt]	ASTM D-445	35	38.9	96
Viscocity @100ºC [cSt]	ASTM D-446	6.9	8--9	11
Viscocity 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]	Microoxidation	0.0199	0.0497	0.0329

Fig. 1: Autoclave

Fig. 2: Gear wear-test

final mixture was allowed to cool to room temperature to obtain the grease. For structure stabilization of palm-grease, it was homogenized using high speed double stirrer until it was thoroughly homogeneous. The final product had a smooth, paste-like texture. Similar procedure was used to prepare the other greases made with varying composition of base oil, fatty acid, lithium hydroxide and additive.

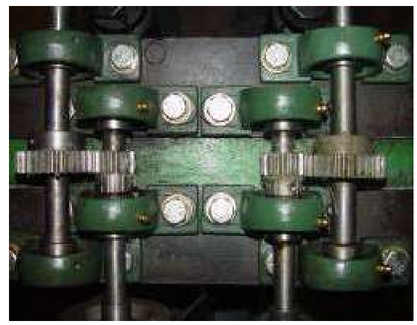

Fig. 3: Gear wear test

Rigidity Measurement: Samples of the palm-grease were tested with penetrometer (ASTM D 217), dropping point test (ASTM D 566).

Lubrication Performance Test: Lubrication performance of palm-grease were tested using 4-ball wear tester and gear wear tester as shown in Figure 2 and 3. Both apparatus were_ used to assess lubrication performance of grease by comparing the amount of wear obtained after the tests. The 4-ball wear test method was intended to measure anti-wear property of the palm grease in simulated ball bearing by weighing the wear particles produced in the ball specimens. These tests are performed with 8.73 mm steel balls. Testing conditions were selected to simulate boundary lubrication: low speeds (146 rpm; 0.2 m/s), loads 30 kg (3.34 GPa maximum hertzian pressure), 2 hrs of testing time.

Gear wear test method was intended to assess antiwear characteristics of the palm-grease in a gear. In this test, a pair of gear was run under load. Each test was carried out at ambient temperature with 10 hours runs at 25 rev/s and the applied load of 10 kg. The amount of wear particles were measured by AAS. Grease that provides better lubrication performance would show smaller amount of wear.

RESULTS AND DISCUSSION

Palm-grease Rigidity and Appearance: Figure 4 shows a palm-grease, as a result of ordinary camera. It was creamy and the texture was soft and sticky.

The rigidity of the palm greases with lithium soap 15% at various base oil composition were determined by measuring its depth of penetration with penetrometer (ASTM D 217), as shown in Figure 5. Two 2 curves in the figure represent base oil 1 (modified RBDPO) and base oil 2 (modified RBDPO + epoxy RBDPO). At composition 100% base oil 1 and base oil 2, the palm-greases shows penetration level 200 and 150 respectively, which mean that these palm greases have higher rigidity than grease NLGI grade 2 (depth of penetration 265-295). As the base oil composition decreases to 80%, 40%, 20% by blending with mineral oil HVI 160S, the palm greases getting higher penetration and at composition 0% it reach penetration level 340, which means it is softer than grease NLGI Grade 2

The curves indicate that with the same amount of lithium soap, the palm-greases could give higher rigidity than mineral-greases or we can say that to produce the same level of rigidity, palm-greases need smaller amount of the lithium thickener than of mineral-grease. To manufacture a palm-grease NLGI Grade 2, both the base oil 1 and base oil 2 at composition 100% need amount of lithium soap less than 15%. The base oil 2 could give higher rigidity than the base oil 1, at the same lithium soap composition.

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 palm-grease with lithium soap 15% at various modified RBDPO composition are shown in Figure 6

The dropping point of palm-grease using base oil 1 and using base oil 2 is 170 and 210°C, respectively. As the composition of modified RBDPO reduces to 80%, 40%, 20% by blending with mineral oil HVI 160S, the dropping point decreases and at composition 0% l or 100% mineral oil HVI 160S the dropping point reaches 150°C. These facts indicate that at the same amount of lithium soap thickener, the palm-grease could get higher dropping point than mineral-grease. An also, the base oil 2 could give higher dropping point than base oil 1.

Fig. 4: Palm-grease

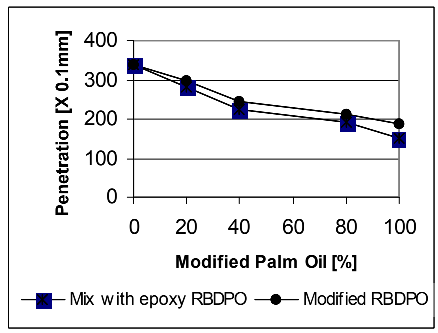

Fig. 5: Penetration of the palm-grease at various base oil composition

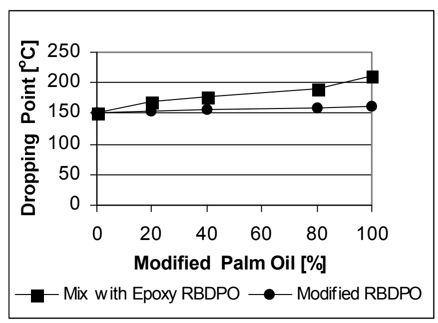

Fig. 6: Dropping point of the palm-grease

Suggested Reason for Rigidity Difference Palm-grease and Mineral-grease: Theoretically, rigidity of grease is determined by fibrous formation by the thickener. Since the fact in this trial showed that at the same lithium soap composition, the palm grease could get higher rigidity than the mineral grease, as shown by Figure 5, so the rigidity of the palm grease was affected by the base oil

Table 2: Results summary of lubrication performance of the palm-grease

	Grease produced in this research					Commercial grease	
	Modified RBDPO (base oil 2)	Mix Base Oil			HVI 160	Mineral oil	
Base oil composition	-	80%	40%	20%	-	-	-
Thickener			Lithium soap 15%			Lithium soap	
Additives	No	No	No	No	No	Yes	Yes
Penetration [X 0.1 mm]	153	190	225	284	338	-	-
NLGI number	5	4	2	2	1	-	-
Dropping point [°C]	210	190	178	170	150	200	200
Anti wear properties							
Amount of wear from 4-ball Test [mg]	0.4	0.8	1.2	2.0	3.6	0.8	0.8
Amount of wear from Gear Test [ppm]	65	65	102	194	209	50-100	50-100
Appearance	light brown	light brown	light brown	light brown	light brown	colored	colored

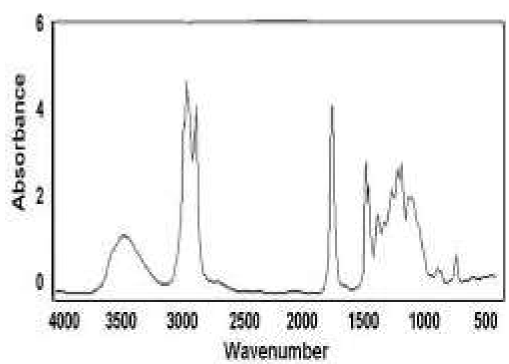

Fig. 7: Typical FTIR spectrum of modified RBDPO

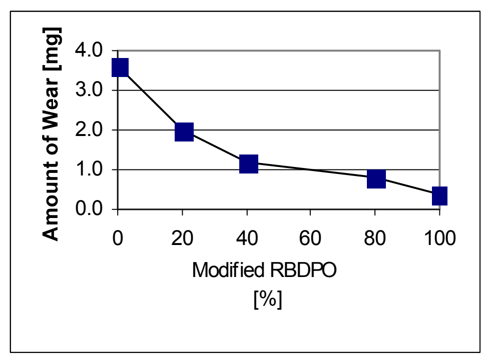

Fig. 8: Amount of wear using 4-ball wear tester

which has specific chemical and or physical interaction to the lithium soap. In contrast to mineral-oil having only non-polar paraffinic hydrocarbon, typical modified palm oil (base oil 1 and base oil 2) entirely retains more polar due to its functional group such as ester -COOC-, hydroxide -OH, ether -COC-. The interaction between lithium soap with those relatively polar species in base oil may alter the grease to be more rigid. And the base oil 2 gave the palm grease higher rigidity than base oil 1 because the contribution epoxy RBDPO which contains oxirane ring -COC-.

In addition, as mentioned in grease preparation, lithium soap was made by reacting 12-hydroxy-stearate with LiOH and more than stochiometric amount the base was intentionally added to the grease formulation. This excessive LiOH might lead to the formation of additional soap. Consequently, two kinds of soaps were formed, i.e. the product of saponification reactions between lithium hydroxide with 12-hydroxy-stearate and the excessive LiOH with free acids or acid products from modified RBDPO. This additional soap might also give contribution to the rigidity or consistency of the palm grease

Results Obtained from 4-ball Wear Test and Gear Wear-test: 4-ball wear test is used to model grease lubrication in ball bearing. In this test, the lubrication performance of the grease was determined by measuring the amount of wear particles produced due to friction among the balls. The test was carried out under boundary lubrication condition.

Figure 8 shows the amount of wear obtained from 4-ball wear test of the palm-grease with lithium soap 15% at various base oil composition. As shown in Table 2 and also Figure 8 palm-grease using 100% base oil 2 (modified RBDPO + epoxy RBDPO) produces amount of wear 0.4 mg. As the base oil composition reduces to 80%, 40%,

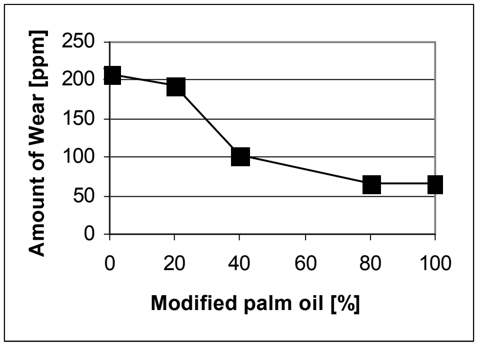

Fig. 9: Amount of wear using gear wear tester

20%, the amount of wear increases. At base oil composition 0% or 100% mineral oil, the grease gives highest the amount of wear. This experimental result implies that the palm-grease has better antiwear properties than mineral-grease.

Several researchers reported that the lubricating power of the greases was not much affected by their bulk physical characteristics, their consistency and their greater effectiveness over the base oil was probably due to chemical/ physical interaction between the thickener and the working surfaces of the metal [3]. Therefore, although the palm-grease was more rigid than the mineral-grease, it must be thought that the superiority of the palm-grease over the mineral-grease in its antiwear property was not due to its higher rigidity. The higher ability of palm-grease to give wear protection is seemed to be related to polarity of oxygen containing species in the base oil. In Figure 7, the FTIR spectrum of the modified RBDPO shows hydroxide (OH) peak (3200-3600 cm^{-1}) and carbonyl (C=O) peak (1700-1730 cm^{-1}) clearly. The small peak at 820- 850 cm^{-1} attributed to epoxy group.

The result of performance tests of the palm-grease using gear wear test are shown in Figure 9, which shows the amount of wear particles plotted against base oil composition. The amount of wear obtained from both the 4-ball wear test and gear wear test show decreasing trend, as the composition of the base oil increasing.

The antiwear properties of the palm-Grease were also compared to commercial mineral-grease, as presented in Table 2, where the penetration test, dropping point test and performance test of the palm-grease, have been plotted in Figuer 5, Figure 6 and Figure 8 respectively. The results of both the 4-ball wear test and the gear wear test show that the palm-grease product could not surpass the mineral-grease (commercial) in their antiwear property. Considering that the palm-grease was not formulated with additives yet, the above result was good enough. The ability of palm-grease to give wear protection can be promoted even higher by formulation with EP additives which contain more active component than ester -COOC-, hydroxides -OH, oxirane ring -COC- containing species in the base oil.

CONCLUSIONS

In this study, biogrease based on modified palm oil has been made using lithium soap as thickener. The tribological performance, especially the antiwear property of the palm grease have been tested. The palm grease shows better antiwear property than the mineral-grease based on HVI 160S, as shown by the smaller amount of wear produced in the 4-ball wear test and gear wear test. The experiment result here conform the superiority of vegetable oil over the mineral oil in their ability to protect surface from metal to metal contact, when they are used as base oil in grease. The ability of the palm-grease to give better antiwear property than the mineral grease were considered to be influenced by the existence of several polar functional groups such as hydroxides –OH, oxirane ring -COC-, besides functional groups ester -COOC- which is characteristic of triglycerides.

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