Grease formulation and characterization from waste automotive engine oil with the use of complex thickener

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Abstract. Waste engine oil one of the most abundant wastes in Malaysia, and through the reutilization of waste automotive engine oil helps to create a sustainable environment. The objective of this research is to develop the best formulation of lithium complex grease derived from waste automotive engine oil as base oil. The main focused parameter in this study is the different formulation ratio of base oil, thickener and co-thickener. Lithium 12-hydroxystearate is mixed with azelaic acid to produce lithium complex 12-hydroxystearate. Two different type of base oils, i.e. fresh automotive engine oil (FAO) and waste automotive engine oil (WEO) are used to formulate Li-complex grease. The grease derived from FAO is used to compare the physical properties derived from WEO. The texture of the formulation of base oil higher than 82 weight percentage was very fluid. The formulation of grease is carried out by differencing the ratio of the waste automotive engine oil, lithium complex 12-hydroxystearate and azelaic acid, which are 82:18, 80:20 and 70:30. The properties of the grease formulated is conducted through several tests, such as ASTM approach, Fourier Transform Infrared Spectroscopy (FTIR) characterization, oil separation and thermogravimetric analysis (TGA). Such interesting properties included consistency, chemical compound of the grease, oil separation and thermal stability. Based on the finding, the best formulated Li-complex grease is WG3, classified NLGI 3. The significant peak derived from FAO and WEO to observe is 1710 cm\(^{-1}\) as this peak indicated the oxidation stability. From the result, the intensity of carboxylic acid is weak that ranged 1709 – 1711 cm\(^{-1}\). Hence, this indicated the grease formulated exhibited better oxidation stability. Furthermore, the formulated grease was thermally stable as the onset temperature was 250.09 °C. In conclusion, the formulation of Li-complex from WEO can be used as an alternative source of base oil in the grease industry, due to the good properties exhibition and preserving the environment as well as the increment of fossil fuel’s demand and cost.

1. Introduction
The depletion of natural resources and environmental issue have putting pressure on industries to find the natural resources scarcity as well as reducing the impact to the environment caused by industrial waste materials. Due to the effect of lubricants exert on the environment, every year, it is expected more than 10 million tons of waste oil such as engine, hydraulic and industrial oils are dumped to the environment [1]. To solve the problem, more research on biodegradable grease using vegetable oil are being actively researched at present day. Several studies have been done by Universiti Malaysia Pahang...
(UMP) researchers related to reutilizing waste oil such as waste cooking oil and waste transformer oil [2, 3].

Greases mostly acted to reduce wear and friction in machinery as it is an important machine element making the demand for their improvement in performance to be ongoing in the industry. Thickener, oil and additives is the most common element in grease [4]. The compositions for grease is commonly include base oils at 70-95%, thickeners at 3-30%, and additives at 0-10%. The thickener forms an entangled network which holds or traps the oil and contribute to the appropriate rheological and tribology behaviour of the grease [5]. The most commonly used of thickening agent are soaps, such as calcium, aluminium, lithium and sodium.

Lithium complex grease is commonly formulated from 12-hydroxystearate and azelaic acid [6, 7]. 12-hydroxystearic acid is a saturated long chain fatty acid with one hydroxyl group on aliphatic chain and is described to be a good gelator [8]. Greases produced from lithium 12-hydroxystearate have higher dropping point when compared to lithium stearate. The improvements in properties basically connected to the capability of the 12-hydroxystearate anion to the hydrogen bond. Lithium 12-hydrostearate has been described as the “foundation stone of the current generation of lubricating grease” [9].

Two problems are taken in consideration in this field of study. Firstly, it is the improper handling of WEO towards the environment. Improper handling of waste oil can cause waste emulsion. Secondly, it is the cost effective of crude oil. Due to its higher demand, this has also indirectly threatened public health and pose a serious threat to the environment at the same time. Consequently, the increase in prices of crude oil and environmental concerns have induced the idea of finding alternatives to replace mineral oils [10]. Since base oil accounts for the highest composition for about 70-95 weight percentage, there is a great need for the reutilization of waste automotive engine oil into recycled products. Recycling is beneficial to the environment and also to economic development as it prevents resource scarcity, decreases the demand of landfilling and saves energy too [11]. Hence, it is wise to reutilize WEO as base oil in grease production for its economic value and environmentally friendly aspect.

In this research, the main objective is to develop the best formulation of lithium complex grease from WEO which is something new to be discovered as the base oil for this research. Grease formulated from FAO was used as reference to compare the grease derived from WEO. This new formulated grease derived from WEO was analysed for its exhibited properties through several tests such as consistency test, oil separation, FTIR characterization and TGA analysis.

2. Experimental work

2.1. Material
Waste automotive engine oil (WEO) and fresh automotive engine oil (FAO) were collected from automotive shop located in Kuantan. Lithium 12-hydroxystearate with industrial grade from China was purchased with Orioner Hightech Sdn. Bhd. Azelaic acid (solid form and 98% purity) was purchased from Revlogi Materials (RM).

2.2. Pre-treatment of waste engine oil (WEO)
The pre-treatment of WEO is needed to remove any contaminants such as suspended solid in the waste oil. WEO is filtered using vacuum filter pump. Glass microfiber filer paper with diameter of 47mm was used to remove the impurities contained in WEO. Next, in order to remove any volatile component and water content in the WEO by evaporation process, the oil was heated at temperature ranging 90 °C-120 °C.

2.3. Formulation of Lithium 12-HSA grease from FAO (FGi) and WEO (WGi)
To compare the properties of formulated grease by WEO, grease containing FAO was also formulated. The formulated grease consists of two type, with and without the addition of complexing agent which is azelaic acid.
Lithium 12-hydroxystearate, WEO and azelaic acid were weighed according ratio, i.e., 70%-82% (w/w). First, WEO was preheated at temperature ranged 90°C - 120°C. Azelaic acid is melted at a higher temperature until the acids were completely melted. Mixture of azelaic acid and WEO is homogenized for about 15 to 20 minutes. Lithium 12-hydroxystearate was added portion wise into the mixture. The mixture was homogenized for thickening process to disperse the thickener [3]. The remaining WEO was added to control the texture of the grease and the homogenization process was continued. After that, the grease was allowed to cool down. The steps were repeated to formulate with different ratio of base oil, thickener and azelaic acid. Then, the same ratios were repeated to formulate Li-complex from FAO 2.4.

Grease Analysis

The formulated grease was analysed through several tests to determine their properties. The tests that were carried out were consistency test, oil separation test, Fourier Transform Infrared Spectroscopy (FTIR) characterization and Thermogravimetric Analysis (TGA).

2.4.1. Consistency Test. Consistency test was carried out to decide where the consistency of the grease belong to according to NLGI (National Lubricating Grease Institute). The NLGI ranged from 000 to 6 (table 1). According to Japae et al. (2019) the test was in accordance of ISO 2137 which determined the consistency of the lubricating grease when only small samples of greases were available [3]. The NLGI obtained indicated the consistency level of the grease. Greases of higher NLGI grade are firm, tend to stay in place and are better option when leakage is a concern [2].

| NLGI Grade | Consistency               |
|------------|---------------------------|
| 000        | Very soft                 |
| 0          | Soft                      |
| 1          | Soft                      |
| 2          | Creamy texture (buttery)  |
| 3          | Semi-solid                |
| 4          | Stiff                     |
| 5          | Stiff                     |
| 6          | Hard solid                |

2.4.2. Oil separation test (ASTM D 1742). ASTM D-1742 is used to examine the separation of oil at room temperature condition of grease after storing it for some period of time. The grease started to lose its original consistency and ability when the oil begins to separate in grease. The test is done by storing the grease in a partially filled or normally filled container to test the tendency of the grease to separate oil. According to Suhaila et al. (2018), the sample is considered stable if the oil separation is less than 4%. The grease exhibits better stability when lesser oil separation is observed [12]. However, this method is not suitable for grease with NLGI No.1 grade [13].

2.4.3. Fourier transform infrared spectroscopy (FTIR) characterization. Fourier transform infrared spectroscopy is functioning to monitor the additive degradation, builds up of contaminant and the base stock ageing in oil lubricants. Besides, the ability of FTIR to detect a functional-groups by wide range correlated to the chemical changes in lubricants. This will allow the assessment of the overall quality of lubricants and decided whether a lubricant is required to be replaced or not [14]. The FTIR method is also carried out on lubricating grease and its extracted base oil or its separated thickener to detect the difference in the level of the components of the grease during chemical deterioration and base oil evaporation [15]. In short, FTIR was carried out to identify the functional group of the components, the presence of contamination and the oxidation stability of the grease samples. The grease samples formulated were characterized at the wavenumber of 500 – 4000 cm\(^{-1}\).
2.4.4. Thermogravimetric (TGA) analysis. The thermal stability and phase transitions of the lubricating grease have attracted several researchers’ attention [16]. It was therefore the analysis was carried out to determine the thermal behaviour of the grease samples formulated. TGA can provide qualitative information from a simple experiment. The test was conducted under an inert air flow via nitrogen gas or oxygen gas at a certain heating rate within a range of temperature [17].

3. Result and Discussion

3.1. Consistency of the formulated grease
The results of the grease samples from the testing were in accordance to the NLGI consistency grade. Table 2 shows the results obtained on the consistency number of each grease sample. Sample of greases that fell under the NLGI grades of 00 to 0 were FG6 and WG5. Their applications are suitable to be used in a centralized lubrication system and enclosed gears. These greases were categorized into the fluid to semi-fluid range. Sample greases of FG5, WG3, WG4 and WG6 were recorded from NLGI of 1 to 3. Greases for bearings are typically found in NLGI grade 1, 2 and 3 [18]. NLGI grade of 4 to 5 were FG1, FG2, FG3, FG4, WG1 and WG2. The most common of NLGI grade used in the automotive bearings would be NLGI grade 2 [19]. Grease of NLGI 2 have a superior properties balance making it easy to pump through the dispensing systems [20]. NLGI grade 4 is suitable to be used for a device that move at high speed which is like greater than 15,000 rotations per minute. It is because these devices cause more friction and produce higher heat, hence, a stiffer and channelling grease is a better choice [21].

Table 2. Properties of each grease sample.

| Sample Grease | NLGI  | Description              | FAO | WEO | Li-12 HSA | Azelaic Acid | Oil Separation |
|---------------|-------|--------------------------|-----|-----|-----------|--------------|----------------|
| FG1           | 4-5   | Hard - Very hard         | 70  | -   | 27        | 3            | -              |
| FG2           | 3-4   | Medium Hard - Hard       | 80  | -   | 18        | 2            | -              |
| FG3           | 4     | Hard                     | 82  | -   | 16.2      | 1.8          | -              |
| FG4           | 5     | Very Hard                | 70  | -   | 30        | -            | -              |
| FG5           | 1-2   | Soft – Medium            | 80  | -   | 20        | -            | -              |
| FG6           | 00    | Semifluid                | 82  | -   | 18        | -            | -              |
| WG1           | 4-5   | Hard – Very Hard         | -   | 70  | 27        | 3            | -              |
| WG2           | 4     | Hard                     | -   | 80  | 18        | 2            | -              |
| WG3           | 3     | Medium-Hard              | -   | 82  | 16.2      | 1.8          | -              |
| WG4           | 3     | Medium-Hard              | -   | 70  | 30        | -            | -              |
| WG5           | 0-00  | Very fluid – Semifluid   | -   | 80  | 20        | -            | -              |
| WG6           | 2-3   | Medium – Medium Hard     | -   | 82  | 18        | -            | -              |
3.2. Oil separation
Oil separation occurs when the grease is being kept for a longer period of time. All the grease samples were observed. Table 1 showed the results obtained for the oil separation of grease after being kept in a container for one month. Based on the observation, no oil separation happened for all the grease formulations. Lithium 12-hydroxystearate and azelaic acid will acts as thickener to house the oil in the thickener system. In short, the complexing process makes strong adsorption interactions is developed between the soap, lithium 12-hydroxystearate and complexing agent, azelaic acid during the preparation of grease [22]. According to Suhaila et al. (2018), the sample is acceptable if the oil separation is less than 4% [12].

3.3. FTIR characterization
Table 3 shows the characteristic peaks and corresponding molecular groups and bonds of the grease sample in the spectral range of 4000 to 500 cm$^{-1}$. Figure 1 and figure 2 show the FTIR peaks of grease samples from FAO and WEO respectively whereas figure 3 presented the peaks of all grease formulations. The two figures showed that very strong absorbance usually in the range of 2849 – 2954 cm$^{-1}$. The range of these are the characteristics of the asymmetrical and symmetrical vibrations of hydrophobic groups, i.e., methyl, CH$_3$ and methylene groups, CH$_2$. These spectrums originated from lithium 12-hydroxystearate molecules [23]. According to Abdul and Bilal (2012), their research revealed the spectra of azelaic acid was at 1695 cm$^{-1}$ [24]. The main peak observed was the dicarboxylic acid peak at wavenumber range of 1709 – 1711 cm$^{-1}$. The absorbance of peak at 1709 – 1711 cm$^{-1}$ is weak. In FTIR analysis, it is essential to observe the peak at 1710 cm$^{-1}$ as it indicated the oxidation of hydrocarbon with the formation of carboxylic acid. The higher the intensity of the peak, the less oxidation stability of the lubricant. However, the intensity of this peak is weak hence it indicated better oxidation stability of the formulated grease [25]. The mode of -COO- carbonyl stretching modes is seen at 1559, 1578 and 1579 cm$^{-1}$. The -COO- carbonyl groups were found in all formulation as lithium 12-hydroxystearate were used as thickener. Base oil components were also found at the wavenumber 1376 cm$^{-1}$. The absorbance of 720 – 721 cm$^{-1}$ might be related to the 30 % of the oil bound by the molecular attraction forces between the oil and thickener components [26].

Table 3. Characteristic peaks and corresponding molecular groups and bonds of the grease.

| Characteristic peak/cm$^{-1}$ | Functional group assignment | Band | Source |
|-------------------------------|-----------------------------|------|--------|
| 2849                          | Symmetrical stretching vibration of CH$_2$ group | C-H | Azelaic acid |
| 2954                          | Vibration of CH$_3$ group   | C-H |        |
| 1709 - 1711                   | Dicarboxylic acid           | COOH| Thickener |
| 1578                          | Asymmetric stretching vibration of COO group | COO | Thickener |
| 1579                          | Asymmetric stretching vibration of COO group | COO | Thickener |
| 1559                          | Symmetrical stretching vibration of COO group | COO | Thickener |
| 1452                          | Asymmetrical deformation vibration of CH$_3$ group | C-H | Base oil |
| 1376                          | Bending vibrations of CH$_2$ groups | C-H | Base oil |
| 720 - 721                     | CH$_2$ rocking vibration    | C-H |        |
3.4. TGA analysis

Based on figure 4, the figure depicted the sample grease have high thermal stability until about 250 °C where the start of decreasing weight of the sample grease remarkably. In the temperature range 190 – 540 °C, the TG curve displayed two weight loss steps. At the first onset temperature of 250.09 °C it displayed that the grease undergoes thermal degradation at that temperature with a total mass loss of
86.06 %. °C. In the present study, the first one which range 190 – 360 °C was most probably happens due to the elimination of low molecular weight products. According to Tripathi and Vinu [17], temperature ranged 150 – 350 °C the evaporation hydrocarbons presented in the low end of molecular weight distribution, and degradation of base oil components occur. Based on Santos, Santos [27], this step is the most crucial as it determines the thermal stability of the lubricant. Next, the second weight loss step which ranged 448 – 540 °C was related to the decomposition of higher molecular weight compounds. According to El-Adly and Turky [16], the commercial of Li-complex grease undergone thermal degradation and decomposition during the temperature range 250 – 500 °C. When comparing the result with the literature, the result of thermal degradation for grease sample, WG3 is the same. This meant that the sample grease was intrinsically stable at higher temperature

Figure 4. TGA analysis of WG3.

4. Conclusion
In conclusion, the idea of utilizing treated waste engine automotive oil is for the formulation of lithium 12-hydroxystearate complex grease is viable. The best formulation of lithium 12-hydroxystearate from waste engine automotive oil grease is WG3. The consistency number obtained is 3, which falls under common grease grade. The FTIR results obtained of utilizing WEO do not show significant difference with the one using FAO except for the presence of dicarboxylic peak which indicated the oxidation stability of the grease. The grease samples formulated can be concluded good as there was no sign of oil separation happened. The formulated grease is also thermally stable and has high heat resistance as the degradation happens at temperature at 250 °C. Thus, waste automotive engine oil can be a promising base oil in the grease production industry. It can be an alternative source of base oil for grease production to replace the mineral oil derived from crude oil.

Further experimental work related to tribology especially on the viscosity is required to compare with the commercial grease available in the market. The addition of solid additives can be suggested to improve the tribology of the grease. Lastly, more parameters can be study such as temperature and the speed of homogenizer during the process of grease formulation.

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