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Formulation and evaluation of bio-grease from the blend of chemically modified rice bran oil and Calophyllum inophyllum oil

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Abstract

Vegetable oils are a highly promising alternative to produce various lubricants, owing to their biodegradability and eco-friendliness. In comparison to mineral oil, these oils possess a higher flash point and viscosity index, along with superior lubricating properties. Additionally, most of the vegetable oils are easily accessible in local markets in India. However, their industrial application is limited by poor thermal and oxidative stability, which can be addressed through chemical modification, the addition of appropriate additives, or by blending these oils. Greases, characterized by their semi-solid consistency, are widely used lubricants. Most of the grease production is based on mineral oils as base oil and lithium soap as a thickener. These materials are not only non-biodegradable but also scarce and have health implications. Consequently, biodegradable grease represents an eco-friendly and healthy alternative. Grease made using vegetable oils with the required properties has the potential to bring about revolutionary changes. The present work focuses on the feasibility of using chemically modified blended rice bran oil (RBO) and *Calophyllum inophyllum* oil (CIO) as a bio-lubricant. The oils undergo a two-step modification process, involving a transesterification reaction followed by epoxidation. Significant improvements have been observed in the chemical properties (acid, peroxide, and iodine values) of transesterified epoxidized rice bran oil *Calophyllum inophyllum* oil mixture–50:50 (ETRCIO) when compared with Unmodified Rice bran oil *Calophyllum inophyllum* oil mixture–50:50 (RCIO). The acid value, peroxide value, and iodine value improved by 91.66%, 87.08%, and 15.78% respectively. The rheological, tribological, and chemical properties of the blended samples have been evaluated and compared to pure oils using American Society for Testing and Materials (ASTM) and Indian Standards (IS). Additionally, ETRCIO was used to develop a bio-grease, and its tribological properties were extensively analyzed. The mean coefficient of friction (COF) and wear scar diameter (WSD) of the ETRCIO grease sample improved by 10.20% and 29.32% respectively when compared with that of commercially available grease. These findings indicate that the ETRCIO bio-grease exhibits superior tribological properties in comparison to commercially available grease.

Research highlights

• The study explores the potential of vegetable oils as a biodegradable and environmentally friendly alternative for producing lubricants, specifically focusing on rice bran oil and *Calophyllum inophyllum* oil.

• The oils undergo a two-step chemical modification process (transesterification followed by epoxidation) to improve their thermal and oxidative stability, making them suitable for industrial use.

• The chemically modified and blended oils showed significantly improved chemical properties.

• The rheological, tribological, and chemical properties of the blended samples were evaluated according to ASTM, and IS standards and compared with those of pure oils.

• A bio-grease was formulated using these chemically modified oils, exhibiting better tribological properties than commercially available grease, indicating its potential as an eco-friendly and health-conscious alternative to traditional mineral oil-based greases.

Keywords: Bio-grease, Transesterification, Epoxidation

Introduction

Vegetable oils are oils derived from natural sources and can be used as a substitute for petrol lubricants due to their biodegradability, non-toxicity, and ease of disposal. Additionally, they are readily available and a sustainable resource. Researchers have conducted numerous studies to investigate the lubricating properties of vegetable oils. While most vegetable oils possess good tribological properties, they often exhibit poor oxidative and thermal stability. However, this can be improved through the addition of appropriate additives or chemical modification. Gulzar et al. [1] conducted a study to examine the impact of CuO and MoS_2 nanoparticles on enhancing the antiwear and extreme pressure properties of chemically modified palm oil. Their findings indicated that MoS_2 nanoparticles exhibited superior properties compared to CuO and had a uniform dispersion. In Alves et al. [2], it was observed that ZnO and CuO nanoparticles did not exhibit favorable anti-wearability when combined with epoxidized vegetable oils such as sunflower and soybean oils. However, ZnO alone displayed excellent performance in reducing friction and wear when combined with mineral oil. Khan et al. [3] investigated the coefficient of friction of virgin coconut oil and found that the addition of Cu and Ag nanoparticles resulted in a decrease in the coefficient of friction, as well as an increase in viscosity and a reduction in cutting force and cutting temperature. In a study by Adhvaryu et al. [4], tribological studies were carried out on vegetable oils that had undergone thermal and chemical modifications to determine their suitability as eco-friendly lubricants. The study revealed that amine phosphorus-containing additives underwent substantial chemical changes in the presence of fatty acids, which improved the anti-wear properties of vegetable oils. In another research by Jayadas et al. [5], it was observed that coconut oil exhibited less weight gain in an oxidative environment compared to other vegetable oils and thus it can be used as a viable base stock for bio-lubricant formulation.

Rice bran oil (RBO) is an edible oil derived from rice husk, which is produced from the hull and bran layers during the milling process of the rice kernel. The oil content of RBO ranges from 10 to 23%, depending on the genotype of the rice [6]. RBO exhibits favorable physicochemical and thermal properties compared to other vegetable oils due to its excellent tribological and thermal properties. While RBO demonstrates superior frictional properties compared to commercially available mineral oil SAE20W40, it has a larger wear scar diameter that can be improved with appropriate anti-wear additives [7, 8]. Furthermore, epoxidized and ring-opened products of RBO have shown better tribological properties than pure RBO. It has been established that the lubricating performance of ring-opened RBO using benzoic acid is superior to that of butanoic acid and lauric acid. The flash temperature parameter (FTP) value of ring-opened RBO using benzoic acid is 33% higher than that of pure RBO. Additionally, energy consumption in the four-ball tester is lower for chemically modified RBO than for pure RBO [9]. The oxidative stability of the ring-opened and epoxidized RBO has also improved significantly [10]. The addition of 0.03 wt.% SiC nanoparticles have resulted in an improvement in the wear scar diameter (WSD) of both RBO and modified RBO, owing to the rolling mechanism. This finding suggests that SiC nanoparticles are a highly effective anti-wear additive [11]. Thus, from the above literature, it is clear that RBO is an excellent base oil for lubricant formulation.

The oil derived from the seeds of the *Calophyllum inophyllum* tree, also known as the 'Beauty leaf' tree, is called *Calophyllum inophyllum* oil (CIO). This tree, which is predominantly found in southern and southeast Asia, is a medium to large-sized evergreen tree. The seeds of this tree contain a remarkably high oil content, comprising 75% of the seed kernels. Within this oil content, 71% are unsaturated fatty acids [12, 13]. CIO is not suitable for consumption and is instead used as biomass for oil extraction. The oil extracted from the seeds of the *Calophyllum inophyllum* tree has a high heating value of 41.90 MJ/kg, making it a promising option for bio-grease formulation [14]. Additionally, *Calophyllum inophyllum* oil has a higher viscosity compared to other non-edible plant-based oils, which is a desirable characteristic for bio-lubricants. The oil also contains a significant percentage of unsaturated fatty acids (71.29% of the total fatty acid), suggesting its potential for conversion into biodiesel. The remaining 28.71% is composed of saturated fatty acids [15]. There are various methods available for extracting CIO from the seed kernels, including high-temperature and pressure oil extraction techniques, which yield large quantities of oil. However, due to its high free fatty acid content, CIO has significantly higher acid values. According to a study, it is not feasible to utilize traditional base-catalyzed trans-esterification for chemical modification [16].

Many researchers over the years have tried to formulate bio-lubricants using vegetable oils as base stock. Recently, the focus is mainly on producing high-quality greases with biodegradable products. In the work of Garcia et al. [17] greases were formulated using castor oil, high oleic sunflower oil, and ricinoleic acid-derived estolide as base stock and lithium soap, kraft cellulose pulp and chitosan as thickeners. Lithium estolide produced a thicker grease and showed good mechanical stability but chitosan and cellulose-based greases were too soft with poor mechanical stability and phase separation was observed during mechanical stability tests. The addition of ethyl cellulose improved stability in cellulose-based grease. In Sanchez et al. [18] bio-grease was formulated based on castor oil and cellulose-derived thickener. Ethyl cellulose, methyl cellulose, and cellulose acetate were used as gelling agents. It was observed that the thermal stability has improved and the temperature at which the maximum rate of decomposition occurs was higher for oleogels and there was poor mechanical stability and a higher leakage tendency. Nagendramma et al. [19] used unmodified Jatropha oil and lithium soap as a thickener to prepare the grease sample. Lithium stearate and lithium oleate soaps were used and ZDDP was used as a performance improvement additive. It was observed that the weld load was better and the wear scar diameter was smaller than commercial greases and the grease was non-toxic in nature.

Kumar et al. [20] formulated bio-greases based on canola oil and mineral oils. Several thickeners were used and 17 different greases were made. The test results showed that compatibility varies significantly from sample to sample, and it is not always necessary to obtain intermediate properties by blending. In another study by Cortes et al. [21] they tried to improve mechanical stability by epoxidizing the cellulose material, keeping castor oil as the base oil. The mechanical stability of grease was improved, and wear scar diameter was reduced slightly. However, an increase in the coefficient of friction was observed. In another study, Panchal et al. [22] tried formulating a bio-grease from transesterified Karanja oil as a base oil and lithium soap as a thickener. Karanja oil methyl ester was transesterified with hexanol, octanol, and neopentyl glycol i.e. three different samples were made. The drop point of samples was around 148 °C which is lower than normal lithium greases. Neopentyl glycol yielded the lowest grease consistency. On the other hand, it had the least mechanical stability. Hexyl ester showed the best mechanical stability, and it was the only sample that came close to conventional grease. The coefficient of friction was comparable with commercial grease tested for all three but wear scar diameter was higher for all. The least wear scar among the three samples was obtained for Neopentyl glycol-based grease. All bio-greases showed excellent performance in weld load compared to mineral oil-based grease. So, Karanja oil-derived lubricant has its strengths and weaknesses.

In the chemical modification of base oils, Transesterification is a common method for altering vegetable oils. It involves the reaction of an ester's organic group with the organic group of an alcohol. This process can enhance the thermal and oxidative stability of vegetable oil-based lubricants, which are typically lower than that of conventional lubricants. Following transesterification, epoxidation can further improve the properties of the bio-lubricant [23]. Research works based on the blending of base oils for bio-lubricant formulation are very less. The blending of different oils can result in a bio-grease with improved properties. For instance, a study on the formulation of bio-greases derived from Mahua and Karanja oil found that bio-grease prepared from their methyl esters and tri-esters showed promising properties, such as a high drop point and good water washout resistance [24]. Similarly, blending chemically modified rice bran oil and *Calophyllum inophyllum* oil could result in a bio-grease with enhanced properties. Literature on rice bran oil and *Calophyllum inophyllum* oil as greases is rare even though it is known to be a good lubricant. It may lead to a bio-grease with excellent properties, and it may be able to minimize the need for additives or chemical modifications. This work aims to formulate and evaluate the tribological properties of bio-grease produced from chemically modified blends of Rice bran oil and *Calophyllum inophyllum* oil.

The chemical modification of oils, as employed in this study, serves to enhance the thermal and oxidative stability of the resulting lubricant. The innovative two-step process, involving transesterification followed by epoxidation, is applied separately to both oils, contributing to improved properties crucial for diverse applications. The selection of *Calophyllum inophyllum* oil, a non-edible feedstock with high heating value and viscosity, diversifies the raw materials used in bio-grease production. The chemical modifications not only alter physical properties such as viscosity but also introduce functional groups, like epoxide groups, influencing the lubricating characteristics of the final product. This approach allows for the development of a bio-grease with superior tribological properties, making it more suitable for demanding applications where stability, lubricity, and resistance to oxidation are paramount.

The innovation of this work lies in the formulation and evaluation of a bio-grease using a blend of chemically modified rice bran oil and *Calophyllum inophyllum* oil. The selection of *Calophyllum inophyllum* oil, a non-edible feedstock with high heating value and viscosity, and the two-step chemical modification process (transesterification followed by epoxidation) applied to both oils separately, are key innovative aspects. This process enhances the thermal and oxidative stability of the bio-lubricant, making it more suitable for various applications. The blending of these modified oils results in a bio-grease with improved properties.

The main objectives of this work are to explore the potential of chemically modified rice bran oil and *Calophyllum inophyllum* oil as a base oil for bio-grease formulation, to enhance the properties of the bio-lubricant through a two-step chemical modification process, and to evaluate the performance of the resulting bio-grease. The rationale behind this work is to contribute to the development of environmentally friendly lubricants. The use of vegetable oils as base oils for bio-lubricants is a growing area of research due to their biodegradability and renewability. However, their application is limited by their poor thermal and oxidative stability. This work addresses these limitations through chemical modification and blending of oils, paving the way for wider use of bio-greases in various applications.

Experimental

Materials

The refined rice bran oil was procured from Kalady Rice Millers Consortium Pvt Ltd. situated in Ernakulam, Kerala. The *Calophyllum inophyllum* oil was acquired from Krishna Ayurvedics located in Thiruvananthapuram, Kerala. All other chemical reagents utilized for the experimentation such as potassium hydroxide, methanol, concentrated sulphuric acid, glacial acetic acid, hydrogen peroxide, phenolphthalein, sodium thiosulphate, chloroform, potassium iodide, starch solution, Wijs solution, calcium hydroxide, 12-Hydroxy stearic acid, acetone and distilled water were purchased from Nice Chemicals Pvt Ltd. situated in Ernakulam, Kerala.

Chemical modification and blending of oil samples

Chemical modification of oil samples

Both the samples of oils were modified separately by a two-step chemical modification process, i.e., Transesterification reaction and then followed by epoxidation reaction. The first step is the transesterification reaction which yields the methyl ester of the oil. The second step is to carry out the epoxidation reaction using this methyl ester of the oil to obtain the final product. Firstly, 200 g of oil (RBO) was heated to 70 °C in a hot air oven for 20 min. This is done to remove moisture content in the oil. The heated oil is left to cool gradually to room temperature. After it is completely cooled, 3 g KOH and 55 ml methanol are added and kept for stirring in a water bath at 60 °C for 1 h (base-catalyzed transesterification). After this, the mixture was kept in a separating funnel for 6 h. Separation occurs slowly and two layers are formed. The upper layer is the methyl ester of the oil, and the lower layer is the triglycerides formed after the reaction. The methyl ester is taken, and water washed three times using warm distilled water (60 °C) to remove any impurities that are present. Following this, it was heated in a vacuum to completely remove the moisture content to obtain the final sample of methyl ester of RBO.

The process of transesterification for CIO differs from that of RBO as it is conducted in two distinct steps. This two-step approach proves to be particularly advantageous for oils with a high FFA content, such as *Calophyllum inophyllum* oil. In the initial step, the transesterification process works to decrease the acid value of the oil, which is crucial for oils with elevated FFA levels. Subsequently, the second step involves the process of epoxidation. *Calophyllum inophyllum* oil, a non-edible oil, boasts an exceedingly high FFA content of approximately 30%. Consequently, the two-step transesterification process plays a pivotal role in reducing the acid value of this specific oil [25]. Conversely, rice bran oil, which possesses a lower FFA content compared to *Calophyllum inophyllum* oil, may not necessitate a two-step transesterification process. As such, a single-stage transesterification process proves to be sufficient for the transesterification of rice bran oil [26]. In this study, the first step of transesterification for CIO is acid-catalyzed transesterification where the stirring takes place in the presence of 64 ml methanol and 2 ml concentrated sulphuric acid initially, with glycerol being separated and then the base-catalyzed transesterification (second step of transesterification) is done, which is the same as that of transesterification of RBO and the remaining glycerol content is separated fully. The final methyl ester of CIO is obtained after water washing and vacuum heating similarly to in the case of RBO transesterification reaction. 5 ml of glacial acetic acid and 2 ml of concentrated sulphuric acid were added to 100 gm of the oil methyl ester. To this add 50 ml of hydrogen peroxide (15 ml in case of CIO) drop by drop. This mixture was vacuum sealed in a conical flask and was kept for magnetic stirring along with heating in a water bath at 65 °C for 4.5 h. After this reaction, the mixture was kept in a separating funnel for 6 h. Two layers will be formed. The lower layer, which is the water formed during the reaction, is released to obtain the epoxidized oil. This is then water washed 5 times using warm distilled water (60 °C) and then vacuum heated to obtain the final sample of transesterified epoxidized rice bran oil (ETRBO) and transesterified epoxidized *Calophyllum inophyllum* Oil (ETCIO).

Blending of oil samples

The overall qualities of vegetable oils can be greatly improved by blending them together. By combining different oils, a balanced composition of fatty acids can be achieved, resulting in enhanced functional and nutritional value [27]. Blending is especially important for oils that are rich in monounsaturated and polyunsaturated fatty acids, as it increases their oxidative stability, which is crucial because these oils are prone to oxidation and less stable [28]. Additionally, blending can improve the rheological properties of oils, as demonstrated in tribological tests [29]. Therefore, blending vegetable oils can create a superior product with improved properties compared to using individual oils. In this study, a magnetic stirrer was used to blend the oil samples (RBO and CIO, ETRBO and ETCIO). The stirring process was carried out at room temperature for 20 min, with a stirring speed of 500 rpm. The blend composition that yielded the best chemical properties was chosen as the optimum blend.

Physicochemical properties

In this study, we evaluated the physicochemical properties of the oil samples using established techniques outlined in IS 548 (part 1) 1964. Specifically, we measured the acid value, peroxide value, and iodine value of the samples. Additionally, we determined the density of the oil samples as per ASTM standards.

Acid test

The acid test involved utilizing a 0.1N solution of potassium hydroxide (KOH) as the titrant. To prepare the solution, 1.4 g of KOH pellets were dissolved in deionized water in a 250-ml standard flask to make up the mark. To perform the test, 2.5 to 5 g of the oil sample was taken in a conical flask and mixed with 30 ml of methanol and 3 drops of Phenolphthalein indicator. The solution was titrated against the standard KOH solution, and the burette reading was recorded when the color changed to pink. The acid value was determined using the following formula:

$$\text{Acid value (AV)} = (56.1 \times \text{V} \times \text{N})/\text{W} \quad (1)$$

where V represents the volume of the titrant used (final burette reading-initial burette reading), N represents the normality of the standard solution (0.1 N), and W represents the mass of the oil sample.

Peroxide test

A standard titration solution was prepared by taking 6.2 g of Sodium thiosulphate in a 250-ml standard flask and diluting it with deionized water to make it up to the mark. To prepare a 0.01-N final titrant, 25 ml of this standard sodium thiosulphate solution was transferred to another flask. The analysis of the oil sample was carried out by taking 2.5 to 5 g of the sample in a conical flask and adding 18 ml glacial acetic acid, 12 ml chloroform, and 0.5 ml saturated potassium iodide solution. The mixture was stirred occasionally for 1 min. Then, 30 ml of deionized water and a few drops of starch solution were added. The solution was titrated against the prepared 0.01 N standard sodium thiosulphate solution, and the burette reading was noted when the color of the titrate changed from black to colorless. The peroxide value was calculated using the following equation.

$$\text{Peroxide value (PV)} = [(\text{B} - \text{S}) \times \text{N} \times 1000]/\text{W} \quad (2)$$

where S = volume of the titrant used (final burette reading-initial burette reading), B = blank value, N = normality of the standard solution (0.01N), W = mass of the oil sample.

Iodine test

To prepare the standard sodium thiosulphate solution (0.1 N), first take 0.29 to 0.31 g of the oil sample in a conical flask. Then, add 25 ml chloroform and Wijs solution, followed by placing the mixture in a dark place for 30 min. Next, add 50 ml of deionized water and 0.5 ml of saturated potassium iodide solution. The solution will turn red in color. Titrate this solution against the prepared 0.1 N standard sodium thiosulphate solution. When the red color of the solution starts to diminish, add a few drops of starch solution. Note the burette reading when the color of the titrate changes from black to colorless. Finally, calculate the iodine value using the appropriate equation.

$$\text{Iodine value (IV)} = [12.69 \times \text{N} \times (\text{B} - \text{S})]/\text{W} \tag{3}$$

where S = volume of the titrant used (final burette reading—initial burette reading), B = blank value, N = normality of the standard solution (0.1 N), W = mass of the oil sample.

Density

The density of vegetable oils is a crucial factor in the formulation of bio-lubricants. It directly influences the performance and efficiency of the lubricant. Higher-density oils tend to have better lubricating properties, making them ideal for use in high-performance applications [23]. Moreover, the density of the oil can affect its flow characteristics, which is an important consideration in the design of lubrication systems [30]. Therefore, understanding the density of vegetable oils and manipulating them through blending or other means can lead to the production of more effective and environmentally friendly bio-lubricants. In this work, a known volume of the oil sample is taken in a beaker and its mass is measured at room temperature (ASTM D369). Density is calculated using the equation,

$$\text{Density} = \text{Mass of oil sample/volume of oil sample} \tag{4}$$

Rheological properties

Viscosity

The measurement of the samples' kinematic viscosity was conducted in accordance with ASTM D445 Standards, utilizing a Cannon–Fenske viscometer. Prior to the measurement procedure, the viscometer was thoroughly cleaned with acetone. The oil sample was then introduced into the viscometer, securely plugged with a cork, and maintained at the required temperature within a water bath for a period of 10 min. Following this, the cork was removed and the duration of time taken for the oil to surpass the designated mark was carefully measured using a stopwatch. The kinematic viscosity was subsequently determined by means of the following equation:

$$\text{Kinematic viscosity (incst)} = \text{Time taken for the oil sample to rise (in seconds)} \times 0.10235 \tag{5}$$

Hot oil oxidation test

A hot oil oxidation test (HOOT) was undertaken to examine the oil samples' oxidation stability, following the American Oil Chemists Society AOCS Cd-12–57 standards. The oil was maintained at a temperature of 100 °C for a duration of 120 h. The viscosity of the sample was recorded at 40 °C at intervals of 24, 48, 72, 96, and 120 h, with the percentage change in viscosity being calculated.

Grease formulation

The bio grease was formulated using blends of pure oils and chemically modified oils. The concentration of thickener used was 9.6%. Initially, 9.67 g of calcium hydroxide was taken in a beaker, and then to it add 10 g of distilled water, followed by 4.83 g of 12-Hydroxy stearic acid, and finally, 135.5 g of oil was added to the beaker. The mixture obtained was then stirred at 90 °C for 1 h and 45 min using a magnetic stirrer. After this, the mixture was transferred into a double-walled induction heated vessel and heated at 150 °C for another 15 min. The finally obtained mixture was kept undisturbed for cooling and solidification.

FTIR analysis

Fourier transform infrared spectroscopy (FTIR) is a technique employed to examine the functional groups that are present in oil and grease. This technique provides specific information on the chemical bonding and molecular structure of the grease and oil, thereby providing insight into the organic and inorganic materials involved in the substance. The FTIR principle is based on the presence of molecules in a lubricant that absorbs infrared light to varying degrees due to their chemical structure. In this study, we utilized an ATR-FTIR spectrophotometer (JASCO FTIR-4700) with a resolution of 4 cm and a wave number range of 390–4450 cm^{-1} to investigate the functional groups present in oil and grease.

Tribological properties

This study has conducted an assessment of the coefficient of friction (COF) and wear scar diameter (WSD) of the samples. The evaluation was carried out using a standard four-ball tribo-tester, in accordance with ASTM D 4172 (for oil) and ASTM D 2266 (for grease). The tribo-tester consists of three chrome steel balls that are confined in a ball port, with another rotating chrome steel ball pressed against them. The balls, each made of AISI 52100 steel and having a diameter of 12.7 mm, were cleansed with acetone before being placed in the ball port and filled with the sample. A collet was utilized to attach the fourth ball to the rotating shaft. The test conditions were set to a load of 392 N, speed of 1200 RPM, temperature of 75 °C, and duration of 3600 s. The wear scar diameter of the lower balls was measured using an optical microscope that was attached to the tribo-tester. The average wear scar diameter of the three balls was taken as a measure of wear obtained during the test run. The average coefficient of friction of the test run was calculated from the average frictional torque on the handle, which was dynamically recorded.

Cone penetration

The lubricating grease samples were evaluated for consistency using the ASTM D 1403 method. The results were expressed in a range of NLGI grades, starting from 000 for semi-fluid greases and going up to 6 for solid block greases.

Results and discussion

Physicochemical and tribological properties of pure base oils, chemically modified base oils, and their blends

As a preliminary study, the physicochemical and tribological properties of pure RBO and CIO were evaluated as shown in Table 1. To improve the oxidative stability and shelf life, the blending of these oils was performed at three different ratios. The chemical and tribological properties of CIO-RBO blends at different ratios were evaluated and shown in Table 2. 50 CIO: 50 RBO (RCIO) sample was chosen for further studies. This was done because it had the best tribological results when compared with the other two samples and had comparable chemical properties. To improve the oxidation and thermal stability, the oils were chemically modified by the 1st stage of transesterification followed by the epoxidation method (ETRBO, ETCIO) separately and then blended in a 50:50 ratio (ETRCIO). Various properties of these samples are tabulated in Table 3.

Rheological properties of pure base oils, chemically modified base oils, and their blends

The kinematic viscosity of the samples was measured using a Cannon–Fenske viscometer according to ASTM D445 standards as shown in Fig. 1. It was observed that CIO had a higher value of viscosity when compared with that of RBO at room temperature. The

Table 1 Properties of pure RBO and CIO

Oil sample	Density (g/cm^3)	Chemical properties			Tribological properties	
		A V (mgKOH/g)	P V (meq/Kg)	I V (gI/100 g)	Mean COF	Mean WSD (micrometer)
RBO	0.701	1.13	7.71	99	0.058	595
CIO	0.876	36.50	9.78	93	0.037	537

Table 2 Properties of blended RBO and CIO

(CIO:RBO)	AV	PV	IV	Mean COF	Mean WSD
30:70	11.42	8.51	97	0.043	577
50:50	18.17	8.65	95	0.036	561
70:30	25.48	9.22	93	0.039	565

Table 3 Properties of RCIO and ETRCIO

Oil sample	Density (g/cm^3)	Chemical properties			Tribological properties	
		A V (mgKOH/g)	P V (meq/Kg)	I V (gI/100 g)	Mean COF	Mean WSD (micrometer)
RCIO	0.789	18.17	8.65	95	0.046	555
ETRCIO	0.751	1.51	1.11	80	0.042	549

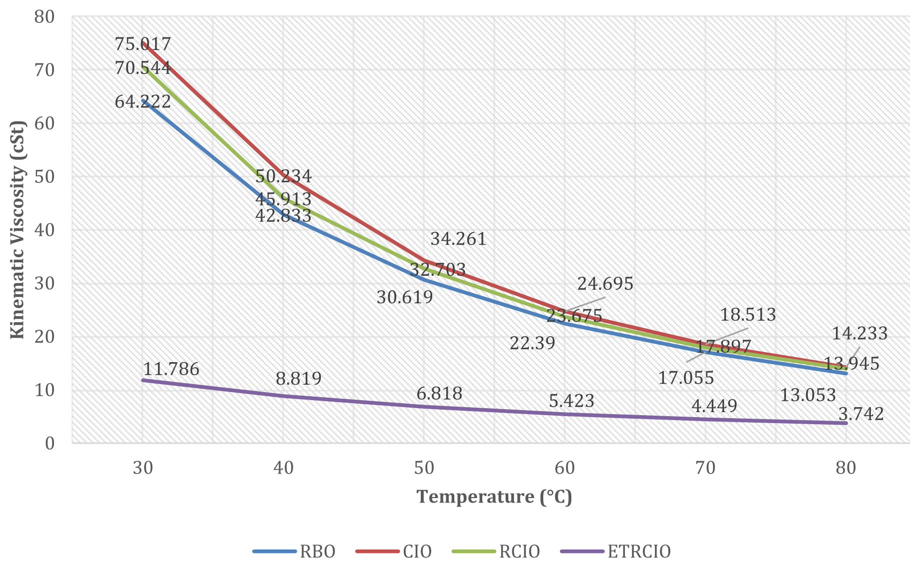

Fig. 1 Kinematic viscosity of RBO, CIO, RCIO, and ETRCIO

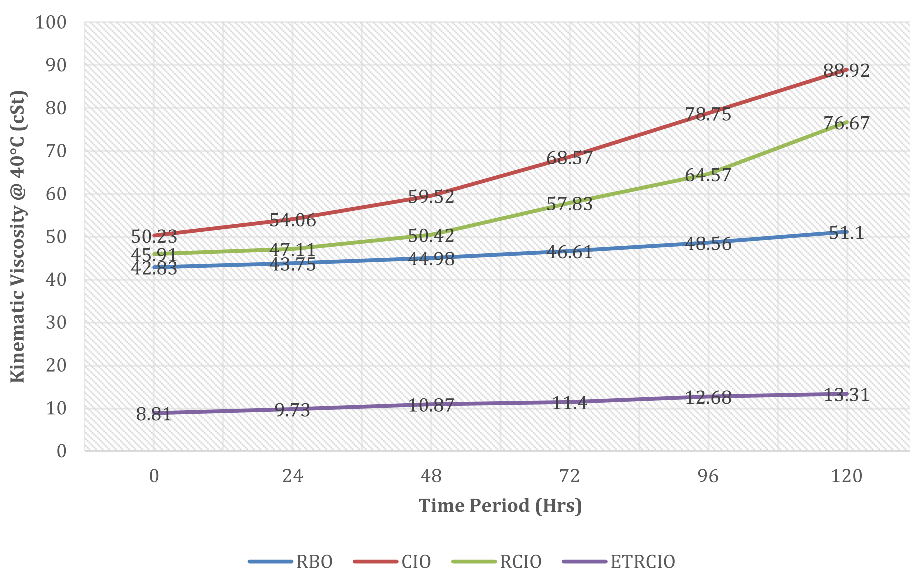

Fig. 2 HOOT results of RBO, CIO, RCIO, and ETRCIO

viscosities of ETRBO and ETCIO were also lower than those of the corresponding pure oils. This is because, upon chemical modification of these oils, the glycerol is removed and separated out which is the main viscous constituent in the base oil.

Oxidative stability of pure base oils, chemically modified base oils, and their blends

The hot oil oxidation test (HOOT) was used to analyze the oxidative stability of the samples, and the results are presented in Fig. 2. The HOOT method is commonly employed for measuring the oxidative stability of pure and chemically modified base oils. The test involves placing a sample of the oil in a sealed vessel with a copper coil and 5 g of water before pressurizing it to 620 kPa (roughly 90 psi) using pure oxygen. The vessel is then immersed in a hot oil bath that is heated to 150 °C while being rotated at 100 rpm. Under these conditions, the oil undergoes oxidation or hydrolysis, resulting in an increase in acidity or acid number. The HOOT results are highly informative about the oil's ability to resist oxidative degradation, which is a critical factor in lubrication and biofuel production applications. The HOOT results of ETRCIO show that there is a 51% viscosity change for the sample, while for RCIO it was 67% change in viscosity. For pure RBO, the viscosity increment was 19% and for CIO it was 51%. Thus, ETRCIO had very little change in viscosity during the test. This indicates that ETRCIO was more oxidatively stable than RCIO.

FTIR analysis

Figures 3 and 4 depict the FT-IR spectra of RCIO and ETRCIO correspondingly. The CH vibrations of the CH, CH2, and CH3 groups in the samples were observed around 3000 cm^{-1}, as is apparent in Figs. 3 and 4. A well-defined band, indicative of the presence of carbonyl groups, was observed at 1742 cm^{-1}. The existence of methylene groups (CH2) was confirmed by strong peaks around 2920 cm^{-1} and 2851 cm^{-1}. The asymmetric deformation vibrations of CH2 and CH3 groups were attributed to a peak at 1460 cm^{-1}, while the bending vibration of CH_3 groups was represented by a peak at 1372 cm^{-1}. Prior research has demonstrated that the robust peak around 721 cm^{-1} can be ascribed to the aromatic stretching vibration [40]. Upon comparing the FTIR spectra, it can be deduced that the RCIO system encompasses the functional groups of typical rice bran oil. It was also observed that the FTIR spectra of both RCIO and ETRCIO were

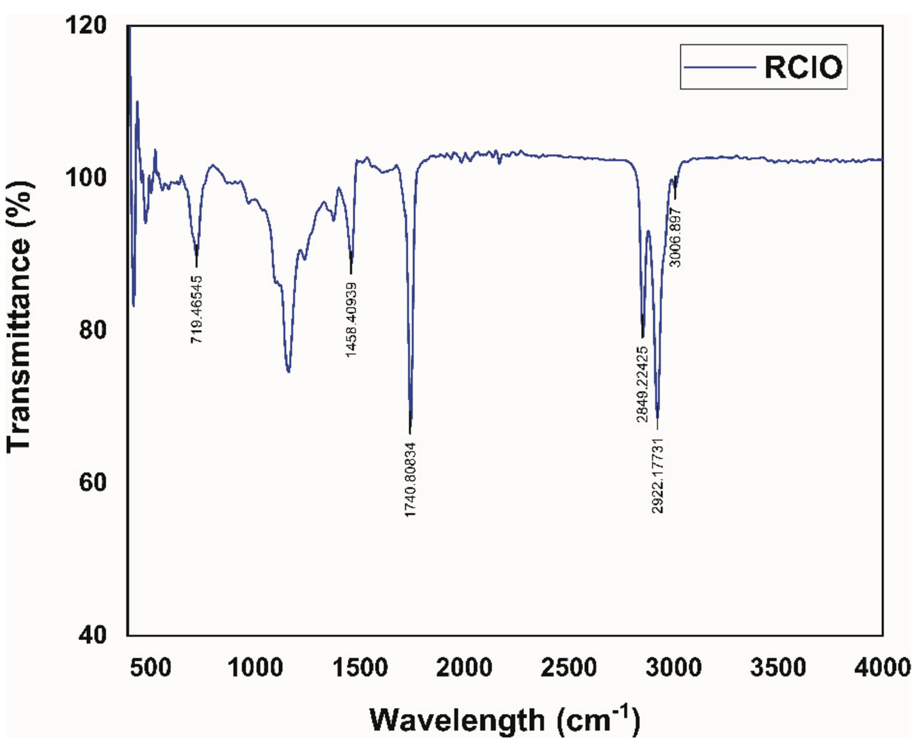

Fig. 3 FTIR of RCIO

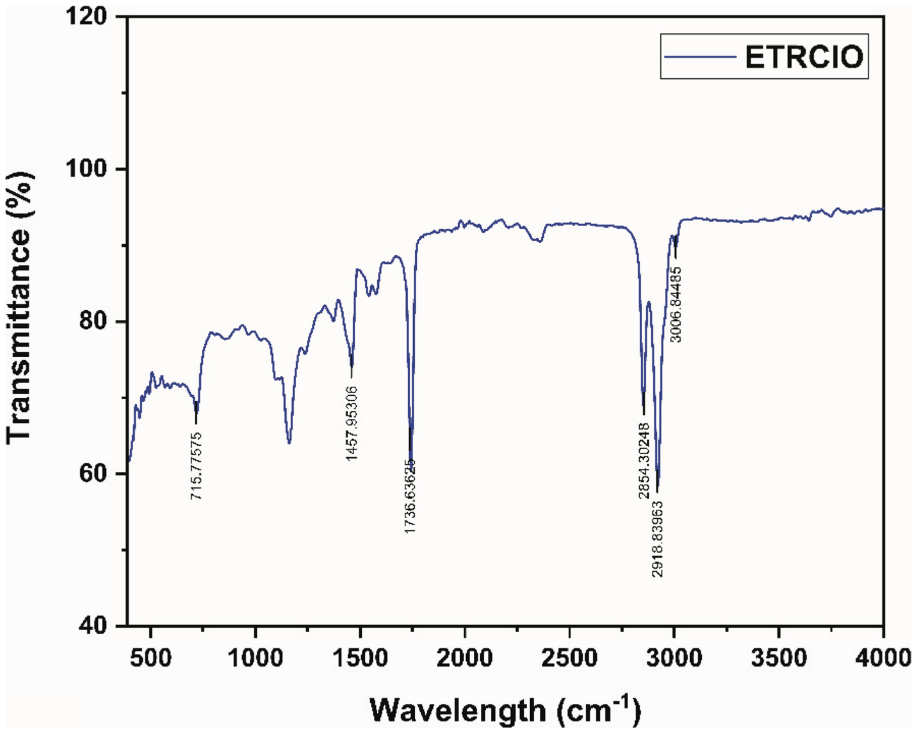

Fig. 4 FTIR of ETRCIO

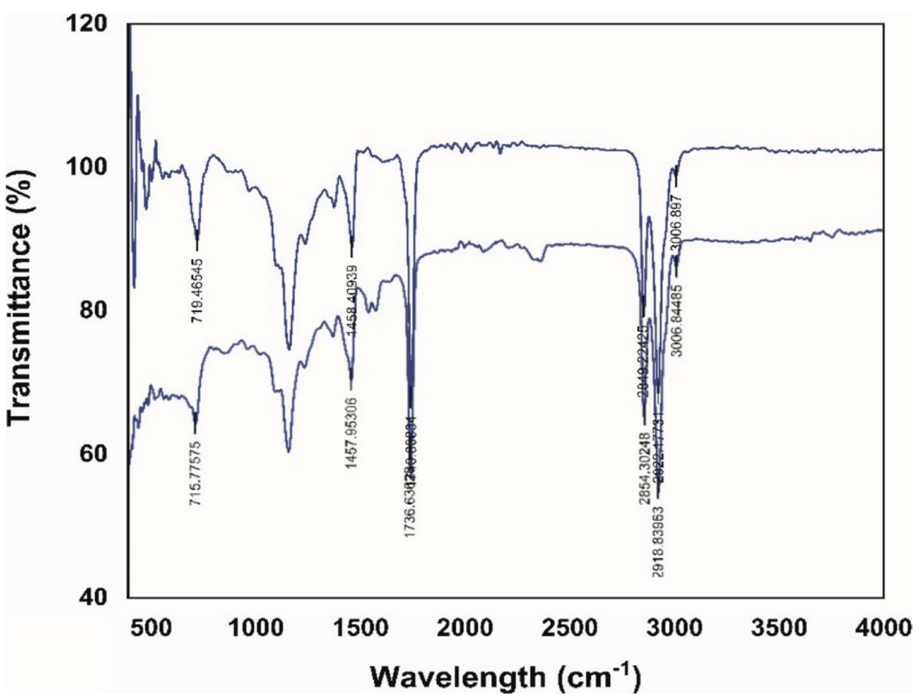

Fig. 5 Combined FTIR of RCIO and ETRCIO

Table 4 Tribological properties of bio-grease

Grease sample	Mean COF	Mean WSD (micrometer)
RCIO grease	0.093 ± 0.01	665.667 ± 5
ETRCIO grease	0.086 ± 0.01	630.540 ± 5
Commercial grease [23]	0.096 ± 0.01	892.132 ± 5

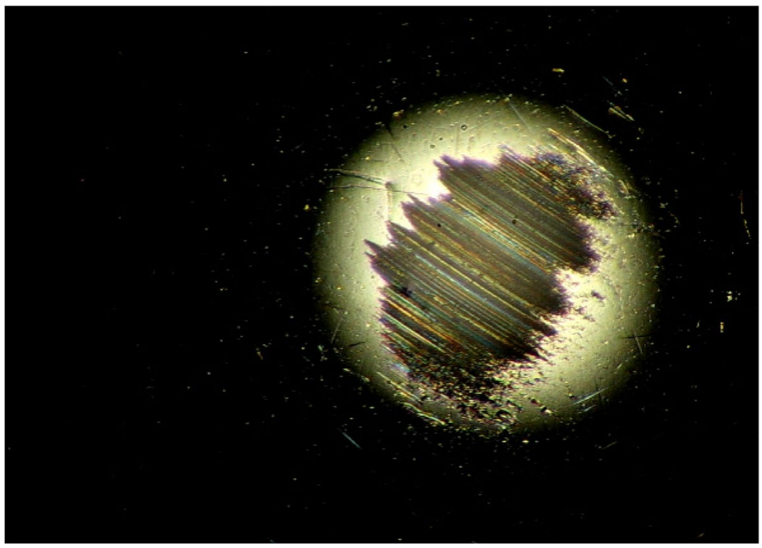

Fig. 6 Optical image of wear scar formed when RCIO grease was used

similar, except for the discrepancies in peak intensities. Figure 5 shows the combined FTIR images of both samples for better comparison and understanding.

Tribological property evaluation of grease

Bio-grease was formulated using RCIO and ETRCIO samples as base oils. The tribological properties were evaluated and the results were compared with that of commercial grease as shown in Table 4. From the tribological property results, it was clear that both RCIO and ETRCIO grease had better tribological properties than commercial grease. Among them, ETRCIO had good tribological properties due to the improvement in the oxidation stability of the chemically modified blended base oils that were used in the formulation.

The optical images of the wear scar formed on the chrome steel balls during the tribological tests conducted using a four-ball tester were analyzed deeply. It can be observed from Fig. 6 that the scar formed has deeper and broader grooves indicating more material wear. It is also visually observed from Fig. 7 that when ETRCIO grease is used narrow grooves are formed indicating that material wear is lesser.

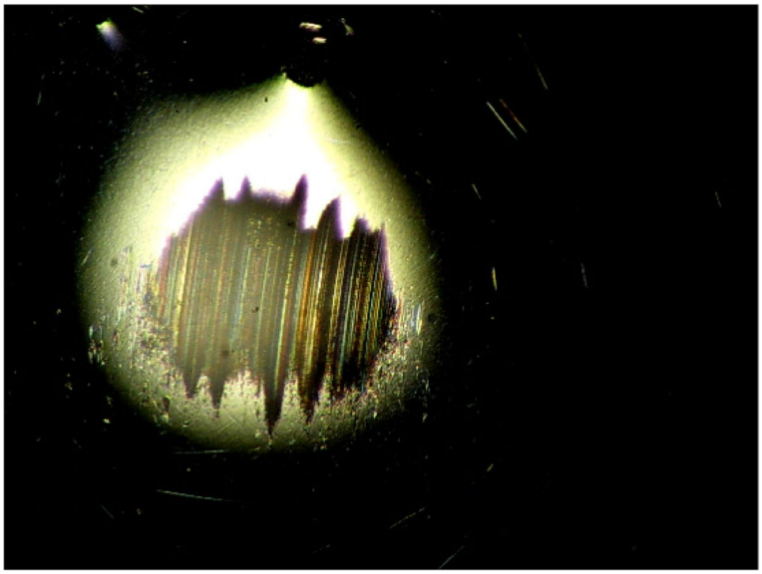

Fig. 7 Optical image of wear scar formed when ETRCIO grease was used

Cone penetration test

The NLGI grade of the formulated grease was determined by means of the cone penetration test. The NLGI value serves as an indicator of the relative hardness of the grease employed. Based on the results of this study, it was observed that ETRCIO grease conforms to NLGI grade 3. Typically, grease of this grade is suited for use as a lubricant in high-load and continuous applications. Therefore, ERTCIO grease may be applied to components such as rolling and sliding bearings.

Conclusions

The chemical properties of RBO and CIO base oils were evaluated as per standard protocols. It was noted that RBO had better chemical properties than CIO. An optimized blend of oil (50:50) was found by analyzing the chemical and tribological properties of three different blend compositions. RCIO was found to have properties intermediate to that of RBO and CIO. Oils were then chemically modified separately by making use of a 2-step chemical modification process to obtain ETRBO and ETCIO. The tribological, rheological, and chemical properties of both pure base oils and chemically modified oils were evaluated. Results indicate that ETRCIO had better chemical properties and oxidative stability. Bio-grease which was formulated using ETRCIO exhibited better tribological properties when compared with commercial grease. Hence, ETRCIO grease can be used as an alternative for applications falling under NLGI grade 3 like bearings. This formulated bio-grease can act as a cheaper replacement for the synthetic grease commercially available in the market. Since it is formulated from biodegradable base stocks, it can further be treated as an environmentally friendly grease.

Abbreviations

RBO Rice bran oil
CIO *Calophyllum inophyllum* oil
RCIO Rice bran oil, *Calophyllum inophyllum* oil blend (50:50)

ETRBO	Transesterified epoxidized rice bran oil
ETCIO	Transesterified Epoxidised *Calophyllum inophyllum* Oil
ETRCIO	Transesterified epoxidized rice bran oil, *Calophyllum inophyllum* oil blend
HOOT	Hot oil oxidation test
NLGI	National Lubricating Grease Institute
COF	Coefficient of friction
WSD	Wear scar diameter

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Authors' contributions
MAP contributed to conceptualization, investigation, methodology, writing—original draft, reviewing and editing. SR contributed to supervision, conceptualization, investigation, methodology, writing—original draft, reviewing, and editing. SPS contributed to conceptualization, investigation, methodology, writing—original draft, reviewing, and editing. DER contributed to conceptualization, methodology, writing—reviewing, and editing. PB contributed to conceptualization, methodology, writing—reviewing, and editing. All authors have read and approved the final manuscript.

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Declarations

Competing interests
The authors state that they have no competing interests and are believed to be solely accountable for the manuscript's text and work.

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