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Low-Temperature Chemical Modification Challenges of Tallow, Butter, Palm Oil, and Palm-Based Biolubricants as Alternative Substitutes for Fossil Oils

Nuhu Buhari Lenfa[1], A. Anterinwa[2], B. A. Aliyu[3], A. Yakubu[4]
[1,2,3]Modibbo Adama University, Yola, Nigeria
[4]Ibrahim Badamasi Babangida University, Lapai, Nigeria
buharilamido202020@gmail.com

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Abstract

Plant-derived oils such as Shea butter and palm kernel oil—abundant in African countries, particularly Nigeria—exhibit significant potential for use in lubrication, industrial processes, and transportation applications. Similarly, animal fats including butter and tallow may serve as viable alternatives for biolubricant production. This study investigates the low-temperature performance—specifically the cloud and pour points—of biolubricant oils synthesized from palm oil, Shea butter, butter, and tallow using various laboratory-based methods, including methanolic solvent extraction. The research addresses the environmental impact of conventional lubricants, which often contain harmful substances such as heavy metals and are frequently disposed of indiscriminately. Experimental results demonstrate that the pour point of palm oil modified with polymethacrylate (TPMA) improved to –9.5 °C, compared to –5 °C without additives. The Shea butter–polymethacrylate blend (SBPMA) exhibited a pour point of –3.5 °C, while modified palm oil (POPMA) improved from 7.2 °C to –5 °C. Butter oil derived from milk (BOPPG) showed a cloud point of –5 °C, whereas the Shea butter–polypropylene glycol blend (SBPPG) had a pour point of –6 °C. Notably, the tallow oil–polypropylene glycol blend (TOPPG) exhibited the lowest cloud point at –8 °C. These improvements are attributed to the inclusion of polymethacrylate and polypropylene glycols, which enhance the oils' low-temperature properties. The findings highlight the significance of chemical modification in overcoming the limitations of biolubricants under cold conditions, positioning them as more sustainable and environmentally friendly alternatives to fossil-based lubricants.

Keywords: Biolubricants; Low-Temperature Properties; Chemical Modification; Shea Butter; Palm Oil; Tallow

INTRODUCTION

With concern over global climate change and depleting petroleum reserves growing, it is therefore expedient for the search for environmentally sustainable alternatives of these fossil fuels. One area of interest which could serve to reduce both reliance on petroleum and anthropogenic impact on the environment, is the use of vegetable oil-based lubricants in place of the commonly used petroleum-based lubricants. These products, known as "biolubricants", carry several environmental, health, and performance benefits over current petroleum-based lubricants. The main purposes of biolubrication are to protect the surfaces from corrosion, reduce oxidation, reduce wear due to contact, prevent heat loss from the surfaces in contact, act as insulator in transformer applications, as sealing agents (against dust, dirt and water), biodegradable, and improve efficiency of machines (Amit and Amit, 2012; Jamat and Nadia, 2010; Tirth et al., 2017; Dabi et al., 2018)

Viscosity is the chief property of any biolubricant oil which is responsible for preventing friction between two surfaces in contact (Amit and Amit, 2012).

The application range of lubricants is determined by their physico-chemical properties; a basic requirement is to remain in a liquid form over a broad range of temperature. The temperature limits are determined by the pour point at low temperature and flash point at high temperature (Salimon et al., 2010). During the earlier stage of the development of biolubricants, the focus was on the products based on pure vegetable oils, which in contrast to mineral oils, are rapidly and completely biodegradable and have low ecotoxicity (Ceccutti and Aguis, 2008). Although the technical properties of plant oil-based fluids are quite comparable with mineral based fluids, they have drawbacks of sensitivity to hydrolysis and oxidation at high temperatures and poor low temperature flow properties and are hence limited to total loss applications and those with very low thermal stress (Erhan, 2005).

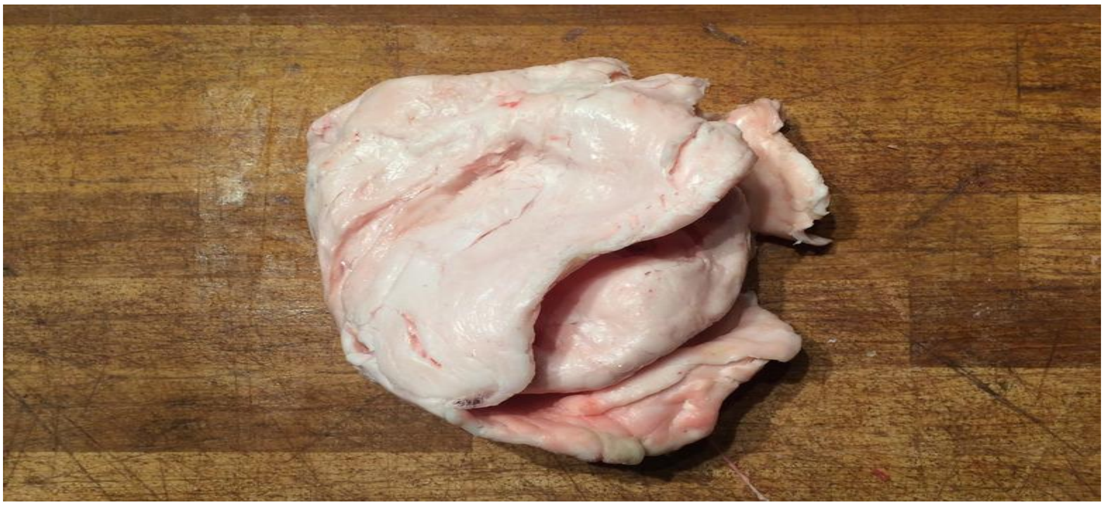
In order to satisfy the new environmental regulations, the scientific community is developing new lubricants with greater biodegradability and less toxicity. In this sense, the lubricants obtained from bio-based sources (biolubricants) have emerged as potential alternatives to replace traditional mineral oils synthesized from petroleum (Erhan et al., 2008).

Biolubricants derived from plants and animals display excellent physicochemical properties, such as high viscosity indexes and flash points as well as good resistance to shear and high biodegradability, in such a way that these compounds can be considered renewable and readily biodegradable allowing them to be used in various industrial applications, including as emulsifiers, lubricants, plasticizers, surfactants, plastics, solvents, and resins (Soni and Agarwal, 2014; Shashidhara and Jayaram, 2010 and Hsien, 2015).

Therefore, low temperature modifications such as cloud and pour points were carried out on the biolubricant in order to enhance their physical and chemical characteristics.

Butter (source: Google.com, 2024)

Palm oil (Source:Wikipedia, 2024)



Animal fat or tallow (source: google.com, 2024)

MATERIALS AND METHODS

Sample Collection and Preparation

Collection and preparation of oils from source materials

Palm kernels was collected from the Head of Department, Chemistry, Modibbo Adama University, Yola, Adamawa State; Shea butter nuts were obtained from Lapai Local Government Area of Niger state; Milk for Butter was locally sourced from Damare Village, Girei Government Araea of Adamawa State and Animal fat was purchased from the Abattoir, Yola, Adamawa State, Nigeria.

Extraction of Bio-lubricants

Shea Butter Biolubricant

In the experiment, 30 g of 0.45 mm particle size of the prepared shea nut particles was placed in a wrapped cloth in place of the thimble and placed into the received portion of the Soxhlet extractor. 150 cm^3 of methanol was transferred into the flask and placed on an electro thermal heating mantle. The Soxhlet extractor related to a condenser having rubber tubing for inlet and outlet water flow for cooling. The miscella, a mixture of oil and solvent, was subjected to evaporation to recover the solvent and oil (Prasanna and Rahul, 2018).

Palm kernel oil extraction.

The freshly collected seeds were washed and dried at room temperature in order to remove dirt and other contaminants. The dried kernels were shredded to smaller sizes and heated to 80 °C so as to elevate the moisture content and also to allow for penetration of solvents. The 100 g of the crushed sample was placed in o Soxhlet with diethyl ether as (about 300 cm^3) as solvent (Bong, et *al*., 2018).

Synthesis of Biolubricant from Animal Fat (Tallow)

The beef tallow collected from a local butcher was subject to several rendering processes to separate fat from protein-rich tissues. For boiling water (BW) fat extraction, the fat tissues were boiled with water (enough to cover the fat material) in a pressure cooker for 40 min (1.5 atm; 112 °C). After the residues were removed, the liquid is cooled at room temperature, and the fat layer will be removed with a drainer. The cooking time was optimized to extract the maximum fat. Acetone fat extraction, at reflux temperature, was accomplished in a glass 500 cm^3 capacity round flask equipped with a reflux column heated by a nest-shaped heating mantle. The fat tissues were then boiled with acetone (1.28 $w_{fat}/w_{acetone}$ ratio) for about 4 hours. After removing the solid material, the liquid was now cooled at room temperature and the fat layer removed with a drainer. All the extraction methods were replicated 3 times to evaluate their reproducibility (Soares Dias, *et al.,* 2013).

Synthesis of Biolubricant from Buttermilk

About 4 litres of raw cream (40 % fat) was batch pasteurized at 68.3 °C for 30 minutes each and was then cooled, stored in separate containers and aged overnight at 7 °C. A part of the pasteurized cream was manually churned or a butter churn machine without addition of color. Break point will be reached about 55 to 60 minutes, and the buttermilk will be drained and stored in containers (https://www.journalofdairyscience.org/)

Physicochemical Properties of the Oils

The oil samples were mixed in a container to obtain homogeneous whole Osemeahon (2024) were studied as well as those obtained from the addition of lubricant additives separately in order to ascertain the effects of additives on the biolubricants. The blends and samples containing additives were code-named for easy identification and classification Maitera (2024).

Determination of Pour Point

Pour Point is the lowest temperature at which a fluid particularly lubricants and biolubricants, will flow or pour when it is cooled under standard conditions. It is an important property of lubricants as it affects their performance in cold weather. Pour Point 20ml of the oil sample was measured into an enclosed container fitted with a thermometer that can read a negative temperature up to -30 ^{O}C. it was chilled and checked at intervals of 5 min until the oil stopped flowing (ASTM D-97). The temperature at which the oil had difficulty flowing was recorded as the pour point.

Determination of Pour Point

Cloud point (CP) is the temperature at which the first sign of wax formation for biolubricant can be detected. It is the temperature at which first sign of haziness is observed. The wax crystals formed can clog filters and openings, thereby leaving deposits on surfaces such as a heat exchanger, and increase the viscosity of the biolubricating oil.

Test jar was filled to the level mark, closed tightly by the cork carrying the thermometer and placed into a bath of crushed ice. Test jar was removed from the jacket quickly without disturbing the specimen. Inspection for cloud point was done and jacket replaced. Operation was done without exceeding time duration of three (3) seconds. Since cloud point is the temperature of a liquid specimen when the smallest observable cluster of hydrocarbon crystals first occurs upon cooling under prescribed conditions, observation was done, and cloud point was reported to the nearest 1 ^{O}C. At this point, clouds are observed at the bottom of the test jar, which is confirmed by continued cooling. (Emmauel et al., 2016).

Addition of Additives to Biolubricant Oils

Selected additives such as polymethacrylate for pour point, polyalkylene glycol for cloud point, diphenylamine for oxidation stability and butylated hydroxytoluene for thermal stability were added to the biolubricant oils to improve their efficiency (Zainal *et al*., 2018).

Effects of Additives on the Performance of Biolubricants

This improvement in the stability of the final product through chemical modifications makes its application more viable, considering that one of the main limitations in the direct use of vegetable oils as bio-based lubricants is their low oxidative stability, low hydrolytic stability, poor low temperature behaviours such as pour point cloud point. Each of the biolubricants-containing additives was code named as follows: TPMA for Tallow, BPMA for Butter, SBPMA for Shea butter and POPMA for palm oil.

RESULTS AND DISCUSSION

Effects of Polymethacrylate PMA additives on the pour points Biolubricants

Table 1: PMA additives on Biolubricants Oils.

Biolubricants	Pour points ^{O}C
Shea Butter, SBPMA	-3.5
Palm Oil, POPMA	-5
Butter from Milk, BPMA	-7
Tallow, TPMA	-9.5

It can be seen from figure 1 below that the pour points of the biolubricants varies across the oils upon addition of Polymethacrylate additive as shown in figure 4.2 above. Figure 1 shows that tallow biolubricant obtained from animal fat (Tallow), TPMA had a pour point value of -9.5 ^{O}C is higher than -5 ^{O}C obtained without the addition of any additives that is an increase of about 5 ^{O}C. This agrees with the study carried out by Yohannes and Betelhem, (2024) in which a pour point of -5 ^{O}C was obtained on chicken tallow fat. Similarly, however, a pour point of -6 ^{O}C was recorded for butter oil BPMA obtained from animal milk when the additive was added. This implies an 8 ^{O}C rise in the pour point value upon additive introduction. Shea butter, SBPMA also exhibited a rise in the low temperature pour point value of -3.5 ^{O}C while palm oil, POPMA had a significant change of pour point value from 7.2 ^{O}C to about -5 ^{O}C indicating a difference of 12 ^{O}C raise.

Menkiti et al. (2017) reported an improvement in the pour point of crude jatropha oil from – 7 ^{O}C to – 12 ^{O} Cf or jatropha oil-based bio-lubricant. Bilal et al. (2013) reported improved pour points of jatropha oil from 5 ^{O}C to – 7 ^{O}C for its bio-lubricant. Aji et al. (2015) reported pour points of 1.30 ^{O}C for neem-based bio-lubricant, 0.20 ^{O}C for jatropha based bio-lubricant and -30 ^{O}C for mineral oil SAE 50. Singh et al. (2018) reported pour point of -21 ^{O}C for mineral oil SAE 40. Shah et al. (2019) also reported pour point of -15 ^{O}C. The cold flow property of plant oils is extremely poor, and this limits their use at low operating temperature, especially as automotive and industrial fluids. Plant oils tend to form macrocrystalline structures at low temperature through uniform stacking of the 'bend' triglyceride backbone.

The chemical modification of plant oils is an attractive way to solve these problems. Transforming alkene groups in plant oils to other stable functional groups could improve their oxidative stability, whereas, reducing structural uniformity of the oil by attaching alkyl side chains would improve its low-temperature performance. A method to improve the low-temperature flow property is to introduce branching sites at the epoxy carbons. The branched products have significantly improved low-temperature flow characteristics and friction-wear properties.

Polypropylene Glycol additive, PPG was added to the biolubricant oils and code named SBOPPG for Shea butter, POPPG for Palm Oil, BOPPG for Butter from milk and TOPPG for tallow. As seen in table 2 below.

Table 2: Polyglycols, Polypropylene glycols, PPG additives on the cloud points Biolubricants Oils.

Biolubricants	Cloud points ^{O}C
Shea Butter SBOPAPG	-6
Palm Oil POPPG	-2
Butter from Milk BOPPG	-5
Tallow TOPPG	-8

As seen from table 2 below, the cloud point of the palm-derived lubricant, POPPG, was reduced from 7.2 ^{O}C as seen in table 1 to about -2 ^{O}C. In a similar study, the cloud point was reduced to 0 ^{O}C for biolubricants after double transesterification as carried out by Yohannes et al., (2024). On the other hand, the shea butter oil, SBOPPG drastically shifted from 24 ^{O}C value to -6 ^{O}C upon addition of polyglycol additive. About -5 ^{O}C was recorded for butter oil from milk BOPPG depicting a rise of about 11 ^{O}C. As seen in Figure 1 below, Tallow oil TOPPG biolubricant however showed cloud point of -8 ^{O}C. These results suggest that the cold flow properties of the biolubricants are adequate to permit their use at extreme temperatures.

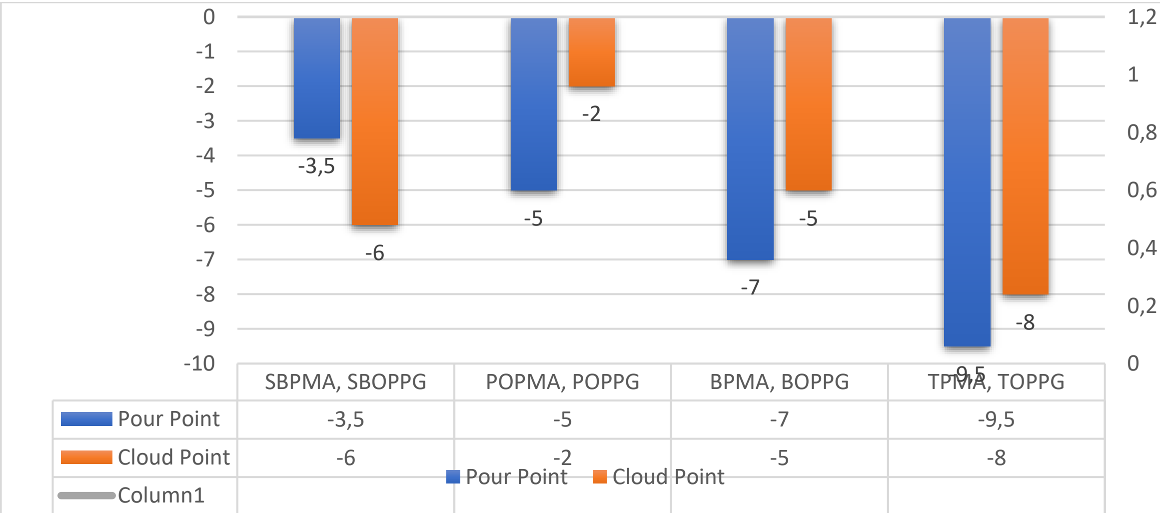


Figure 1: Plot of Cloud and Pour Points of polymethacrylate, PMA and Polypropylene Glycol, PPA additives respectively

CONCLUSION

The cloud and pour points carried on the four biolubricant oil sample revealed improved stabilities when polymethacrylates and polypropylene glycol additives were added respectively.

Tallow-based biolubricant oil was seen to have exhibited the best pour and cloud points. Similarly, butter oil showed better low temperature performances as a result to the additives added. However, although shea butter and palm oil-based biolubricant showed increased performances, their values are comparatively lower from the results of the analysis carried out. Therefore, the results of this study indicate the significance of the quality biolubricant production, modification and possible applications.

Conflict of Interest

The authors affirm that there are no conflicts of interest associated with this publication.

Authors' Declaration

The authors confirm that the research presented in this article is entirely original. They accept full responsibility for any claims or issues arising from the content herein.

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