The Tribological Performance of Nano-Activated Carbon as Solid Additives in Modified Calophyllum Inophyllum Based-Metalworking Fluid

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Abstract Biolubricants have attracted attention in today's market as a new alternative to commercial lubricants due to their environmentally friendly and renewable properties. The refinement of bio-lubricants has improved their tribological and physical properties. However, to optimize the performance of lubricants when machined under high-temperature conditions, additives must be added to the lubricant. In this study, the tribological properties of modified Calophyllum inophyllum (MTO) oil combined with nano-activated carbon (NAC) as additives were investigated using the four-ball wear test method. This bio-lubricant consists of modified Calophyllum inophyllum oil in combination with NAC at concentrations of 0.01, 0.025, and 0.05 wt%. The coefficient of friction for the balls and their wear diameter are evaluated and compared. The kinematic viscosity and viscosity index of MTO were tested according to ASTM standards. The results show that a lubricant with added NAC is more effective in reducing wear and friction than a bio-lubricant without nano-activated carbon. The bio-lubricant combined with NAC reduced the wear diameter of the lubricated balls compared to the bio-lubricant without additives. The nano-additives have converted the sliding effect into a ball-bearing effect between the interfaces of the balls, creating a better oil protective film that helps form a gap between the mating surfaces during tribological testing.

Keywords Nano-activated carbon · Modified calophyllum inophyllum oil · Tribology

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R. Abd. Aziz et al. (eds.), *Intelligent Manufacturing and Mechatronics*, Springer Proceedings in Materials 40, https://doi.org/10.1007/978-981-99-9848-7_34

1 Introduction

The lubricant has been used for decades to decrease friction and wear between surfaces in contact and to reduce heat formation during continuous motion between the mating surfaces [1]. For instance, lubricant is used in the automotive industry and other industrial areas as a cooling agent, metalworking fluids, engines, and hydraulic pumps. Lubricants originally derived from mineral-based oil such as petroleum due to their efficacy to reduce wear, have good hydrolysis stability and economical properties [1]. However, petroleum-based oil possesses poor biodegradability, poor flash point value, and high toxicity [2, 3]. The increasing understanding of worker health concerns and environmental pollution is the main objective for the development of lubricants derived from renewable resources [4].

Lubricants from petroleum-based contain a variety of complicated mixtures made up of countless chemical compounds. Additionally, these bio-lubricants perform better in terms of being ecologically friendly and toxic-free, making them a viable substitute for petrochemical products. Bio-based lubricants have been acknowledged and utilized as engine oil, biodiesel, metalworking fluid, and hydraulic oil. Bio-based lubricants are often derived from vegetable oil and animal fat [5]. However, due to competition between the feedstock industry and the lubricant industry, bio-lubricant prices are more expensive than mineral-based lubricants [6]. To overcome this issue, the non-edible source has been utilized as an alternative and several modifications have been made to ensure this non-edible vegetable oil is suitable for use according to ASTM standards [7].

In this study, the Tamanu oil (Calophyllum Inophyllum), was selected for its exceptional rheological and tribological characteristics, owing to its sustainable, and biodegradable nature. Tamanu, being a non-edible plant, has make it a favourable option for substituting traditional sources of lubricating oil. From an edible plant thus eliminating the edible oil from being used as a lubricant [8]. However, crude Tamanu oil (CTO) cannot compete with the synthetic ester (SE) in today's marketplace due to its inherent properties, which include extremely high viscosity, poor thermal and oxidative stability, and a high amount of monounsaturated acid [9]. To improve the existing physical and chemical properties of Tamanu oil for metalworking fluid applications, chemical modification is used. The chemical modification involves the elimination of the hydrogen component on the beta-carbon positive side of the DNA structure by using a catalyst to initiate the chemical processes [3]. To enhance the efficiency and performance of lubricants, additives are used to aid in reducing friction and wear produced by the cutting tool while also lowering energy loss in the system [10]. The dispersion of a small weight percentage of nanoparticles can help to provide a gap between the cutting tool and the workpiece surface. In the synthesizing process of nano-fluid, the size and concentration of nano-additives play a major role in their tribological performance [11]. Lubricants that have nano-additives with adequate concentration can significantly reduce friction and wear as they formed an excellent tribo-film layer protecting the surface [12]. In this study, the CTO triglyceride structures are altered chemically by using the catalysts sodium methoxide (NaOCH3) and trimethylolpropane (TMP) ester [13]. The inclusion of nano-activated carbon from Tamanu shells was evaluated at various concentrations for its effectiveness in assisting in reducing the wear formed on the ball. The tribological performance of MTO at various concentrations of NAC was investigated using a four-ball test to determine the potential of the newly developed metalworking fluids (MWF).

2 Methodology

2.1 Chemical Modification for Crude Tamanu Oil (CTO)

The crude Tamanu oil (CTO) was transformed into a bio-based metalworking fluid (MWF) using a chemical modification process and the inclusion of additives to enhance the tribological and physicochemical properties of the oil. Fatty acid methyl ester (FAME) was created by chemically modifying the CTO utilizing a two-step acid-based transesterification technique. To produce modified Tamanu oil (MTO), FAME was mixed with trimethylolpropane (TMP) ester and 1% weight sodium methoxide (NaOCH3) at a molar ratio of 3.5:1 for 24 h as the catalyst for the reaction. As shown in Fig. 1, the transesterification process was executed in a flask with three necks and a Graham condenser on top.

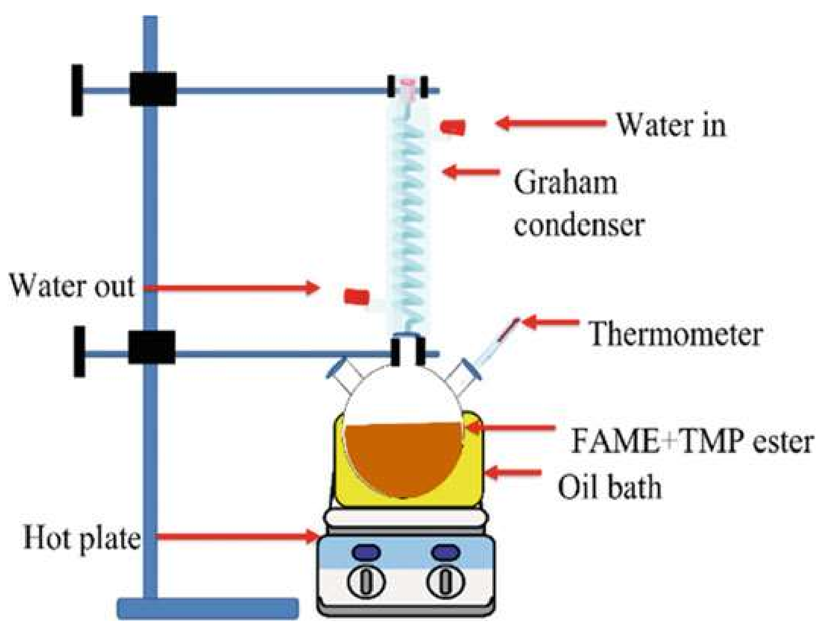

Fig. 1 Transesterification process

2.2 Nano-Activated Carbon (NAC) Synthesis Process

The main material used for the nano-activated carbon is Tamanu shells and the process is depicted in Fig. 2. The shell was dried under 12 heating bulbs with 100 W for 24 h to dry up the shells after husk extraction from the shells. Subsequently, the shell is charred in the furnace for 2 h at 450 °C after it undergoes a cleaning process in an ultrasonic machine for 3 h. The charred shells were ground in pestle and mortar for the first phase of the size reduction process. Then, a sieve of 30 μm in size was used to filter the carbon powder. In the second size reduction process, the ball-milling process is carried out for 24 h at 350 rpm to reduce the size of the carbon powder to 1 μm.

The carbon powders were activated by using a chemical activation process with sodium hydroxide (NaOH) as an activation agent at a molar ratio of 1:2.5. The carbon powder was soaked for 24 h before it is carbonized in the furnace for 2 h at 450 °C to activate the pores. After the activation process, the pH of the powder was neutralized with hydrochloric acid (HCl) and distilled water until a pH of 7 was reached. After neutralization, the powder was filtered with a filtration bottle and dried in a vacuum oven at 100 °C for 5 h. Then, the activated carbon powder undergoes the final phase of the size reduction process by using the ball-milling process. The parameters for

Fig. 2 Synthesis process for nano-activated carbon (NAC); **a** Dried and charred Tamanu shells, **b** ball-mill machine, **c** activation process and **d** nano-activated carbon powder

Table 1 Ball-milling parameters

Parameters	Value
Weight per ball	7.5–7.8 g
Number of balls	23
Milling speed	350 rpm
Milling hours	24–72 h

the ball-milling process are shown in Table 1 below. Then, the size and surface morphology of the nano-activated carbon is analyzed under FESEM (JEOL).

2.3 Dispersion Process of NAC into the Biobased MWFs

MTO was mixed with nano-activated carbon (NAC) at different concentrations of 0.01, 0.025, and 0.05 wt%, respectively (the additive concentration was calculated based on the weight of the MTO sample). MTO and NAC were mixed using an ultrasonic device for 2 h at 60 °C. Figure 3 shows the appearance of MTO before and after the addition of NAC. Table 2 shows the prepared MTO samples with and without the addition of NAC. Subsequently, the physicochemical and tribological properties of the lubricants were tested according to ASTM D445 (kinematic viscosity), ASTM D2270 (viscosity index), and ASTM D4172 (four-ball wear test).

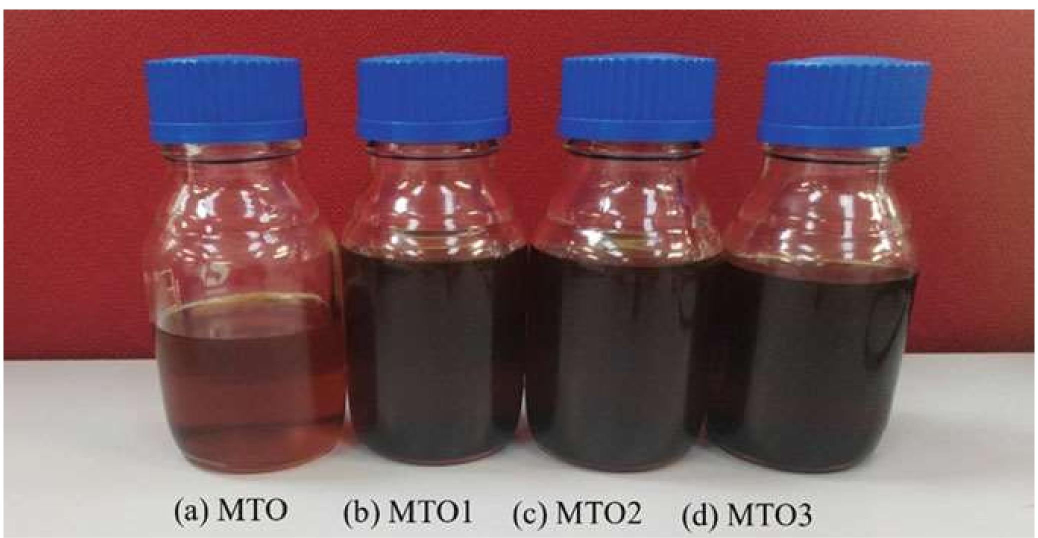

Fig. 3 Lubricant sample: **a** Modified Tamanu Oil (MTO), **b** MTO1, **c** MTO2 and **d** MTO3

Table 2 The descriptions of the MTO samples for this study

Sample	Concentration of additives (wt.%)
MTO	–
MTO1	0.01
MTO2	0.025
MTO3	0.05

2.4 Tribological Test

The research on metalworking fluid's tribological properties revolves mainly around friction and wear mechanisms. Figure 4a shows the DUCOM TR-30 L four-ball tribo-tester used to perform the tribology test in this research, which follows the ASTM D4172 standard method. The ball used in this test is a chromium steel ball (AISI 52,100) with a diameter of 12.7 mm and a hardness value in the range of 62 to 66 HRC. Three fixed steel balls were assembled in the ball cup, secured with a retaining ring, and covered with 10 ml of lubricant. The fourth ball, called the rotating ball, was attached to the collet, and tightened on the spindle. Figure 4b shows the setup diagram for the test sample. After the tribological test, the wear scar diameter (WSD) was measured on the three steel balls supported in the ball cup to determine the effectiveness of the oil used to minimize wear. After the test, the topological surfaces of the three-ball bearing were identified using an optical microscope (Olympus BX51M metallurgical microscope) and the coefficient of friction (COF) for each lubricant sample was determined using Winducom software. The results for WSD and COF of all lubricant samples were compared to a reference oil, which is a synthetic ester (SE). SE is the commercial metalworking fluid for MQL applications derived from mineral oil.

3 Result and Discussion

3.1 Rheological Properties

Figure 5 displays the viscosity index and kinematic viscosity at 40 and 100 °C for each lubricant sample. When temperatures change during the machining process, kinematic viscosity is essential for preserving the lubricant's fluidity. MTO and MTO with nano-additives had higher kinematic viscosities than SE (5.20 mm^2/s), demonstrating the lubricant's potential to form tribo-films and withstand high-temperature conditions. As depicted in the graph, SE possesses the lowest kinematic viscosity and viscosity index while MTO and MTO with nano additives have excellently improved their kinematic viscosity and viscosity index. While for the viscosity index of MTO (198.03), has increased by 31.84% after the modification process compared to SE(150.21) indicating the effectiveness of the chemical modification technique in

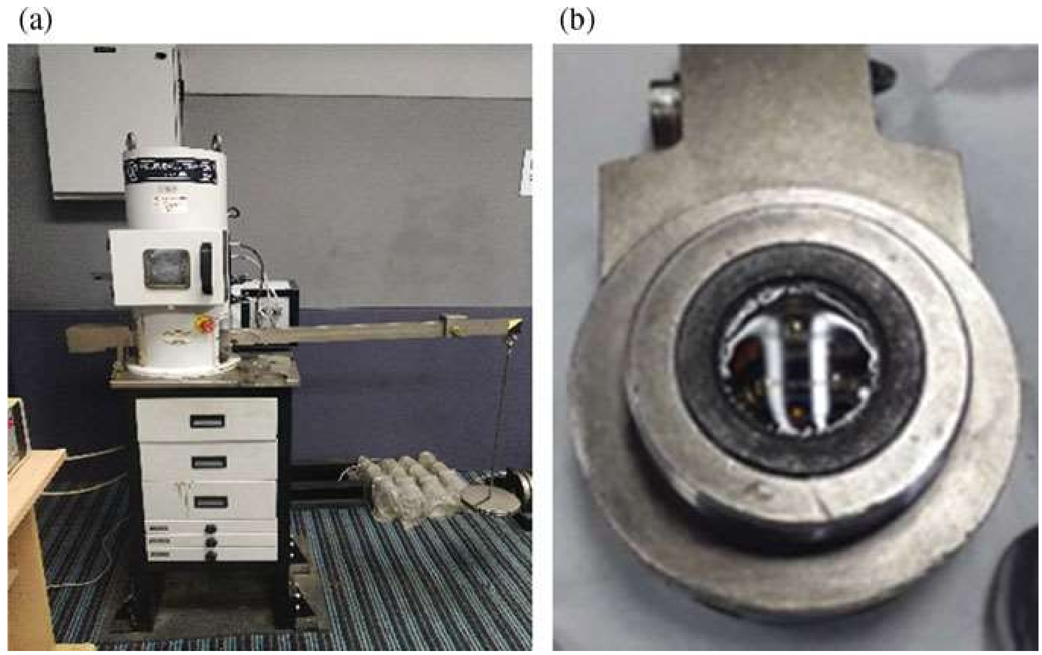

Fig. 4 Tribological test for lubricants; **a** DUCOM TR -30 L four-ball tribo-tester and **b** Ball-pot containing lubricant and three stationary balls

altering the triglyceride structure of Tamanu oil by replacing the beta carbon with triglyceride ester structure [14]. MTO3 has the highest viscosity index (236.15) and kinematic viscosity(6.80) due to the high concentration of nano-activated carbon in the oil as depicted in Table 3 below. The high content of nano-activated carbon has decreased the space for the particles to move in the oil [15]. The nanofluids become denser and more viscous than other lubricant samples.

3.2 Results for Tribological Performance of Each Lubricant Sample

Table 4 shows the tribological performance of the lubricants in terms of their coefficient of friction (COF) and wear scar diameter value (WSD). The nano-activated carbon presence in the fluid was able to generate a lubricating film between the contact surfaces that acted as a cushion layer protecting the interface of the balls from direct load applied, improving the COF and WSD values [16]. Furthermore, the nanoparticles have generated a rolling effect at the mating surfaces, potentially converting sliding motion into ball-rolling motion [17]. The fatty acids in MTO provided effective lubrication properties as they contained fatty acids that can produce a lubricant layer that attaches to the contact surfaces [18]. The polar carboxyl group in the fatty acids remained tightly packed, providing a sufficient lubricating coating

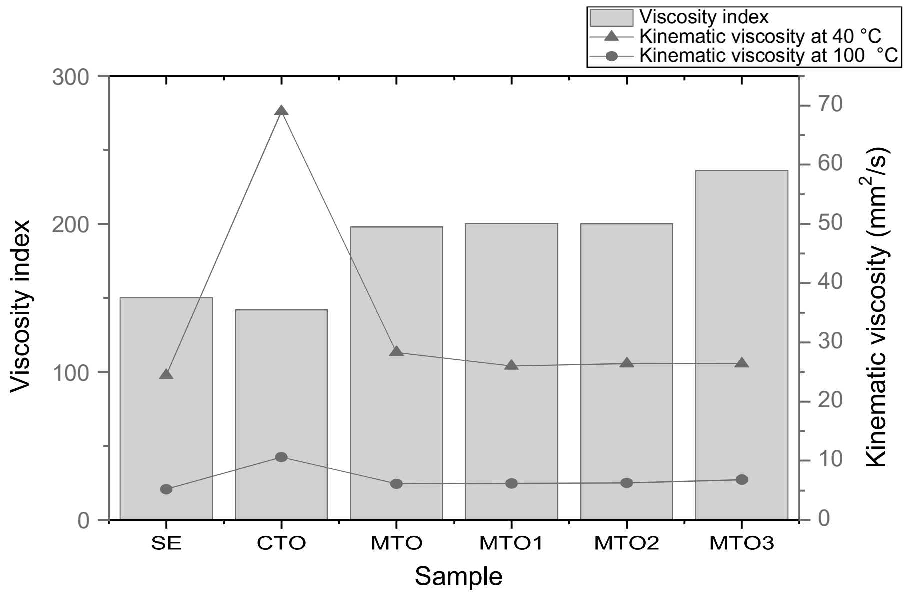

Fig. 5 Viscosity index against kinematic viscosity of lubricants sample chart

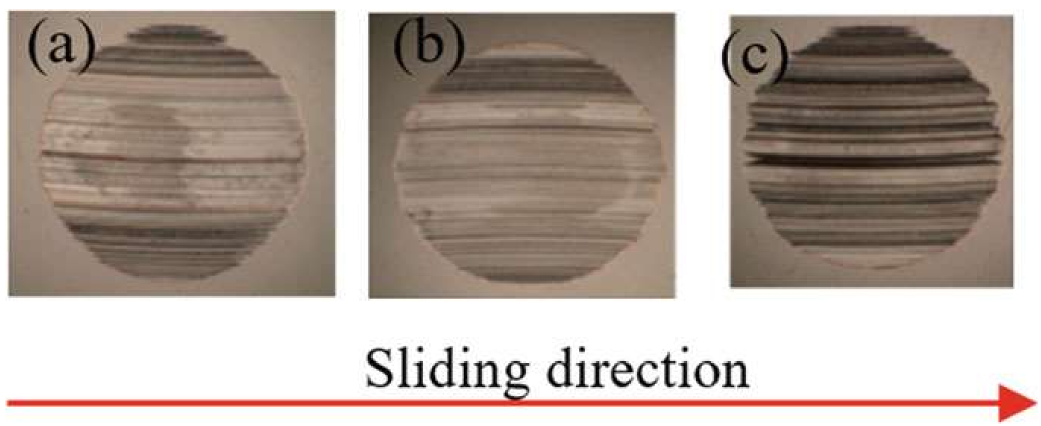

Fig. 6 Worn surface after tribological test; **a** MTO1, **b** MTO2, and **c** MTO3

Table 3 Rheological properties of lubricant samples

Physical properties	Temp (°C)	SE	MTO	MTO1	MTO2	MTO3
Density (g/cm$^{3)}$	40	0.97	0.93	0.93	0.95	0.98
	100	0.91	0.86	0.87	0.88	0.93
Kinematic viscosity (mm^2/s)	40	24.43	25.81	26.00	26.44	26.37
	100	5.20	6.10	6.17	6.25	6.80
Viscosity index	–	150.21	198.03	200.27	200.17	236.15

Table 4 Tribological results after four-ball wear test

Lubricant sample	Wear scar diameter (μm)	Coefficient of friction (COF)
SE	779.30	0.102
MTO1	674.70	0.064
MTO2	724.20	0.055
MTO3	739.50	0.059

that may reduce friction [1]. Moreover, among three nano-activated carbon concentration ratios, MTO2 has presented an excellent improvement of COF(0.055) and better WSD(724.20 μm) surface. There was less formation of deep grooves on the scar surface of MTO2 compared to MTO3 as depicted in Fig. 5. While for MTO1, the concentration of nano-activated carbon is not enough to fill the gaps between the contact surface and for MTO3, the concentration of nano-activated carbon has exceeded the needs and cause agglomeration of nano activated carbon between the contact surface [19]. This situation proved that an adequate quantity of nanoparticles can provide a smooth rolling motion between the contact area as there will be no agglomeration between particles at the interface (cf. Fig. 6) thus lowering the COF value.

4 Conclusion

In this research, the tribological performance of four MTO samples as the eco-friendly lubricant was examined by conducting physical and tribology test using a four-ball wear test, and the performance of this eco-friendly lubricant were compared with SE. The presence of nano-activated carbon has significantly improved the physical properties of the MTO. The addition of 0.05 wt% of nano-activated carbon in MTO shows the highest viscosity index of 236.15 respectively. While the inclusion of 0.025 wt% of nano-activated carbon in MTO is the optimum concentration based on the results obtained from the COF value and scar formation on the ball after the tribology test. MTO2, which is MTO + 0.025 wt% has the smallest COF value and less groove formation on the ball. Based on the overall results, the addition of nano-activated carbon has excellently improved the tribological properties of the MTO and their performance has exceeded the SE fluid. In conclusion, MTO with nano-activated carbon could replace the application of SE as an eco-friendly metalworking fluid and reduce the dependency on mineral-based metalworking fluid for a sustainable machining process.

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