Journal of Physics: Conference Series

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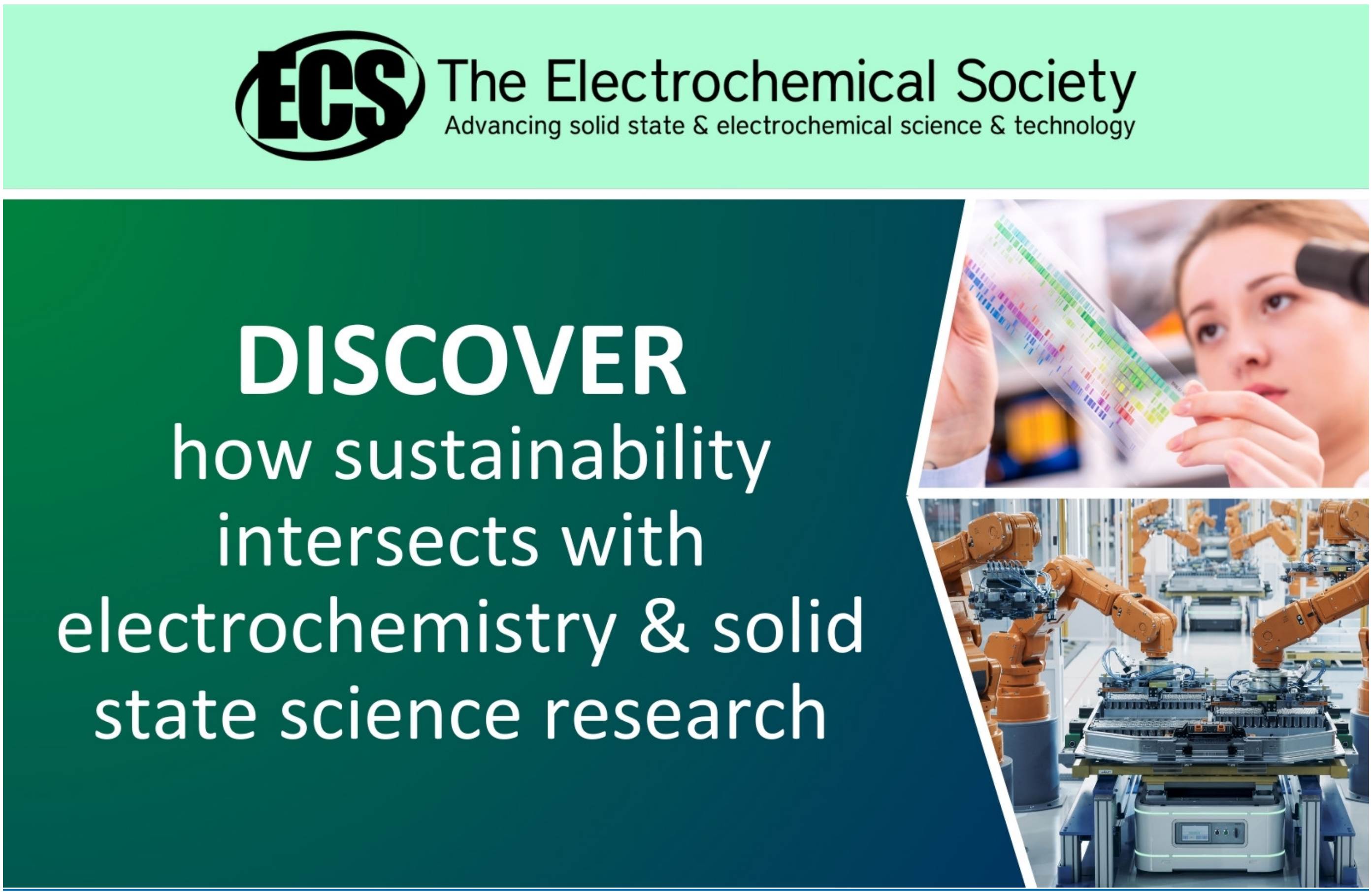
To cite this article: R.N.R Ismail *et al* 2024 *J. Phys.: Conf. Ser.* **2688** 012020



A Tribological Analysis of PAO-Based Hybrid SiO_2-TiO_2 Nanolubricants

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Abstract. Friction and wear are caused by contact between sliding surfaces over time. It is possible to reduce friction in a compressor by improving its lubrication. The nanoparticle lubrication will aid in reducing wear and friction of the piston mechanism of the compressor. This work aims to analyse the tribology properties of performance of the system employing Polyalphaolefin (PAO)-based hybrid nanolubricants. A two-step method was used to disperse SiO_2 and TiO_2 nanoparticles in the PAO lubricant at volume concentrations of 0.01% and 0.05% using a two-step method. Then, hybrid nanolubricants are observed visually, and their coefficient of friction (COF) is evaluated using a four-ball tribometer. The SiO_2-TiO_2/PAO hybrid nanolubricants were found to have a higher than 80% sedimentation ratio up to 180 hours and to be visually stable for up to 30 days. The 0.01% SiO_2-TiO_2/PAO has a lower COF than the base PAO 68 oil. The 0.05%, however, does not show the expected reduction. The COF ratio for volume concentrations of 0.01% and 0.05% is 0.97 and 1.01, respectively. The highest COF reduction of nanolubricants was attained up to 2.53% at 0.01% volume concentration. Therefore, 0.01% SiO_2-TiO_2/PAO is the ideal condition for use and is recommended for further investigations.

1. Introduction

Automotive air conditioning (AAC) systems consume much power on commercial vehicle auxiliary components. Studies show that 90% of fuel consumption increases when air conditioning is operated at idle conditions [1, 2]. Approaches to improving the COP of the system are currently being addressed by focusing on optimising the components. The optimised features include a compressor, evaporator, thermal expansion valve and refrigerant [3]. In the refrigeration industry, the AAC compressor is the most essential auxiliary load on the engine. AAC compressors are typically belt-driven, so speed and sliding contact matter [4]. Sliding contact causes friction and leads to wear over time [5]. A lubricant is therefore required to prevent the piston and cylinder walls from wearing prematurely [6]. While the refrigerant is being compressed, lubrication also reduces the refrigerant's temperature. Thus, employing a suitable lubricant can further increase compressor consistency, maximising performance and lowering power usage [7].

In most AAC systems, vapour compression refrigeration systems are used. The compressor commonly used is piston type. The sliding contact due to piston movement against the cylinder wall has produced friction. Friction produces heat and power loss. Hence, more power consumption is needed to overcome the power loss. Consequently, there is a strong connection between the performance of AAC systems compressor with the friction coefficient (COF) and wear of lubricants. The characteristics of nanolubricants are being explored to boost the COF in order to enhance the performance of the AAC system with nanoparticles dispersion.

It has been known that various types of metallic oxides have been added to lubricants [8]. The tribological properties of nanoparticles have been the subject of several investigations, including ZnO, ZrO_2, TiO_2, SiO_2, CuO, and others. [9-13]. Previously, it has been shown that these nanoparticles may accumulate on the surface of rubbing and improve the characteristics of conventional oils. Additionally, to enhance the behaviour of wear and friction, a low concentration of nanoparticles, such as less than 2wt%, is sufficient; however, for certain nanoxides, 0.5wt% is the optimal concentration. Nanoparticles exhibited a rolling mechanism to reduce surface friction [14]. However, considerations including compatibility between base lubricants and nanoparticles [15] and the stability over time of nanoparticle dispersion might prevent the development and use of nanolubricants [16, 17].

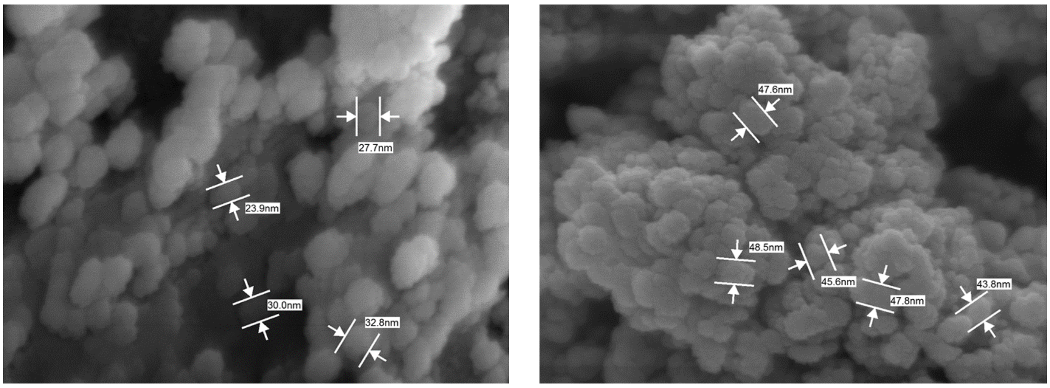
In the automotive industry, nanoparticle-enhanced lubricants demonstrate definite improvements in lubrication [18-20]. The application of a newly developed hybrid nanolubricant, based on polyalphaolefin (PAO), as a potential replacement for the conventional polyalkylene glycol (PAG) lubricant, poses certain limitations and potential challenges. These challenges include concerns related to the compatibility between nanoparticles and their base lubricants, the long-term stability of nanoparticle dispersion, increased viscosity, reduced specific heat, and elevated production costs. The hybrid nanolubricants is expected to enhance stability, tribological behaviour and the compressor work performance. Research on the investigation of tribological performance of hybrid nanolubricants is still lacking, however numerous studies on the performance of AAC systems with nanolubricants have been presented in the existing literature. There is yet to be a tribological evaluation of nanolubricants based on PAO in AAC compressors. Hence, the objective of this study was to evaluate the preparation and stability of hybrid nanolubricant, as well as the tribological behaviour of AAC compressors employing SiO_2-TiO_2/PAG hybrid nanoparticles.

2. Materials and Methods

Silicon dioxide (SiO_2) and Titanium dioxide (TiO_2) metal oxide nanoparticles were taken into consideration for the preparation of nanolubricants in the current work. The spherical of 99.9% pure TiO_2 nanoparticles were purchased from HWNANO (Guangzhou, China). The SiO_2 nanoparticles, in contrast, with a purity of 99.9% were acquired from DKNANO (Beijing, China). **Table 1** displays information on the physical properties of the present nanoparticles. During the preparation of nanolubricants, the necessary safety measures and protective gear were kept in place. The utilisation of Field Emission Scanning Electron Microscopy (FESEM) analysis was employed to characterise the nanoparticles of SiO_2 and TiO_2. The FESEM images of the nanoparticles under investigation are displayed in **Figure 1**.

Table 1. TiO_2 and SiO_2 Physical Properties [21]

Properties	Units	TiO_2	SiO_2
Thermal Conductivity	k [W/m.K]	8.4	1.4
Density	ρ [kg/m^3] @ 20°C	4230	2220
Specific heat	c [J/kg.K]	692	745
Average particle size	d [nm]	50	30
Molecular mass	m [g/mol]	79.86	60.08
Surface characteristics	-	hydrophilic	hydrophilic



SiO_2 TiO_2

Figure 1. Micrograph image of nanoparticles using FESEM analysis

Polyalphaolefin (PAO) was chosen as the based lubricant among other synthetic oils. PAO is the most common synthetic oil used in industrial and automobile lubricants. The PAO lubricant is suitable for AAC systems and industrial end users. It is frequently used in aftermarket applications as a universal compressor oil. The PAO base lubricant used in this investigation is PAO 68. When compared to other oils, PAO-Oil 68 does not collect moisture from the surrounding air. This suggests that issues brought on by humidity, including the formation of acids or ice on components, may be readily remedied with PAO. Therefore, PAO Oil 68 has a far wider variety of applications and storage stability compared to other conventional lubricants. The properties of PAO Oil 68 are shown in **Table 2**.

Table 2. Base lubricant characteristics.

Properties	PAO 68
Viscosity @ 40°C, 100°C (cSt)	68, 10
Density @ 15°C (g/cm3)	0.835
Flash Point (°C)	260
Water Solubility	Insoluble
Colour	Light Yellow

3. Preparation of Hybrid Nanolubricants

Two-step method was used to prepare the present hybrid nanolubricants. In this experiment, TiO_2 and SiO_2 nanoparticles were used. **Equation 1** was considered in the determination of mass of nanoparticles for a specific volume concentration of nanolubricants. Various researchers have utilised a similar equation to prepare nanolubricants [22-24].

$$\text{Volume concentration, } \phi = \left(\frac{\frac{m_n}{\rho_n}}{\frac{m_n}{\rho_n} + \frac{m_{PAO}}{\rho_{PAO}}} \right) x100\% \qquad (1)$$

where; m_n is the nanoparticles mass, ρ_n is the nanoparticles density, m_{PAO} is the PAO mass and ρ_{PAO} is the PAO density. In the process of preparing hybrid nanolubricants, many instruments were employed, including a high precision weight scale, a magnetic stirrer (FAVORIT magnetic stirrer with hotplate HS0707V2), and an ultrasonic homogenizer water bath (Fisherbrand FB15015). The sequential steps involved in the preparation of nanolubricants are depicted in **Figure 2**. In the beginning, the mass of the nanoparticle was determined using the equation provided for volume concentrations of 0.01% and 0.05%. With the aid of a magnetic stirrer, PAO was mixed with nanoparticles using the two-step procedure to produce nanolubricant. The hybrid lubricants used in the study were composed of two distinct nanolubricants that were blended 50:50 for a total volume of 30 mL. The nanolubricant was stirred for up to 30 minutes using the magnetic stirrer. After the magnetic stirrer process, the hybrid nanolubricants were transferred to the ultrasonic homogenizer at 100 W for 2 hours, a straightforward visual sedimentation observation approach leveraging photography was employed to evaluate the stability condition of nanolubricants. Furthermore, the absorbance ratio of the hybrid nanolubricants at the peak wavelength was measured by altering the sample sonication period from 0 to 7 hours (0 to 7H) using a UV-VIS spectrophotometer.

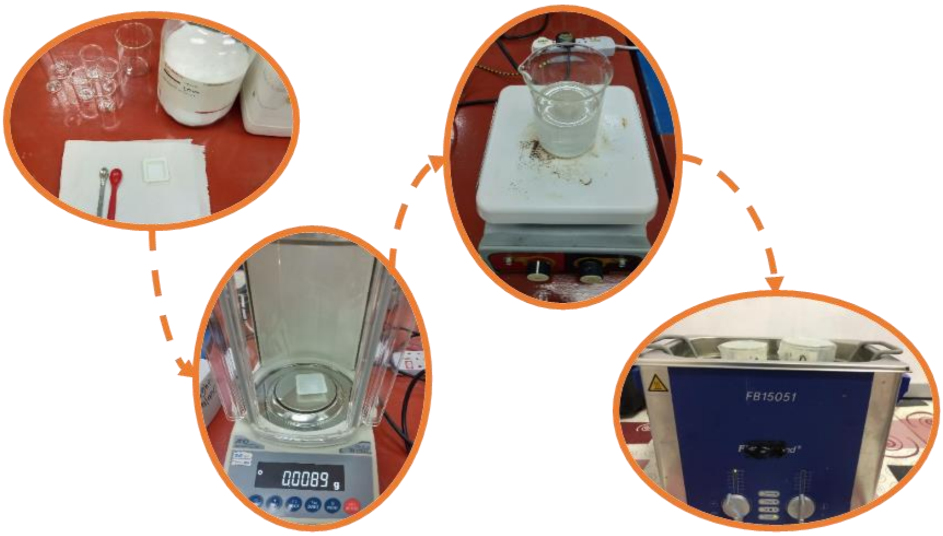


Figure 2. Flowchart of Nanolubricant Preparation

4. Tribological Properties Measurement

Figure 3 illustrates the ASTM D4172-94 standard-compliant Koehler Four-ball Tribo Tester used to evaluate the COF and wear rate of the TiO_2-SiO_2/PAO nanolubricants. Starting with pure PAO lubricant, the tribology measurement was then performed with 0.01% and 0.05% volume concentrations of TiO_2-SiO_2/PAO nanolubricant. The test specifications for the ASTM D4172-94 standard are shown in Table 3. The experiment was undertaken at 75 °C operating temperature for up to 60 minutes. An automated temperature controller was employed to control the heating in order to maintain a consistent temperature for the lubricants. The lever arm was loaded with 40 kg, and the speed was adjusted at 1200 rpm. Pure PAO lubricant and nanolubricants were both tested for friction torque. **Equation 2** was used to calculate the COF using the friction torque from experiment with a constant load for all test situations.

$$\mu = 2.23004 \frac{\tau}{F_N} \quad (2)$$

Where μ is the COF, τ is the experimental friction torque in kg·cm and F_N is a constant normal load in kg. The tools and balls should be cleaned before testing using a solvent such as hexane or heptane.

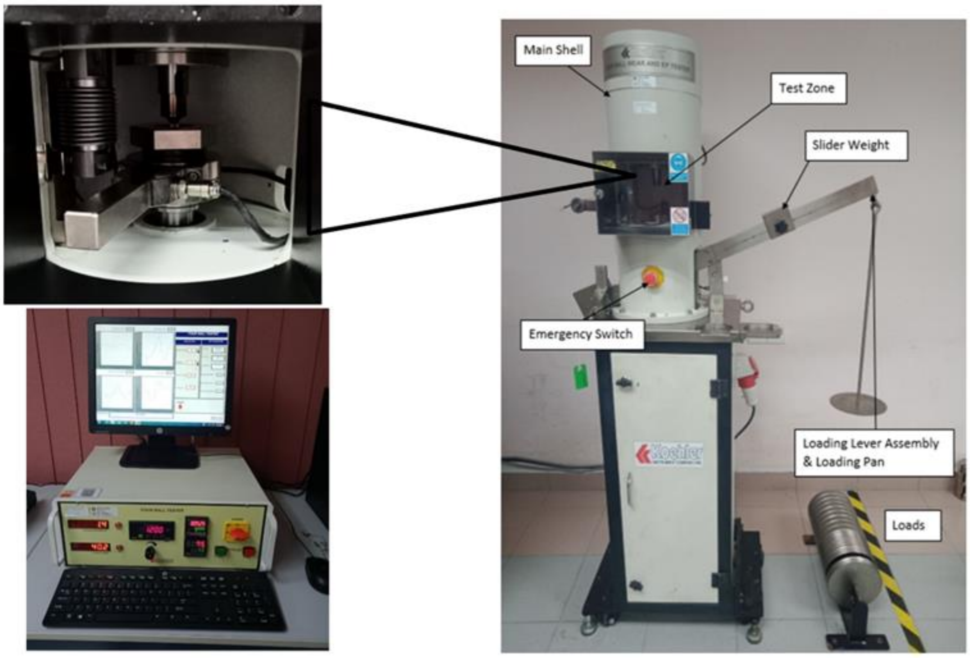


Figure 3. Four-Ball tribology tester and temperature controller

Table 3. The ASTM D4172-94 test specifications

ASTM Standard	Test Specifications			
	Speed (rpm)	Load (kg)	Duration (minutes)	Temperature (℃)
D4172-94	1200 ± 60	40.0 ± 0.2	60 ± 1	75 ± 2

5. Result and Discussion

5.1. Observation Sedimentation Analysis

Figure 4 displays the nanolubricant samples at various volume concentrations for up to 30 days. The hybrid SiO_2-TiO_2/PAO nanolubricant at volume concentrations of 0.01% and 0.05% was stable without sedimentation. Overall, observation showed that even up to 30 days following preparation, there was no discernible separation between the PAO-based lubricant and nanoparticles. It should be emphasised that none of the nanolubricants were prepared with surfactants. Agglomeration decreased the stability of the nano mixture, preventing it from acting as a high anti-friction lubricant as compared to the PAO-based lubricant. The AAC systems may experience decreased performance because of agglomeration since it increases wear and tear. Consequently, the nanoparticles settled down in the system, resulting in increased friction, and the ideal condition of nanolubricants must be established before they can be used. According to visual observation, the SiO_2-TiO_2/PAO exhibited an excellent stability condition for 0.01% and 0.05% volume concentration. Further investigation of these findings was evaluated quantitatively in the next section using a UV-Vis spectrophotometer.

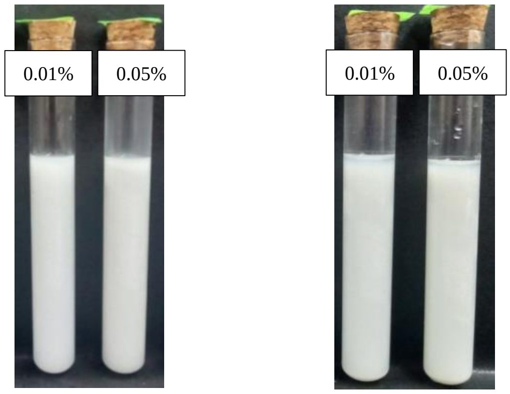


Figure 4. Observation of sedimentation for up to 30 days post-preparation.

5.2. UV-Vis Sedimentation Analysis

Following preparation, the particle shape at various concentrations was examined. The UV-vis spectrometer sedimentation testing first investigated the wavelength for particular peak absorbance of the SiO_2-TiO_2/PAO nanolubricant at 0.01%. According to their absorbance measurements, all nanolubricants exhibited the typical absorption in the 200–400 nm wavelength range. At a wavelength of 286 nm, the peak absorption was shown to be observed. Consequently, the absorbance value of SiO_2-TiO_2/PAO was examined using the peak wavelength. The appropriate sonification time needed to produce outstanding stability was also determined using the UV-Vis spectrometer investigation, which was also performed. To accomplish this, the same SiO_2-TiO_2/PAO nanolubricant concentration was created for various sonification process time durations. **Figure 5** shows the curve of the absorbance ratio across the hours of sedimentation for eight samples (0 to 7H). The graph shows that the absorbance ratio is related to sonication time and decreases with sedimentation time. The particles would settle out increasingly as time passed, affecting the nanolubricants' performance. The 2H sample was observed as the best or ideal sonication period for SiO_2-TiO_2/PAO nanolubricant to achieve stability. The absorbance ratio for the 2H sample remained stable above 80% during the sedimentation period up to 168 hours. This finding is also supported by similar previous work in the literature [8, 21].

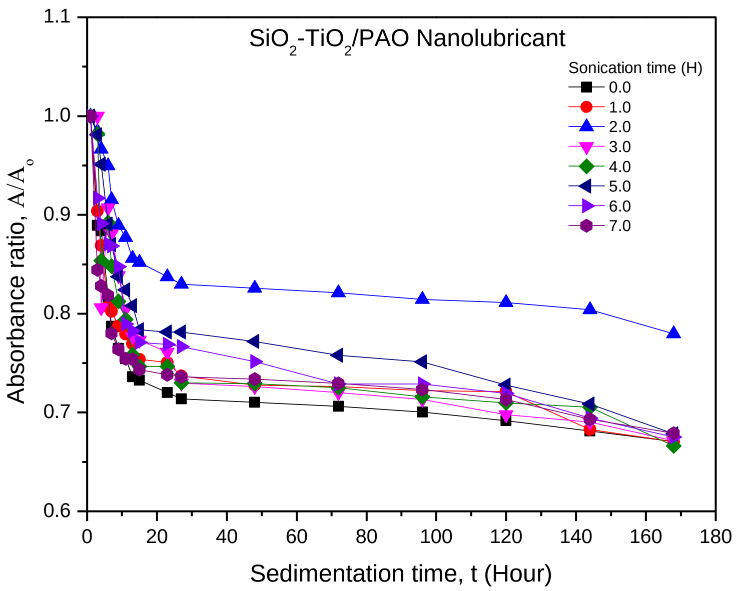


Figure 5. UV-Vis spectrometer of different concentrations.

5.3. Coefficient of Friction Analysis

Figure 6 presents the COF for the hybrid nanolubricant for different volume concentrations. Not all volume concentrations of the hybrid nanolubricants exhibit COF lower than the PAO-based lubricants. With a volume concentration of 0.01%, the hybrid nanolubricant maintains a more significant friction-reduction capability than PAO-based lubricants. This condition illustrates that nanoparticles may efficiently increase the friction-reduction capabilities of the basic lubricant [25]. In addition, the lubricant function reduces friction; by means, the lower the number of COF, the better the lubricant's performance. The figure shows that the average value of COF for PAO is 0.079, while for hybrid nanolubricants with volume concentration at 0.01% and 0.05%, were 0.077 and 0.080, respectively. The COF ratio of hybrid nanolubricants was observed to be 0.97 and 1.01 at volume concentrations of 0.01% and 0.05%, respectively. The COF was decreased at 0.01% volume concentration, while the COF increased as volume concentration increased. The highest COF reduction of 2.53% for hybrid nanolubricant was obtained at 0.01% volume concentration. The decrease of COF in this study was also similar to that presented by Guo, et al. [26]. The addition of nanoparticles to lubricants aids in forming a thin layer of tribo-film that separates the two surfaces that are in contact [26, 27]. Nevertheless, high concentrations of nanoparticles may contribute to the instability of the nanolubricant mixture, such as agglomeration.

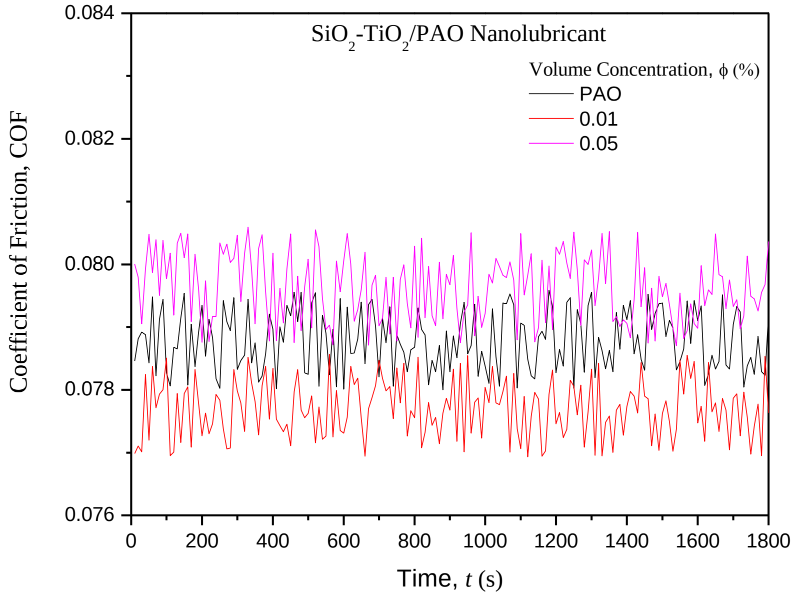


Figure 6. Coefficient of Friction for Hybrid Nanolubricants

The effect of SiO_2-TiO_2/PAO concentration on the average COF is shown in **Figure 7**. The graph demonstrates that lowering the COF will occur as concentration increases. The pattern of decreasing concentration persisted up to 0.01% vol. This might result from the formation of tribo-film on worn surfaces, a solid lubricant filling the gap, or an exceedingly thin lubricating layer that reduces shear stress. The mobility of nanoparticles between the contact surfaces, which transforms pure sliding friction into rolling friction due to reduced interfacial frictional surface action [28], is a nanoparticle mechanism that might lead to a drop in average COF and achieved optimal tribological performance. Furthermore, the observed behaviour can be attributed to the synergistic qualities exhibited by SiO_2-TiO_2 hybrid nanolubricants [29]. Consequently, this leads to a reduction in the average COF for hybrid nanolubricants. While COF reduced when nanoparticles were added to the lubricant, the positive influence on COF value decreased as volume concentration increased. The graph points out that after 0.01% volume concentration, the COF value again increases as the volume concentration of the nanolubricant increases and, in agreement with Zawawi, et al. [30]. According to Zawawi, et al. [30], One of the most important criteria is the optimal concentration of nanoparticles, because an excessive concentration would have a detrimental influence on the COF. The SiO_2-TiO_2/PAO nanolubricant at a volume concentration of 0.01% is therefore the ideal concentration, and any further studies on the performance of the AAC system should use this concentration.

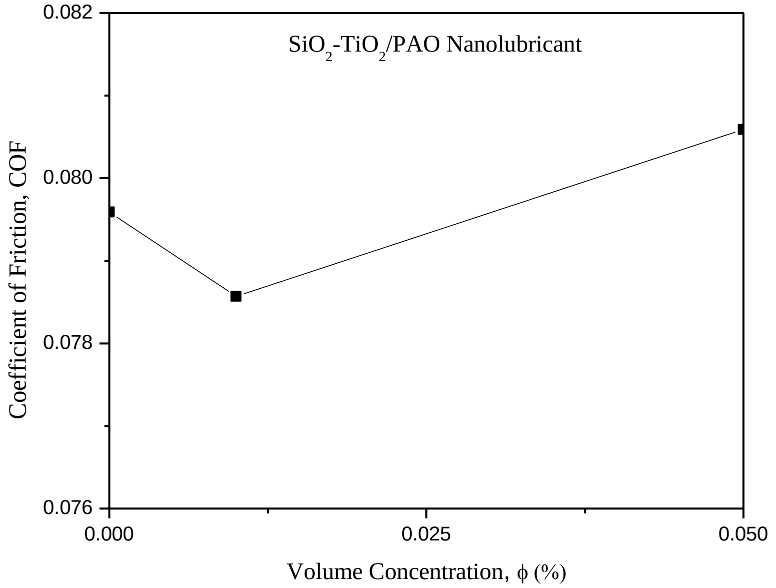


Figure 7. The influence of volume concentration on the COF

6. Conclusions

The friction coefficients of SiO_2-TiO_2/PAO hybrid nanolubricants were measured at 0.01% and 0.05% and 1200 rpm with a load of 40 kg. All nanolubricants did not exhibit sedimentation after 30 days. Upon sedimentation, the 2H sonication sample maintained a sedimentation ratio of over 80% within 180 hours of sedimentation. The SiO_2-TiO_2/PAO hybrid nanolubricant with a volume concentration of 0.01% showed the highest reduction in COF at 2.53% or 0.97. Accordingly, the SiO_2-TiO_2/PAO hybrid nanolubricant with a volume concentration of 0.01% in air conditioning systems is recommended. Further study on the tribological performance of hybrid nanolubricants comprised of SiO_2-TiO_2/PAO hybrid nanolubricants is necessary to extend the current research. It is also advised that future studies focus on investigating the efficacy of hybrid nanolubricants in conjunction with ecologically friendly refrigerants, such as R1234yf. In addition, future study includes a feasibility evaluation of hybrid nanolubricants utilising an AAC with electrically driven compressor (EDC) system is suggested.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Credit Authorship Contribution Statement

N.N.M. Zawawi and R.I.R. Norazura: Conceptualization, Methodology, Writing-Original draft preparation. N.N.M. Zawawi: Data curation, Investigation, Writing-Reviewing and Editing. W.H. Azmi: Visualisation, Supervision, Validation, Writing- Reviewing and Editing.

Acknowledgements

The authors appreciate the financial support provided by Universiti Malaysia Pahang under the Distinguished Research Grant (RDU223021) and additional financial support under the Postgraduate Research Grant Scheme PGRS220387. The authors further acknowledge the contributions of the research teams from the Center for Research in Advanced Fluid and Processes (Pusat Bendalir) and the Advanced Automotive Liquids Laboratory (AALL), who provided valuable insights and expertise to the current study.

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