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Research Paper

Tribology Performance of TiO_2-SiO_2/PVE Nanolubricant at Various Binary Ratios for the Automotive Air-conditioning System

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Abstract

Tribological properties are crucial for air-conditioning system performance. The properties can be improved using nanolubricant. However, the effect of the binary ratio of hybrid nanolubricants on the tribological performance of automotive systems is limited in the literature. Therefore, the present study investigates the tribology performance of TiO_2-SiO_2 nanolubricants for application in automotive air-conditioning (AAC) systems. The dispersion of TiO_2 and SiO_2 into PVE lubricant was carried out using a two-step method. Subsequently, the dispersion stability was assessed qualitatively and quantitatively. The samples were characterised by a volume concentration of 0.010%, with variations in the mixture ratio of 20:80, 40:60, 50:50, 60:40, and 80:20. Coefficient of friction (COF) and wear scar diameter (WSD) values were determined using the Koehler Four-ball Tribo Tester and Light Compound Microscopy. The investigation revealed that each sample experienced a reduction in COF, with the 40:60 ratio demonstrating the best ratio with the most significant decrease of 37.09%. At the same time, the COF decreased by 8.34%, 2.12%, 7.37%, and 15.11% for the nanolubricant samples at 20:80, 50:50, 60:40, and 80:20, respectively. The WSD evaluation showed that the 40:60 ratio has the lowest scar diameter of 0.0344 mm and a 37.09% wear rate decrease compared to pure lubricant. Each sample exhibits superior performance when evaluated for tribological characteristics and performance, particularly in the case of nanolubricants with the 40:60 ratio. The TiO_2-SiO_2/PVE, characterised by a volume concentration of 0.010%, has remarkable efficacy across different binary ratios, making it highly recommended with a 40:60 ratio for lubricating AAC compressor systems.

Keywords: Nanolubricant; Air-conditioning System; Tribology; Coefficient of Friction; Wear Scar Diameter

1. Introduction

Reducing friction and improving lubrication in tribosystems are long-term environmental goals for the automotive industry, component suppliers, and lubricating oil makers. These objectives seek to increase component longevity, reduce wear, and boost overall efficiency. Moreover, the lubrication system plays a crucial role in automotive design and undergoes periodic advancements [1]. The lubrication system's primary function is to prevent wear on the sliding components and maintain stability during machine operation. Nevertheless, it remains common to encounter lubricants that exhibit sliding contact failure due to wear on the sliding boundary surfaces. However, it is essential to note that the fundamental concept underlying the performance of lubrication systems is the provision of lubrication to moving surfaces to minimise gas leakage [2]. Hence, carefully selecting oils and refrigerants is important in compressors, particularly automotive air-conditioning (AAC) systems [3].

The selection criteria for an appropriate lubricant have a notable influence, including the potential for energy conservation and the preservation of optimal performance in compressor components [4], [5]. The presence of specific indicators can serve as evidence of a well-functioning lubrication system, such as an observed rise in the coefficient of performance (COP) and a correspondingly low coefficient of friction (COF) [6]. One potential method for improving a compressor's performance involves reducing the COF, consequently increasing overall performance [7], [8]. An analysis of friction and wear in the reciprocating mechanism of nano additives in increasing the COP of a compressor air conditioning system was conducted by Yilmaz [9]. Compared to pure compressor lubricants, adding 0.5 vol% Cu/Ag alloy nanoparticles to CuO nanolubricants increased COP by 20.88% and 14.55 %. The COF for the lubricants with CuO dispersion was 5.5% and 9.9% lower than those without CuO. Thus, using nanoparticles to enhance the efficiency of air-conditioning systems has facilitated the emergence of research potential.

Presently, there is an increasing trend to enhance the performance of the compressor system by incorporating nanoparticles into fluids [10] and lubricants [11]–[14]. The utilisation of nanolubricants in AAC systems has been well acknowledged for its ability to enhance their efficiency and performance. Moreover, using nano additives results in enhanced tribological performance due to generating rolling effects and forming protective layers. Therefore, it is necessary to evaluate the correlation between the tribological characteristics of nanolubricants and the performance of the AAC system. In a separate experimental study conducted by Ismail, et al. [15], the researchers investigated the effects of incorporating SiO_2/PVE and TiO_2/PVE hybrids with volume concentrations of 0.005 vol.% and 0.015 vol.%, respectively. The findings of this study revealed a notable reduction in the COF by up to 15%. A friction analysis for alternative nanolubricants was conducted by incorporating nanoparticles of SiO_2, TiO_2, and Al_2O_3 into the compressor polyalkylene glycol (PAG) lubricant. The results indicated a favourable outcome, as adding these nanoparticles reduced COF by 23.8%, 15.8%, and 2.3%, respectively [16]. Incorporating Al_2O_3 nanoparticles with a volume concentration of 0.5% into a lubricant compressor base, such as SAE10W40, significantly reduced the COF by 22.67%. Additionally, the diameter of the worn scar was decreased by 20.75% [16].

The concentration, lubricant type, and composition of nanolubricants have emerged as a prominent and evolving area of research. The purpose of these investigations is to enhance the performance of compressors. However, experiments that specifically investigate hybrid nanolubricants with varying mixing ratios are scarce. Zawawi, et al. [17] studied the friction and wear analysis, employing Al_2O_3-SiO_2 dispersed in polyalkylene glycol (PAG). The researchers observed that the COF value and wear rate exhibited an ideal drop to 4.49% and 12.99%, respectively, when the volume concentration was set at 0.02% and the mixture ratio was 60:40. The experimental hybrid nanolubricant, as revealed in recent findings, exhibited exceptional performance. Hamisa, et al. [7] conducted a tribological investigation on air conditioning compressors using microscopes and Koehler four-ball tribo testers. TiO_2 and SiO_2 nanoparticles were dispersed at a 0.01 to 0.1% volume concentration in polyolester (POE) lubricant. The results indicated a 31.6% decrease in COF, while the wear scar diameter (WSD) investigation revealed a 12.4% decrease at a volume concentration of 0.03% and a 50:50 ratio.

Nevertheless, there is currently a lack of study on the impact of the mixture ratio of hybrid nanolubricants, namely TiO_2-SiO_2/PVE, on the tribological performance of automotive systems. Hence, the primary objective of this study was to investigate the effect of varying the mixture ratio of hybrid nanolubricants on the tribological performance of lubrication within the system. The investigations were conducted by formulating PVE nanolubricants with exceptional stability. Subsequently, a study was carried out to assess the compressor's friction torque and COF. This analysis used hybrid nanolubricants at different binary ratios, specifically 20:80, 40:60, 50:50, 60:40, and 80:40, with a volume concentration of 0.010%. In addition, a comparison was made with lubricating oil devoid of nanoparticles. The investigation was undertaken utilising a Four-ball

Tester tribology machine. Then, the worn surfaces and wear scars' diameter were analysed using light compound microscopy.

2. Materials and Methods

2.1. Nanolubricant Properties

The nanoparticles utilised in this experimental study consisted of TiO_2 and SiO_2. The typical diameter of TiO_2 nanoparticles is reported to be 50 nm, while SiO2 nanoparticles exhibit a diameter of 30 nm. The SiO_2 and TiO_2 nanoparticles were acquired from DKNANO and HWNANO, respectively. The TiO_2 and SiO_2 nanoparticles obtained had a high purity level of 99.9% with an average size of 50 and 30 nm, respectively. The lubricant employed in this investigation was the Polyvinyl ether (PVE) variety. The PVE oil utilised in the research was procured from Idemitsu Kosan Co., Ltd. This lubricant is prevalent in refrigeration and air conditioning systems that employ hydrofluorocarbon (HFC) cooling compressors. **Table 1** shows the specification of the lubricant PVE, or FVC68D [18], [19]. FVCD68D is part of PVE, where the chemical Polyvinyl ether is the primary ingredient and other additional ingredients with a viscosity of 68. **Table 2** presents the parameters of TiO_2 and SiO_2 nanoparticles, with respective density values of 4230 and 2220 kg/m³.

The process of hybrid nanolubricants preparation involved the dispersion of TiO_2 and SiO_2 nanoparticles into the PVE lubricant through a magnetic stirrer and agitation technique employing an ultrasonic bath. The two-step method [5], [20], [21] is frequently utilised to prepare hybrid nanofluids, and the nanoparticle volume concentration is calculated using Equation 1 [22].

Table 1. Properties of Polyvinyl Ester (PVE) Lubricant

Property	PVE
Dynamic Viscosity, mm²/s @ 40 °C	66.6
Pour Point, °C	-37.5
Flash point, °C	204
Density, g/cm³ @ 15 °C	0.9369

Table 2. Properties of TiO_2-SiO_2 nanoparticles

Property	TiO_2	SiO_2
Density, [kg/m³]	4230	2220
Molecular mass, [g/mol]	79.87	60.08
Average particle diameter, [nm]	50	30
Specific heat, [J/kg·K]	692	745

$$\phi = \frac{\left(\frac{m_{np}}{\rho_{np}}\right)}{\left(\frac{m_{np}}{\rho_{np}} + \frac{m_l}{\rho_l}\right)} x100\% \quad (1)$$

Where ϕ is volume concentration, m_{np} and ρ_{np} are the mass and density of the nanoparticle, respectively, while m_l and ρ_l are the mass and density of the PVE lubricant. The preparation of TiO_2-SiO_2/PVE hybrid nanolubricants commences with the individual mixing of TiO_2/PVE and SiO_2/PVE lubricants at predetermined binary ratios and volume concentrations. The binary ratios of TiO_2-SiO_2/PVE hybrid nanolubricants were assigned as 20:80, 40:60, 50:50, 60:40, and 80:20 while maintaining a constant volume concentration of 0.01%. Subsequently, the nanolubricants were combined within a single beaker and subjected to agitation using the magnetic stirrer for 1800 seconds. Later, homogenisation was carried out using the ultrasonic water bath for seven hours. This step was done to aid in nanoparticle dispersion, resulting in uniformly distributed nanoparticles that enable a sustained and stable dispersion. The stability of the nanolubricant prepared is significantly influenced by the duration of sonication [23]. Appropriate safety measures were taken while preparing nanolubricants, and sufficient personal protective equipment (PPE) was used.

2.2. Stability of TiO_2-SiO_2/PVE

The nanoparticle dispersion in lubricants results in increased collision probabilities and aggregation tendencies, which subsequently contribute to the sedimentation and obstruction of microchannels. Therefore, various traditional approaches have been developed to evaluate dispersions' dispersion properties and stability [24], [25]. The present work utilises a sedimentation method, spectral absorbency analysis, and zeta potential analysis to assess the dispersion characteristics and stability of hybrid nanolubricants. The sedimentation method is a visual technique used to analyse the changes in nanolubricant or process sedimentation. It is a significant approach for visually assessing the dispersion stability of nanolubricants. The stability was then evaluated with an Ultraviolet-Visible (UV-Vis) spectrophotometer. The UV-Vis used in this analysis is the Drawell DU-8200; the wavelength range is 190 to 1100 nm, and the wavelength accuracy is ±0.8 nm. Accuracy is a consideration because UV-Vis has an essential role in analysing the stability of nanolubricants [26], [27].

Qualitative measurements were carried out to measure the stability of the TiO_2-SiO_2/PVE hybrid nanolubricant using the Zeta potential. The importance of zeta potential lies in its capacity to provide insights into the stability of colloidal dispersions [28]. The zeta potential value is an excellent predictor of nanolubricant stability. A high zeta potential value of a suspension indicates a more vital repulsive force that prevents particles from colliding and forming aggregates [29]. The zeta potential assessment is conducted via the Anton Paar Zeta Potential Litesizer 500. Before this procedure, the input parameters for the PVE lubricant, including refractive index, viscosity, and relative permittivity, were determined. Then, the category was evaluated: 0 to 30 mV is considered stability, 30 to 60 mV is considered acceptable stability, and more than 60 mV is considered exceptional stability [30]–[32].

2.3. Tribology Properties Measurement

The tribological performance of nanolubricant was assessed by employing a Koehler four-ball tribo tester. This experimental setup was utilised to evaluate the coefficient of friction and wear prevention capabilities of TiO_2-SiO_2/PVE hybrid nanolubricants. **Figure 1** depicts the Koehler four-spherical tribo tester, designed per the ASTM D4172-94 standard. The study utilised steel spheres with a diameter of 12.7 mm and a Rockwell C hardness (HRC) of 60 ± 0.2 (chromium steel, grade G20, ISO 3290). Initially, the tribology evaluation using pure lubricants was conducted, followed by the subsequent investigation using TiO_2-SiO_2/PVE hybrid nanolubricants with a volume concentration of 0.01% at different binary ratios. The measurements were performed following the standard operating procedures outlined in ASTM D4172-94. The worn materials WSD were quantified following each test using optical microscopy (Light Compound Microscopy). The wear characteristics and test conditions for standard ASTM D4172-94 are shown in **Table 3**.

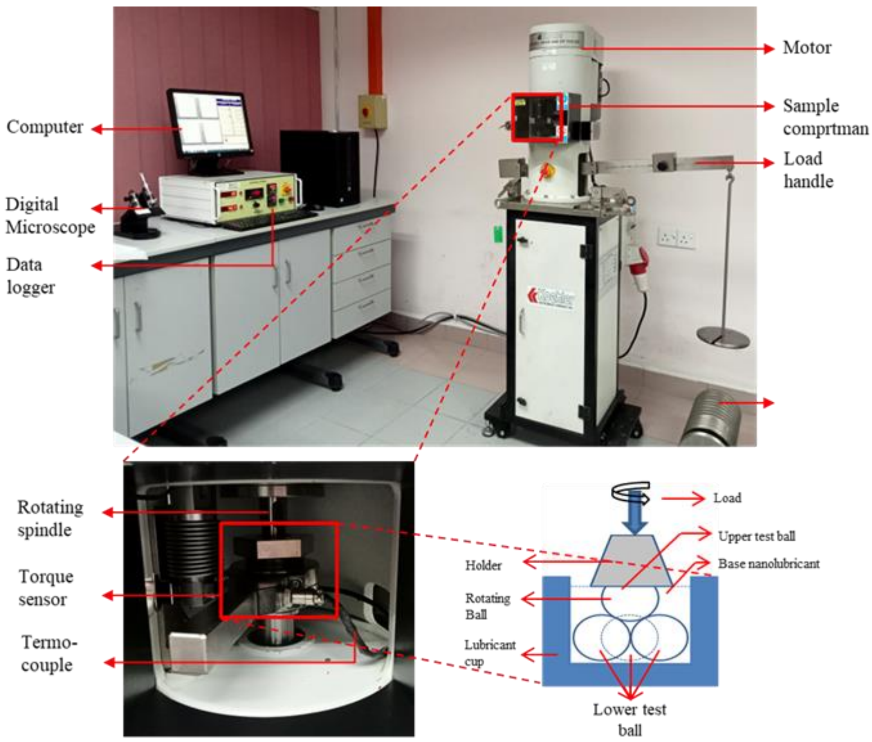

Figure 1. Tribology test using the Koehler four-ball tribo tester

Table 3. Wear characteristics and test condition for the ASTM D4172-94 standard.

ASTM Standard	Method	Test Condition			
		Speed (rpm)	Load (kg)	Duration (m)	Temperature (°C)
ASTM D4172-94	Wear Characteristics	1200 ± 60	40.0 ± 0.2	60 ± 1	75 ± 2

3. Results and Discussion

3.1. Stability Evaluation

The stability of the TiO_2-SiO_2/PVE hybrid nanolubricant was assessed by both qualitative and quantitative evaluations. The stability assessment encompassed visual sedimentation observations, UV-Vis analyses, and zeta potential measurements. **Figure 2** depicts the experimental setup wherein hybrid nanolubricant samples were subjected to a static condition for 30 days at room temperature. Visual observation of the nanolubricant samples carried out on the first day showed that the nanoubricant samples were in normal condition and no agglomeration occurred. Furthermore, findings from the image observations indicate that the nanolubricant sample exhibited limited sedimentation after 30 days. However, it is essential to note that this occurrence might be attributed to the impact of gravitational forces acting on the particles as they fell within the test tube [24].

The evaluation of the stability of the nanolubricant samples was subsequently conducted using UV-Vis analysis. The findings of the study of each sample experiencing stability up to 700 hours are depicted in **Figure 3**. Each hybrid nanolubricants demonstrated stability above a 65% absorbance ratio for up to 700 hours following its preparation, with the most notable performance seen in the mixture ratio of 40:60. This was followed by the 50:50, 20:80, 60:40, and 80:20 binary ratios in descending order of effectiveness.

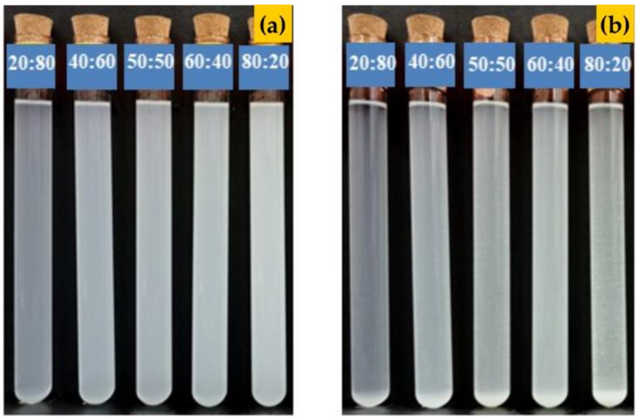

Figure 2. Visual observation at different binary ratios of nanolubricants (a) First day of preparation samples (b) Samples after 30 days of preparation

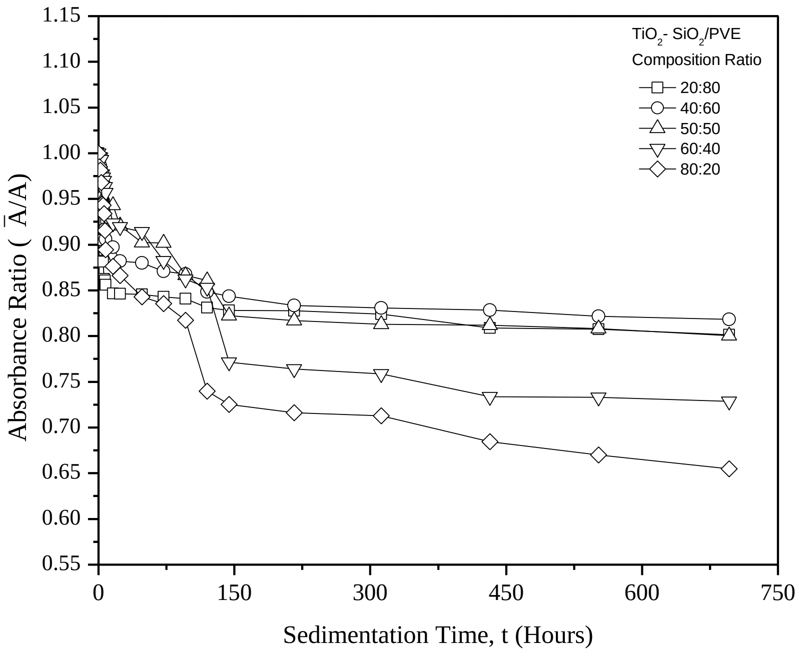

Figure 3. UV-Vis evaluation at different binary ratios of nanolubricants

The zeta potential measurement for TiO_2-SiO_2/PVE hybrid nanolubricants is depicted in Figure 4. All samples have exhibited a notable degree of stability. The assessment findings indicate that the hybrid nanolubricants with a ratio of 60:40 achieved the most excellent zeta potential value of 212.884 mV. Although the 20:80 ratio exhibits 108.235 mV lower than other hybrid nanolubricants, it remains within the range associated with exceptionally high stability, according to Ghadimi, et al. [30]. During the UV-Vis analysis conducted, it was seen that the mixture ratio of 40:60 exhibited the highest absorbance ratio value. This finding was then validated by the zeta potential measurement, which yielded a value of 201.573 mV. Based on these results, the 40:60 mixture ratio was classified as having excellent stability. While the 60:40 ratio had a greater zeta potential value, it exhibited a lower absorbance ratio than the 40:60 ratio when using UV-Vis measurement. Hence, the 40:60 mixture ratio selection for further experimentation was based on its compliance with both UV-Vis and zeta potential measurements.

3.2. Coefficient of Friction

Figure 5 shows the COF of hybrid nanolubricants for various binary ratios. The experimental findings indicated a maximum reduction of 24.19% in the COF when the 40:60 mixture ratio was employed compared to the PVE-based oils. The hybrid nanolubricants with a 50:50 ratio exhibit a minimum reduction percentage of 2.12%. Meanwhile, the other binary ratios of 20:80, 60:40, and 80:20 demonstrate average COF reduction percentages of 8.34%, 7.37%, and 15.11%, respectively. Based on the experimental assessment conducted on tribology, it can be inferred that the hybrid nanolubricants showed enhanced performance compared to the PVE-based lubricant. Notably, the hybrid nanolubricant with a ratio of 40:60 presented the most favourable outcomes. The uniform distribution of various nanoparticle types and binary ratios inside the lubricant, which causes the filling of surface gaps, is one of several causes for the observed phenomena.

Consequently, this decreases the frictional force exerted on the contacting balls [33]. Additionally, the nanoparticles employed in this investigation exhibit a spherical or quasi-spherical morphology, resulting in a rolling motion when interacting with the frictional surface. The findings suggest that the TiO_2-SiO_2/PVE nanolubricant with a 40:60 ratio can generate reduced load conditions during the frictional interaction between sliding surfaces.

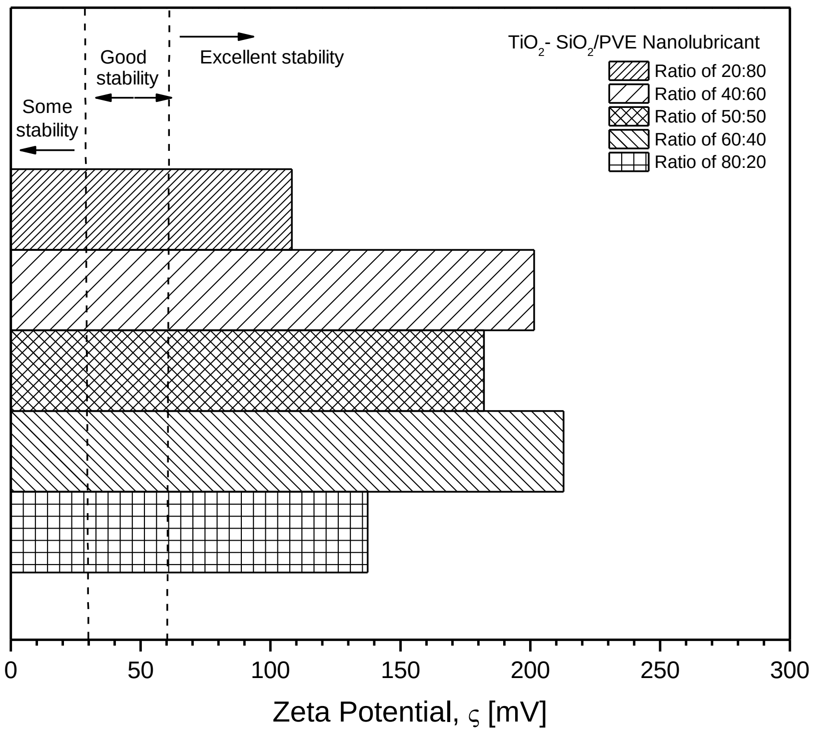

Figure 4. Zeta potential of nanolubricants with variation binary ratios

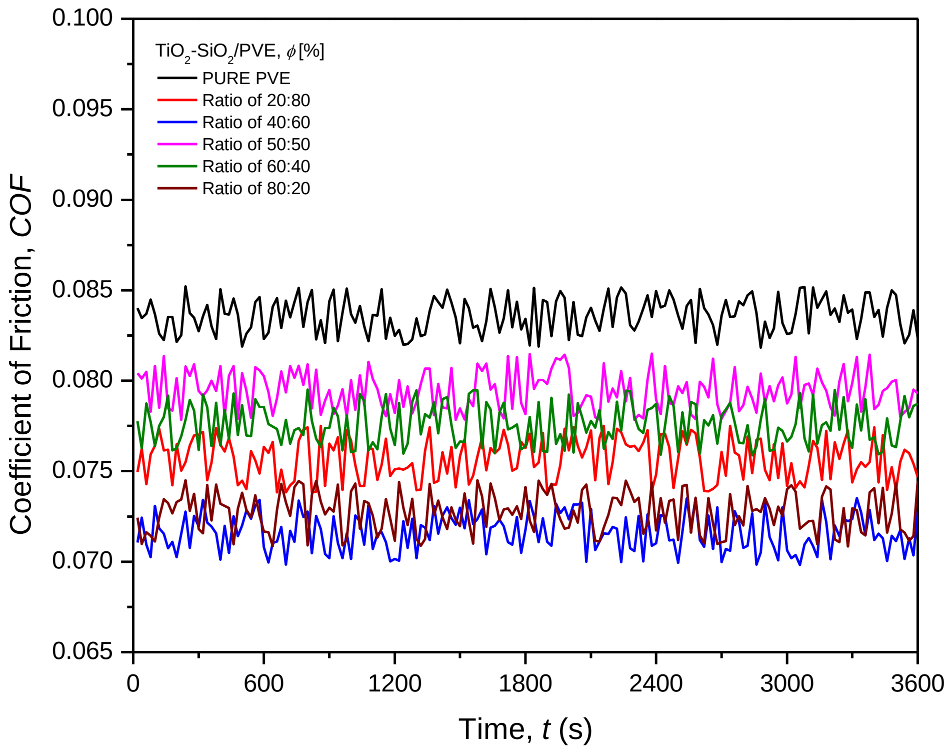

Figure 5. COF of nanolubricants for various binary ratios

3.3. *Wear Scar Diameter*

Figure 6 illustrates the WSD of worn balls following four-ball testing using hybrid nanolubricants with varying binary ratios. Scars resulting from wear exhibit common features, notably the presence of pits that serve as indicators of adhesive wear phenomena. The hybrid nanolubricants showed mostly shallower grooves and more polished surfaces. The observed improvement in surface smoothness with the hybrid nanolubricant may be attributed to the concurrent rise in wear rate [34], as evidenced by the corresponding increase in WSD. The WSD of the worn balls indicated that the ball lubricated with pure PVE had an increment in wear rate compared to the other samples. However, a notable decrease in WSD was seen with hybrid nanolubricants. The reduction in the WSD value compared to the value obtained for pure PVE can be attributed to the efficient lubrication during the testing procedure.

The findings of the WSD exhibit a notable correlation with the COF, wherein samples with a ratio of 40:60 demonstrate the least friction. On the other hand, the remaining samples with different binary ratios exhibited decreased WSD values compared to PVE, but they were not as effective as the 40:60 ratio. **Table 4** presents the same WSD results as in **Figure 6**, however to make the presentation clearer, the WSD legend is arranged again in a tabular form.

This finding demonstrates that every sample of nanolubricants shows anti-wear characteristics, resulting in a reduction in friction and the formation of minor abrasions. Examining the nanolubricant sample with a 50:50 ratio does not guarantee to achieve the lowest WSD value in anti-wear behaviour. Conversely, the sample with

Table 4. The WSD result of experiments tribology with binary ratio variation

Sample	Wear Scar Diameter		
	Radius (mm)	**Area (Sqmm)**	**Perimeter [mm]**
PVE Pure	0.0531	0.0089	0.3339
20:80	0.0359	0.0045	0.2381
40:60	0.0334	0.0035	0.2099
50:50	0.0406	0.0052	0.2564
60:40	0.0377	0.0045	0.2367

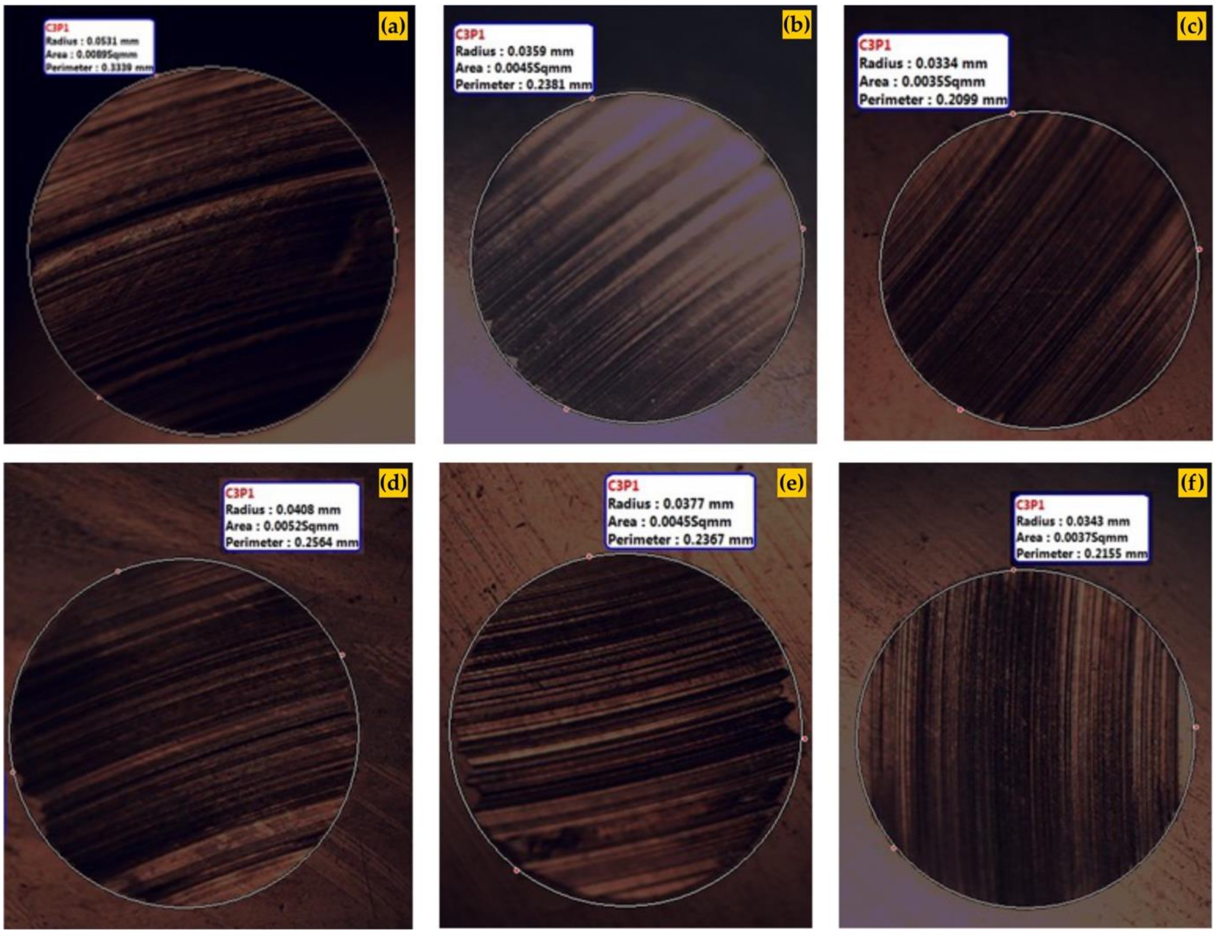

Figure 6. WSDs of worn balls following the four-ball test with binary ratio variation: (a) PVE Pure; (b) Ratio of 20:80; (c) Ratio of 40:60; (d) Ratio of 50:50; (e) Ratio of 60:40 and (f) Ratio of 80:20

an 80:20 ratio exhibits a superior WSD value. However, the ratio of suitability factors has an important meaning in determining the best WSD results. The assessment findings indicated that samples with a ratio of 40:60 at a volume concentration of 0.010% exhibited superior performance in terms of friction reduction and minimising surface abrasions during sliding. Hence, it is recommended that the assessment of ratios be given due consideration instead of only focusing on volume concentration, as is typically done.

Figure 7 illustrates the reduction percentage in WSD by applying TiO_2-SiO_2/PVE nanolubricant. The assessment findings indicated that the hybrid nanolubricant sample with a binary ratio of 40:60 exhibited the greatest decrease percentage compared to the remaining samples, precisely measuring 37.09%. Regarding further samples, such as the ratios 20:80, 50:50, 60:40, and 80:20, their respective reductions of 32.39%, 23.54%, 29.00%, and 35.40% were observed. The assessment findings showed a decrease in the WSD of the sample, suggesting an improvement in the lubricant's performance. This finding may be attributed to the reduced frictional impact exerted on the ball [35], [36].

4. Conclusions

A two-step process was used to disperse TiO_2 and SiO_2 nanoparticles into PVE base lubricants. Based on photographic observations, UV-Vis analysis, and zeta potential measurement, the stability of the hybrid nanolubricants was determined. The results indicate that the sample with a 40:60 ratio is more stable than the other samples. In addition, a qualitative evaluation of zeta potential reveals that the yield of the 40:60 ratio exceeds that of the 60:40 ratio. The tribology experiment showed that the average COF value for the 40:60 ratio was 0.07144, and for other samples, such as the 20:80, 50:50, 60:40, and 80:20 ratios, the average values were 0.0755, 0.0777, 0.0798, and 0.0727, respectively. Evaluation of the

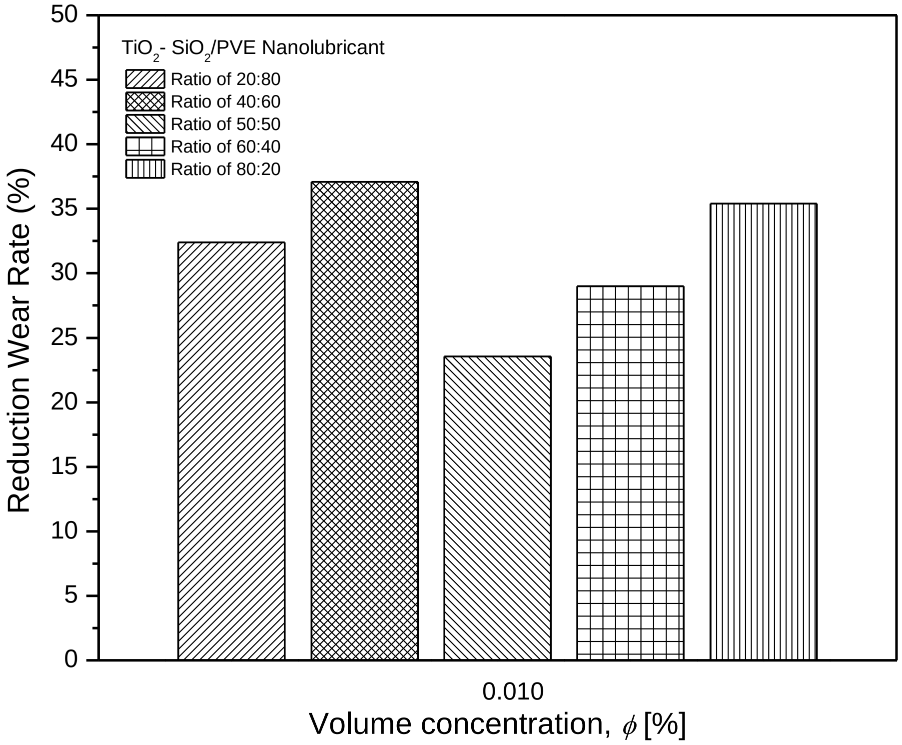

Figure 7. Wear rate reduction using TiO_2-SiO_2/PVE at different binary ratios

WSD value reveals an almost identical trend to the COF evaluation. Compared to the pure base, all samples of hybrid nanolubricant exhibited reduced wear rates. As determined in the assessment, the WSD for nanolubricant samples with ratios of 20:80, 40:60, 50:50, 60:40, and 80:20 was 32.39%, 37.09%, 23.54%, 29.01%, and 35.42%, respectively. Based on the evaluation results of COF and WSD, it can be concluded that the sample exhibiting a combination ratio of 40:60 demonstrates the most favourable outcomes. Hence, it is advisable to utilise TiO_2-SiO_2/PVE hybrid nanolubricants in automotive air-conditioning systems, with a volume concentration of 0.01% and a binary ratio of 40:60. Additional investigation on the others aspect, especially the performance of hybrid nanolubricants is required to enhance the existing knowledge regarding the feasibility of TiO_2-SiO_2/PVE nanolubricants for application in AAC system.

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Author's Declaration

Authors' contributions and responsibilities

The authors made substantial contributions to the conception and design of the study. The authors took responsibility for data analysis, interpretation and discussion of results. The authors read and approved the final manuscript.

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Availability of data and materials

All data are available from the authors.

Competing interests

The authorsdeclare no competing interest.

Additional information

No additional information from the authors.

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