Article

Stability Assessment of Polyvinyl-Ether-Based TiO$_2$, SiO$_2$, and Their Hybrid Nanolubricants

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Abstract: Poor characterisation of nanoparticle suspensions impedes the development of nanolubricants for use in refrigeration and air-conditioning systems. Chemical treatment techniques, such as surfactants, are inappropriate for enhancing the stability of nanolubricants intended for use in vapour-compression refrigeration (VCR) systems. Prior to incorporating nanolubricants into the system, the stability of TiO$_2$ and SiO$_2$ nanoparticles dispersed in PVE was therefore investigated. The nanolubricants were prepared by a two-step method with the aid of an ultrasonication bath homogeniser. Visual observation and ultraviolet–visible (UV–Vis) spectrophotometric analysis were used, and zeta potential analysis was then performed to confirm the nanolubricants' stability condition. The TiO$_2$/PVE nanolubricant was observed to be maintained at a 95% concentration ratio for up to 30 days of evaluation. The TiO$_2$/PVE, SiO$_2$/PVE, and SiO$_2$-TiO$_2$/PVE exhibited zeta potential values of 203.1 mV, 224.2 mV, and 105.3 mV, respectively, after 7 h of sonication. A high absolute value of zeta potential indicates that the electrostatic repulsive forces between nanoparticles are exceptionally strong, indicating an excellent stable suspension. The high values of zeta potentials validated the excellent stability conditions determined by UV–Vis analysis and visual observation. It can be concluded that ultrasonication times of 7 h produced the most stable state for mono- and hybrid nanolubricants.

Keywords: hybrid nanolubricants; polyvinyl ether; refrigeration system

1. Introduction

Cooling and heating are well-known processes that demand energy to fulfil the needs of industries, commercial buildings, and residences. Air conditioners, heat pumps, refrigerators, chillers, and other heating or cooling equipment have become essential in this modern era. With the growth of populations in urban and suburban areas, we must meet the demand for smaller and higher-efficiency devices. An innovative concept of nanofluids has brought a new opportunity to produce such devices, despite other efforts to increase efficiency by enhancing physical components [1–3]. The concept of dispersion of nanoparticles in base fluids has shown tremendous improvement in the heat transfer process for various applications. Today, the advancement of nanofluids has seen additional exploration in multiple applications, such as nanolubricants [4] and nanorefrigerants [5,6]. Sharif et al. [7] reviewed the heat-transfer enhancement mechanism that demonstrated nanolubricants' ability to improve VCR systems' performance. Nanolubricants are one of the relevant areas being explored in nanofluid studies. The dispersion of nanoparticles in engine, machine,

and compressor lubricants has sparked interest in this subject, paving the way for novel nanotechnology applications in this industry. Wang et al. [8] were among the first to present the use of nanolubricants in a VCR system. Following this, numerous investigations of the use of nanolubricants in VCR systems—including domestic refrigerators [9–11], residential air conditioning [12–14], and automotive air-conditioning systems [15]—were undertaken for various applications. All of these applications were distinguished by the base lubricant in their studies. For instance, a domestic refrigerator uses mineral oil (MO) as a lubricant, and residential air conditioning uses polyol ester (POE) lubricant, while automotive air conditioning uses polyalkylene glycol (PAG) lubricant. The type of refrigerant utilised in the application—e.g., hydrochlorofluorocarbon (HCFC)-, hydrofluorocarbon (HFC)-, or hydrocarbon (HC)-based refrigerants—has a significant impact on the lubricant selection. Many research groups have extensively studied mono-nanolubricants [16–18]. Several types of nanoparticles, including Al_2O_3, TiO_2, CuO, and graphite, were dispersed in MO as a base lubricant [9,19–21]. Other popular compressor lubricants used in VCR systems, such as POE, have also attracted much attention for nanolubricant research [13,22,23].

One of the essential aspects that need to be addressed before applying nanolubricants in VCR systems is the stability of nanoparticles in colloidal suspension. This is because the nanoparticles tend to agglomerate due to their large and active surface area. Colloidal chemistry occurs when the critical particle size is reached, the particle remains stable, and no sedimentation occurs [24–26]. Stability and uniformity of nanolubricants can greatly reduce the coefficient of friction and increase thermal conductivity. The settlement time of nanoparticles in colloidal dispersion is one of the crucial issues being discussed [27]. More extended stability approaches are expected to be explored for nanolubricants to gain maximum advantages from the dispersion procedure. Improving the stability of nanofluids is possible by using chemical methods, such as the addition of surfactants, surface modification, or pH adjustments [28]. Moreover, stability can also be improved by physical methods such as ultrasonic agitation, homogenisation, magnetic force agitation, and high-shear mixing [29,30]. However, for nanolubricants—especially for VCR applications—neither surfactant nor surface modification can be adopted, because the lubricant in the VCR system will be compressed together with the refrigerant under high-pressure conditions [31]. Modifying the chemical composition of the lubricant may change its pH value, creating corrosion inside the piping system [32]. The ultimate consequence of this problem is a leaking refrigeration piping system. Therefore, the effort to increase the stability of nanolubricants in the VCR system must be made using alternative approaches.

Utilising two or more nanoparticles in an existing lubricant—known as hybrid or composite nanolubricants—can also increase the stability condition [33], due to the combination of various types of nanoparticles and composition ratios [34], as well as the synergistic effects of different nanoparticles. This method was developed to enhance the heat-transfer characteristics of mono-nanolubricants by combining the thermal and rheological properties of different nanoparticle types. Hybrid nanolubricants aid in improving the physicochemical properties of the lubricant due to the limitations of mono-nanoparticles [35]. Sharif et al. [4] studied the stability and thermal physical properties of Al_2O_3/PAG mono-nanolubricants in an automotive air-conditioning (AAC) system, whereas Redhwan et al. [36] followed up on SiO_2 mono-nanolubricants using the same PAG base lubricant. Later, Zawawi et al. [15] expanded on these findings by using Al_2O_3-SiO_2/PAG hybrid nanolubricants. Interestingly, the dispersion of hybrid nanolubricants has been shown to improve the stability and thermal properties when compared to the mono-nanolubricants. Polyvinyl ether (PVE) lubricant is a relatively new commercial lubricant that is utilised in residential air-conditioning (RAC) systems. Motozawa et al. [37] recently reported the use of CuO nanoparticles in VG68-PVE and explored their thermophysical properties. However, to date, the literature shows that the stability of TiO_2 and SiO_2 mono- and hybrid nanolubricants in RAC systems has not been explored by any researcher. Therefore, this paper aims to evaluate the dispersion behaviour of TiO_2 and SiO_2 nanoparticles in PVE lubricant. A comparison was also made with the hybrid of

both nanoparticles. The stability of the nanolubricants was visually and evaluated using a UV–Vis spectrophotometer. Finally, the zeta potential measurement was performed on the same samples to confirm the nanolubricants' stability.

2. Experimental Methodology

2.1. Material Properties

FVC68D PVE was employed in this study as a base lubricant and was developed by Idemitsu Kosan Co., Ltd (Tokyo, Japan). The FVC68D PVE is a commercially available PVE hermetic compressor for air-conditioning systems that is compatible with both HFC and HC refrigerants [38]. The physical properties of the PVE lubricant are given in Table 1. TiO_2 and SiO_2 nanoparticles with an average size of 50 nm and 30 nm, respectively, were used in the study. TiO_2 with 99.9% purity was procured from HWNANO (Hongwu International Group Ltd., Guangzhou, China), while 99.9% purity SiO_2 was procured from DKNANO (Beijing Deke Daojin Science and Technology Co., Ltd., Beijing, China). Table 2 provides the properties of the nanoparticles used in the present study. Appropriate personal protective equipment (PPE), such as latex gloves, respirators, and goggles, was used by the personnel when handling these nanoparticles. The safety procedure recommended in the material safety data sheet (MSDS) provided by the manufacturer was followed accordingly to prevent and reduce nano-hazard exposure. Transmission electron microscopy (TEM) was used to characterise the nanoparticles' dispersion in hybrid nanolubricants. In the present study, TEM investigation was carried out using a TECNAI G2 F20 X-Twin high-resolution transmission electron microscope (HRTEM) (FEI Company, Oregon, United States). Figure 1 depicts the TEM images of the TiO_2/PVE, SiO_2/PVE, and SiO_2-TiO_2/PVE nanolubricants. The physical attributes, colour, and shapes of the SiO_2 and TiO_2 nanoparticles were found to be comparable. Despite a slight aggregation in the solution, the images show that the SiO_2 and TiO_2 nanoparticles were dispersed randomly. While the TiO_2 nanoparticles were measured between 30 and 50 nm, the SiO_2 nanoparticles had an average size of 30 nm, which is in good agreement with the manufacturer's specifications. The absence of homoagglomeration in the image demonstrates that the hybridisation in the SiO_2-TiO_2/PVE nanolubricant occurred as intended.

Table 1. Physical properties of the FVC68D lubricant [39].

Property (s)	PVE
Appearance	Light yellow
Odour	Characteristic
Physical state	Liquid
Flash point	206 °C/403 °F
Density	940 kg/m^3 @ 15 °C
Viscosity	@40 °C = 66.57 cSt; @ 100 °C = 8.037 cSt

Table 2. Properties of the TiO_2 and SiO_2 nanoparticles [40,41].

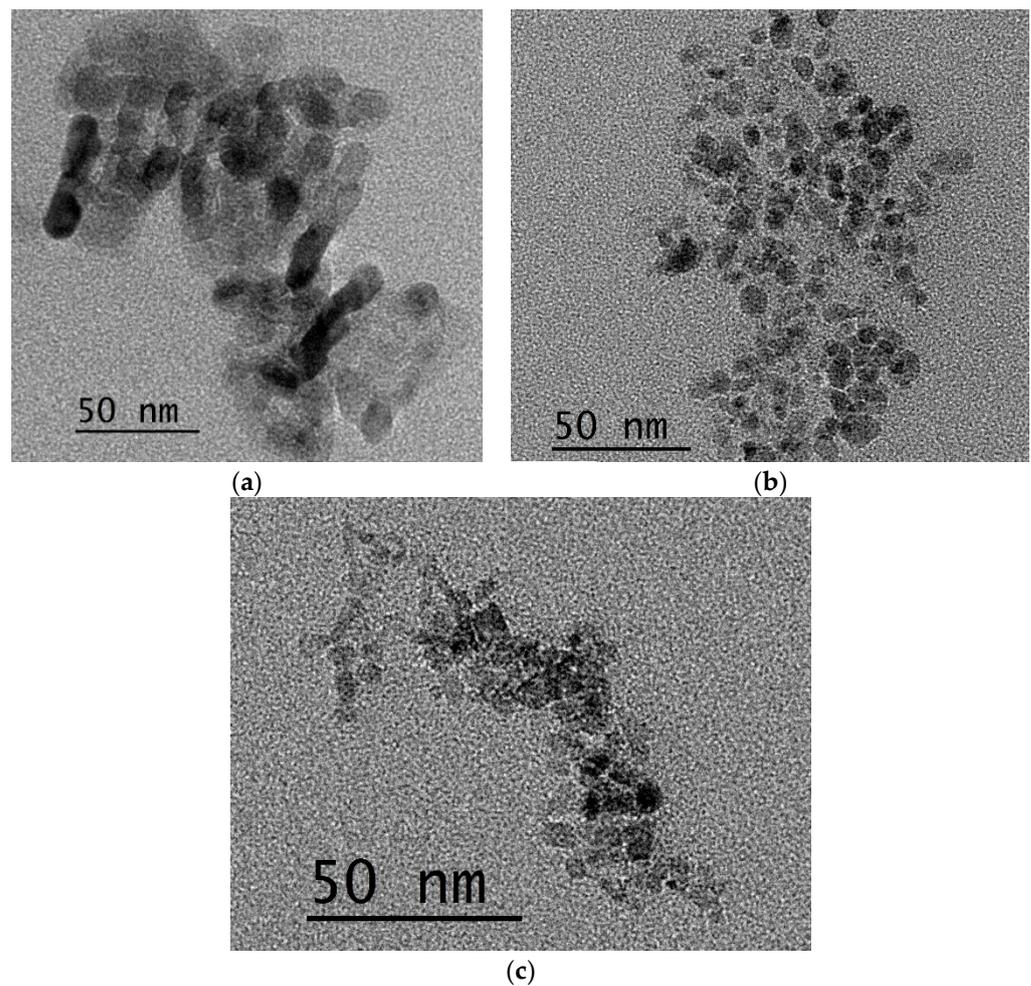| Property (s)	Unit	TiO_2	SiO_2
Molecular mass	g/mol	79.87	60.08
Density	kg/m^3	4230	2220
Average particle diameter	nm	50	30
Specific heat	J/(kg·K)	692	745
Thermal conductivity	W/(m·K)	8.4	1.4

Figure 1. TEM images of PVE-based nanolubricants: (**a**) TiO_2/PVE (0.01% volume concentration); (**b**) SiO_2/PVE (1.00% volume concentration); (**c**) SiO_2-TiO_2/PVE (0.01% volume concentration).

2.2. Preparation of Nanolubricants

A two-step method was used in the preparation of nanolubricants with volume concentration variations. The TiO_2 and SiO_2 nanoparticles each were measured to the desired mass by using a weight scale with an accuracy of 1×10^{-5} g. Equation (1) was used to estimate the mass of nanoparticles required for a given volume concentration [42,43]:

$$\varphi = \frac{m_n/\rho_n}{m_n/\rho_n + m_l/\rho_l} \times 100\% \tag{1}$$

where φ is the percentage of the nanolubricant's volume concentration, m_n is the mass of the nanoparticles, m_l is the mass of the PVE oil, and ρ_n and ρ_l are the density of the dedicated nanoparticles and the lubricant, respectively.

The volume concentrations for the TiO_2/PVE and SiO_2/PVE mono-nanolubricants were determined to be 0.01% and 1.00%, respectively. A total of 500 mL of PVE oil was prepared for each type of nanoparticle for stability evaluation. Then, the nanoparticles were introduced subtly into the lubricant using a magnetic stirrer for a duration of up to 30 min for each sample at a normal, controlled temperature to avoid agglomeration. The SiO_2-TiO_2/PVE hybrid nanolubricant was formulated for the 0.01% volume concentration at a 50:50 composition ratio. The composition ratios refer to the volume percentage of each nanolubricant required to achieve equilibrium in the total volume of the prepared nanolubricants. The composition ratio was selected by considering thermal conductivity and dynamic viscosity to promote heat transfer. Other researchers have also performed

studies on a similar composition ratio of 50:50 for hybrid nanolubricants [44,45]. Firstly, TiO_2 and SiO_2 nanoparticles were dispersed separately in 250 mL of lubricant and went through a mechanical–magnetic stirring process for 30 min. The mixture was then combined and agitated for another 30 min in the same beaker.

All of the nanolubricant samples were homogenised by using an ultrasonic bath. This method employed an ultrasonic vibrator mechanism to break down nanoparticle agglomerations to a smaller size by a transmitting ultrasonic waves through water. The bath, from Fisherbrand (model: FB15051), generates ultrasonic pulses at 50 ± 3 kHz for 230 V power. The nanolubricants were then divided into five 100 mL samples. One sample from each was kept as a reference and labelled "0 h" without going through the ultrasonication process. The remaining four samples were sonicated for between 1 h and 7 h, with a 2 h interval between each sample. The frequency, water temperature, and water volume were all held constant during the sonication process. Every half-hour, the water was replaced to maintain a steady temperature. After the homogenisation process was completed, the nanolubricants were poured into 20 mL glass test tubes and 4.5 mL glass cuvettes for stability assessment purposes. The test tubes and cuvettes were labelled accordingly to avoid unintentional sample exchange. The test tubes were kept at a level and stagnant place for observation, while the samples in the cuvettes were subjected to stability evaluation for the first time.

2.3. Stability Assessment

The stability assessment was carried out by three different methods: The first method was a qualitative technique named the photo-capturing method, or visual sedimentation. This method assesses the nanolubricant sedimentation process through a visual process. It is recommended to evaluate nanofluids' stability because of its straightforwardness and ease of conduct [7,36]. Each set of nanolubricants was left stagnant for a certain period in a level place to ensure that no external movement could disturb the liquid. The same types of nanolubricants with different ultrasonication times were placed side by side in front of the contrast background colour and optimal lighting. Images of the samples were taken on the first day after the preparation for reference. The changes in the samples were identified with photos taken from time to time. Finally, the assessment was performed by visual inspection of the samples by comparing the nanolubricant photos from the first day and after 30 days of preparation.

The second stability assessment method employed in this study was UV–Vis spectrophotometry. The dispersion of nanoparticles in the lubricant changed the particle intensity of the lubricants. The intensity of the light passing through the nanolubricants was measured for each wavelength of light passing through the spectrometer. The absorbance difference between liquids with and without nanoparticles provides a measurable value that can be converted into a concentration ratio. This concentration ratio can be interpreted as the colloidal stability of the nanoparticle dispersion. The concentration ratio was compared according to the Beer–Lambert law [46] for data verification. Then, the nanolubricants were poured into 4.5 mL glass cuvettes to be measured in the UV–Vis spectrophotometer, and the measurement of the absorbance value was taken for up to 30 days. The UV–Vis absorbance measurement was conducted three times to validate its precision and reliability. The concentration ratio (ϕ_r) of each sample was calculated using Equation (2), where ϕ is the absorbance value at the present time, and ϕ_o is the absorbance value at the first hour after the preparation process is completed:

$$\phi_r = \frac{\phi}{\phi_o} \tag{2}$$

The Drawell spectrophotometer (model: DU-8200) is capable of measuring absorbances up to 3000 and wavelengths between 290 nm and 1100 nm. Identification of a constant wavelength for each nanolubricant was carried out using the wavelength scanning method. The nanolubricants were scanned using all wavelengths, and the peak absorbance value

determined the most suitable wavelength for the specified nanolubricant's absorbance measurement [27].

The zeta potential and Zetasizer tests were used to perform the final and ultimate stability measurements in this investigation. The tests were carried out as a verification of the stability assessment based on prior visual observation and UV–Vis measurement. The zeta potential test shows the difference in potential energy between the stagnant layer of fluid that binds the particles and the dispersion medium, while the Zetasizer returns the average agglomeration size of the nanoparticles in the liquid [47]. These zeta measurements were performed using the Malvern Zetasizer ZS. A few drops of the nanolubricants were placed in special cuvettes provided by the manufacturer. The reflective index, viscosity, and dielectric constant for the PVE lubricant were inputted into the machine. Before using the Zetasizer to determine the particle size, the zeta potential of the nanolubricants was first measured. Zeta potential tests were carried out in controlled conditions at 25 °C.

In general, commercial zeta potential meters are intended for measurements in aqueous fluids such as water; however, the zeta potential may also be measured in non-aqueous (in this case, lubricants) and mixed solvents. Nevertheless, the zeta potential measurement in non-aqueous solvents fluctuates with time and hysteresis [48]. This may be due to the low conductivity of non-aqueous solvents as compared to aqueous fluids. Consequently, it is difficult to obtain a constant potential during measurement. To overcome this problem, the present study measured the zeta potential of the mono-nanolubricants more than 3 times to confirm the consistency of the readings. The measurements were conducted sequentially and repeated at least three times, and the cuvettes were cleaned with ethanol every time after completing a cycle. In addition, the zeta potential readings maintained a constant trend of values with a high zeta potential of more than 60 mV. These high potential values can also confirm the excellent stability condition of the examined mono-nanolubricants. The conductive behaviour of the present non-aqueous fluids was improved due to the existence of metal oxide SiO_2 and TiO_2 nanoparticles in the nanolubricants. Subsequently, this thermal behaviour improved the consistency of the zeta potential measurements in the present study.

3. Results and Discussion

3.1. Visual Sedimentation Observation

All nanolubricant samples were observed on the 1st day, the 15th day, and up to the 30th day after preparation. Figure 2 shows the comparison of TiO_2/PVE nanolubricant samples up to 30 days after preparation for different sonication times. The reference nanolubricants that did not undergo ultrasonication were compared to samples of 1 h, 3 h, 5 h, and 7 h sonication. On the first day of observation, all samples looked murky white and were difficult to differentiate with the naked eye. The white intensity of all of the samples decreased slightly when compared to a photo taken on the 15th day. A small amount of sedimentation appeared at the bottom of the test tubes, with no visible separation line. The light intensity of all samples degraded on the 30th day compared to the earlier observations. The reference sample showed a clear image, while the 7 h illustration was the murkiest. The intensity of the white light increased as the sonication time increased. Additionally, white spots appeared on the surface of the test tube for all samples. However, the size of the white spots varied for different samples. For example, the areas in the 0 h sample appeared the biggest, while locations in the 7 h sample were the smallest. No obvious separation line appeared in any of the samples.
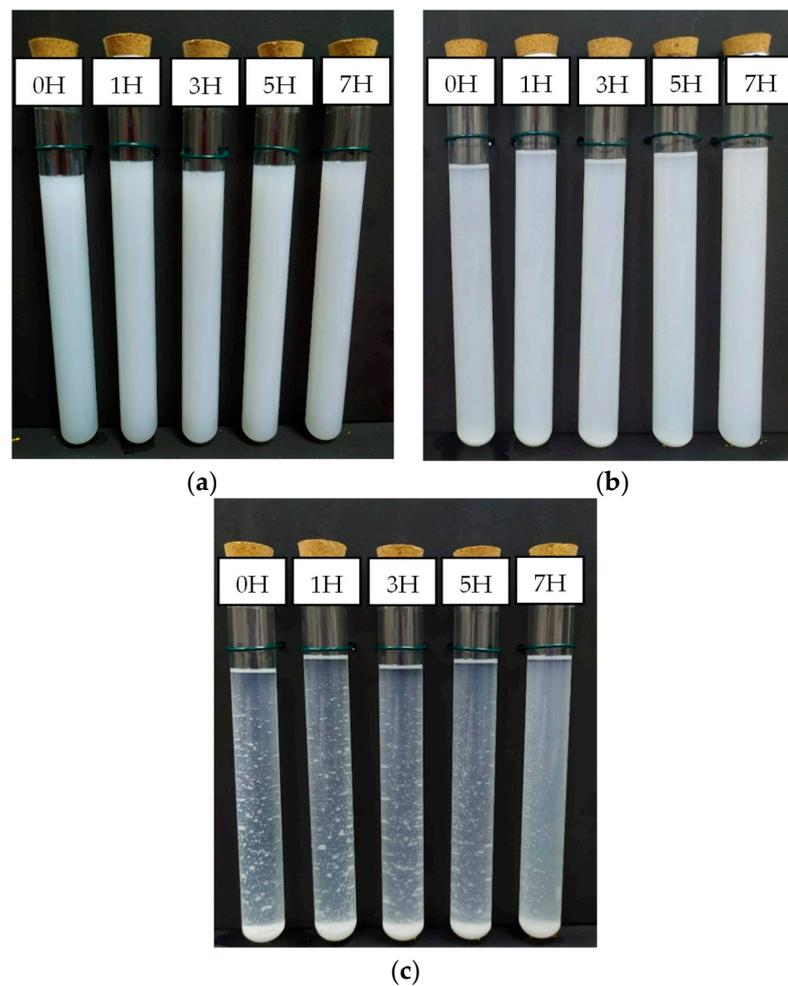
Figure 2. TiO_2/PVE at 0.01% volume concentration with different sonication times: (**a**) after preparation; (**b**) after 15 days; (**c**) after 30 days.

Figure 3 depicts SiO_2/PVE nanolubricants with different sonication times up to 30 days of preparation. The SiO_2 nanoparticles appeared white or colourless after being dispersed in the PVE lubricant. The nanolubricants had similar appearances when comparing all samples on the first day after preparation. A thin white layer of sedimentation appeared at the bottom of the test tubes after the 15th day, and the top layer of all samples became increasingly evident. The thickness of the white layer in the 0 h sample was significant, whereas the white layer in the 7 h sample was noticeably thinner. The white coating within the test tube was thicker for the 0 h sample, whereas the thickness in all other samples decreased as the sonication time increased after 30 days. It appears that the SiO_2 nanoparticles had sedimented significantly after 15 days of preparation.

The sedimentation observation for the SiO_2-TiO_2/PVE hybrid nanolubricants showed the same trend as for the TiO_2/PVE nanolubricants, as shown in Figure 4. On the first day of observation, all samples showed a similar appearance. The colour of the hybrid nanolubricants was almost identical to that of TiO_2, with an opaque white colour for all samples at different sonication times. On the 15th day after preparation, small white spots appeared on the test tubes' walls. When comparing the samples, the differences between them were difficult to discern, due to the similarity in colour observed with the naked eye. The only difference between the 7 h nanolubricants was that the white spots were smaller and the intensity of colour was greater than for the other samples. All samples showed a clearer white with numerous white spots on the wall of the test tube, and sedimentations up to 6 cm in height were observed at the bottom of the test tube after 30 days.
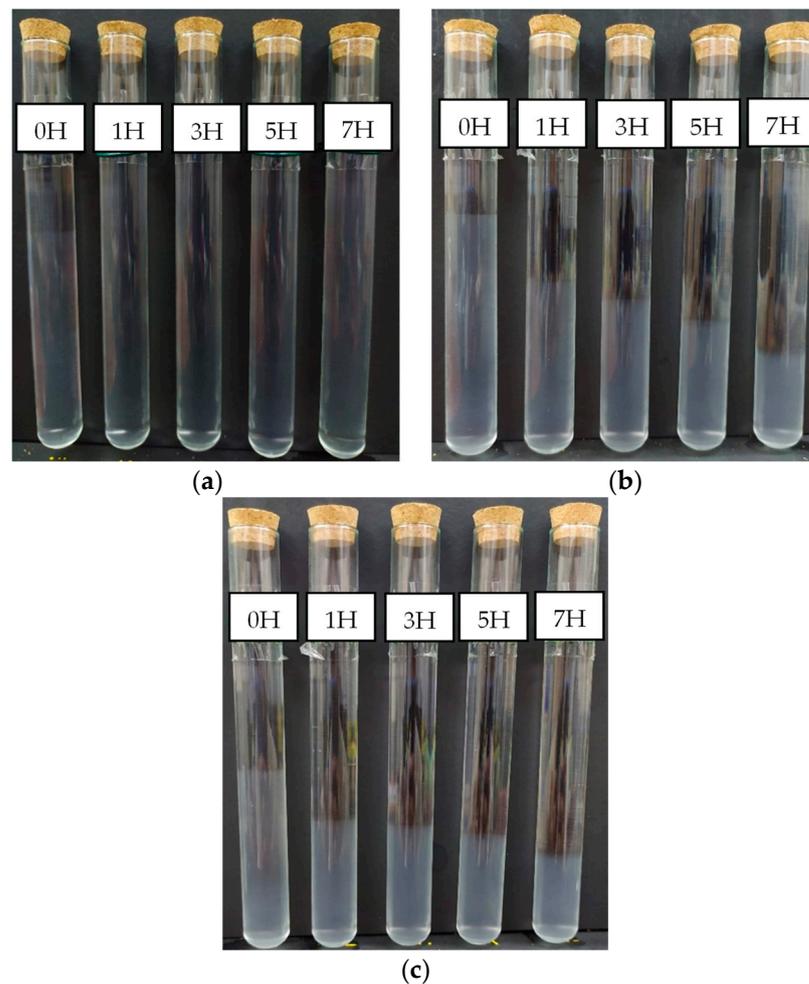
Figure 3. SiO_2/PVE at 1.00% volume concentration with different sonication times: (**a**) after preparation; (**b**) after 15 days; (**c**) after 30 days.

3.2. UV–Vis Spectrophotometer Evaluation

The stability of the prepared nanolubricants was evaluated quantitatively using the UV–Vis spectrophotometer to measure the peak absorbance and identify the suitable wavelength from the scanning results. The absorbance values of the TiO_2/PVE, SiO_2/PVE, and SiO_2-TiO_2/PVE nanolubricants for 0.01%, 1.00%, and 0.01%, respectively, are shown in Figure 5 for wavelengths of 300 to 1100 nm. As shown in the graph, the peak absorbance for all nanolubricants was recorded beyond the absorbance range capability of the UV–Vis spectrophotometer (i.e., more than 3). The absorbance values indicated a value of 3 between 290 nm and 384 nm, after which the absorbance values began to drop. Therefore, an alternative wavelength of 400 nm was identified for the TiO_2/PVE nanolubricants. As shown in the graph, the second highest absorbance for the SiO_2-TiO_2/PVE hybrid nanolubricants occurred at the peak wavelength of 330 nm. Meanwhile, the peak absorbance value for the SiO_2 mono-lubricants was reported at 300 nm. Figure 6 shows the absorbance ratio against concentration for the mono-TiO_2/PVE and -SiO_2/PVE nanolubricants and the hybrid SiO_2-TiO_2 nanolubricants at constant peak wavelengths of 400 nm, 300 nm, and 330 nm, respectively. The Beer–Lambert law states that, under ideal conditions, the suspension volume concentration of nanolubricants (ϕ) is linear to its absorbance ($\overline{A}$) [46,49–51]. The graph indicates that the absorbance values were proportional to the concentration, based on a linear relationship between the nanolubricants' absorbance and their volume concentration. Therefore, the concentration of the nanolubricants can be calculated by measuring their absorbance.
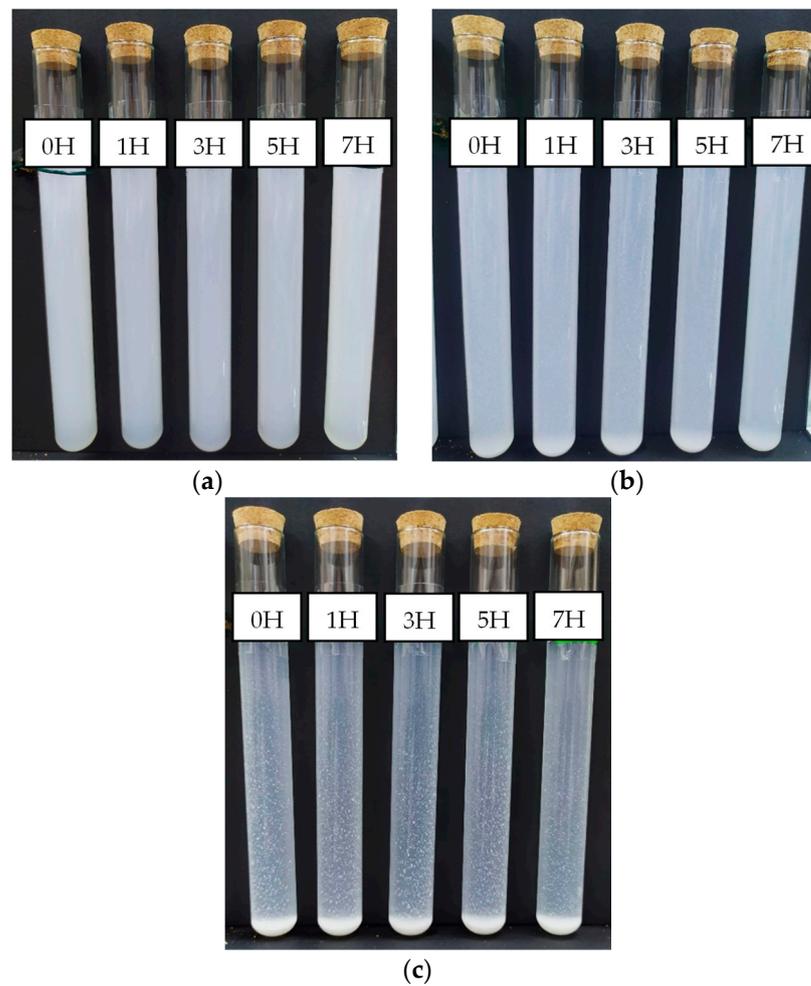
Figure 4. SiO_2-TiO_2/PVE at 0.01% volume concentration with different sonication times: (**a**) after preparation; (**b**) after 15 days; (**c**) after 30 days.
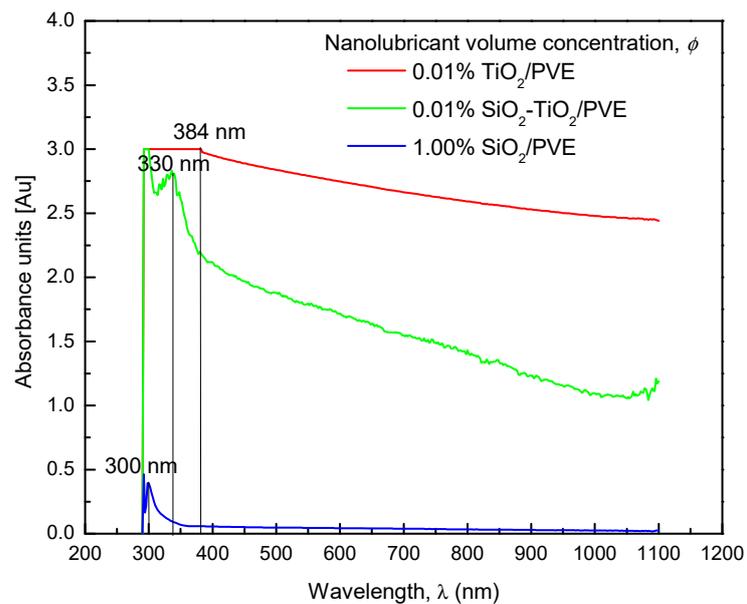

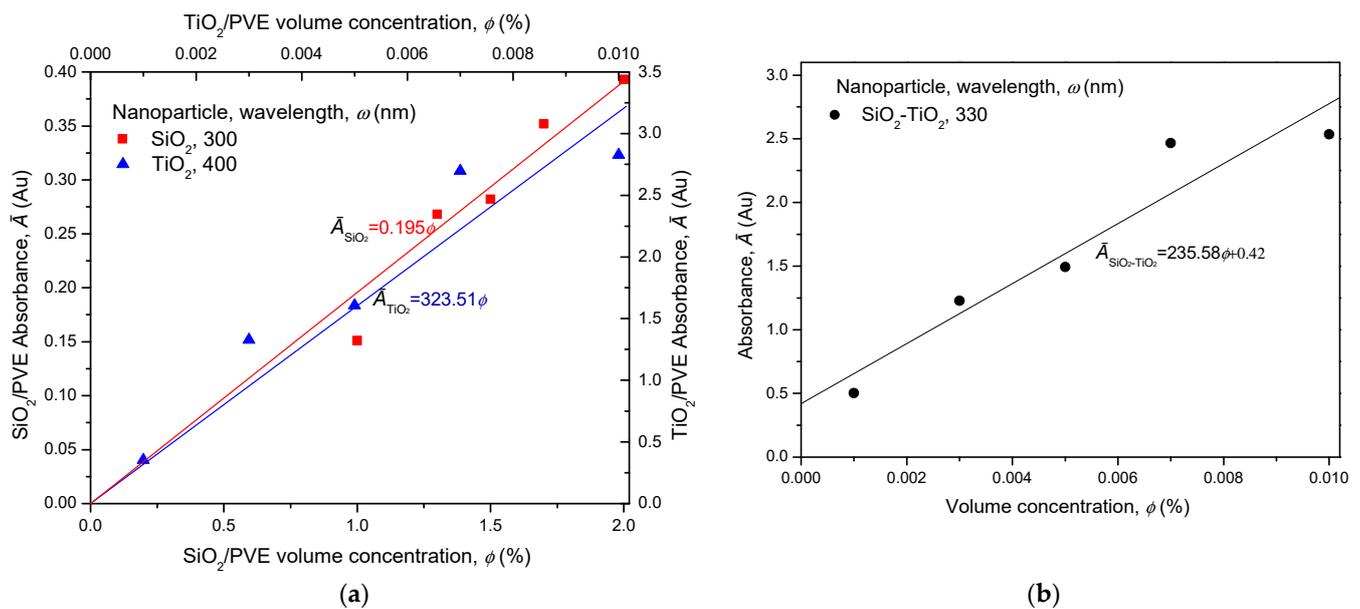**Figure 5.** Absorbance of nanolubricants for different volume concentrations.

Figure 6. Absorbance–volume concentration linear relationships for mono- and hybrid nanolubricants: (**a**) mono-TiO_2/PVE and -SiO_2/PVE nanolubricants; (**b**) hybrid SiO_2-TiO_2 nanolubricants.

Figure 7 shows the absorbance values at five different ultrasonication times up to 30 days for TiO_2/PVE nanolubricants. The absorbance values for all samples ranged from 2.746 to 2.898 and decreased over time. Except for the 0 h sonication, which had an absorbance value of 87%, all samples showed outstanding stability from the first day to the sixth day, with absorbance levels remaining over 2.5 (or 95%). After the 7th day, the absorbance ratio showed that the samples with higher stability had maintained a concentration ratio above 95%, while the samples with lesser stability had begun to decline. After the 9th day, the 0 h sonication decreased below 70%, and by the 30th day it had dropped to 29.5%. Meanwhile, by the 30th day, the 1 h and 3 h sonication absorbance levels had fallen to 77% and 76%, respectively. The 5 and 7 h sonications demonstrated the best stability throughout the assessment period. On the 30th day, the 5 h sonication showed excellent stability, at 94.3%, while the 7 h sonication showed outstanding stability, at 87%. The ultrasonication time is a significant factor that influences the stability of nanolubricants, according to the results of the UV–Vis spectrophotometer evaluation for the TiO_2/PVE nanolubricants. The nanolubricants could maintain their stability for roughly a week without ultrasonication. When the sample was subjected to a 1 h sonication process, the nanolubricant's stability increased to 30 days, or even longer if the assessment was continued for a longer time. These findings also suggest that sonicating the sample for 5 h leads to a longer nanolubricant stability period. In comparison to the recommended sonication time, increasing the sonication time beyond five hours does not result in any improvement in the nanolubricant's stability [52], and triggering particle coagulation leads to agglomeration, which leads to quicker sedimentation [53].
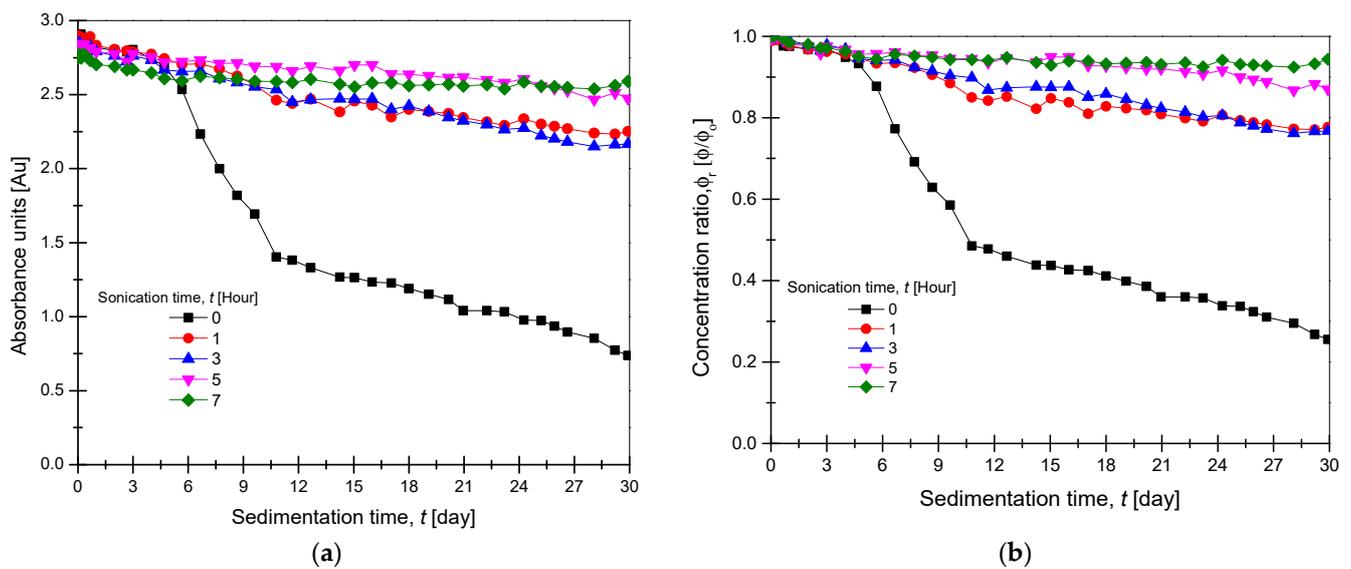
Figure 7. UV–Vis evaluation of TiO_2/PVE nanolubricants for 30 days at a 0.01% volume concentration with different sonication times: (**a**) absorbance value; (**b**) concentration ratio.

Figure 8 illustrates the absorbance values of SiO_2/PVE nanolubricants for five different ultrasonication durations up to 30 days. The absorbance ratio for this SiO_2/PVE nanolubricant showed an unusual pattern compared to TiO_2/PVE, as the value of the absorbance ratio increased over time. The first two days showed a fluctuation in absorbance values until the 3rd day. The peak absorbance ratio was observed on the 27th day after preparation. Then, the values began to decline gradually until the last day of the observation. The highest increment was seen in the 0 h sonication time sample, followed by the 1 h and 3 h samples. The 7 h sample consistently had the most negligible value, while the 5 h sample showed a similar trend to the 7 h sample but with slightly higher values. The phenomenon that was observed for the SiO_2/PVE nanolubricants was due to the charged nature of the particles. After the dispersion process in the lubricant, the SiO_2 nanoparticles were free to move around and clash with other particles. Because of this circumstance, the SiO_2 nanoparticles tended to aggregate in order to achieve particulate stability, resulting in the formation of numerous nanoparticle clusters. Therefore, the nanoparticles tended to settle prematurely over time [11]. Nanoparticle clusters formed in liquids result in instability, due to the size of the agglomeration resulting in sedimentation. As a result, UV–Vis measurements can yield higher absorbance values over time. A larger agglomeration absorbs more light energy due to its higher mass. Visual sedimentation observation also confirmed the UV–Vis results for SiO_2/PVE nanolubricants. The present observations are consistent with those of Sharif et al. [54] in their preparation of nanolubricants for AAC system applications.
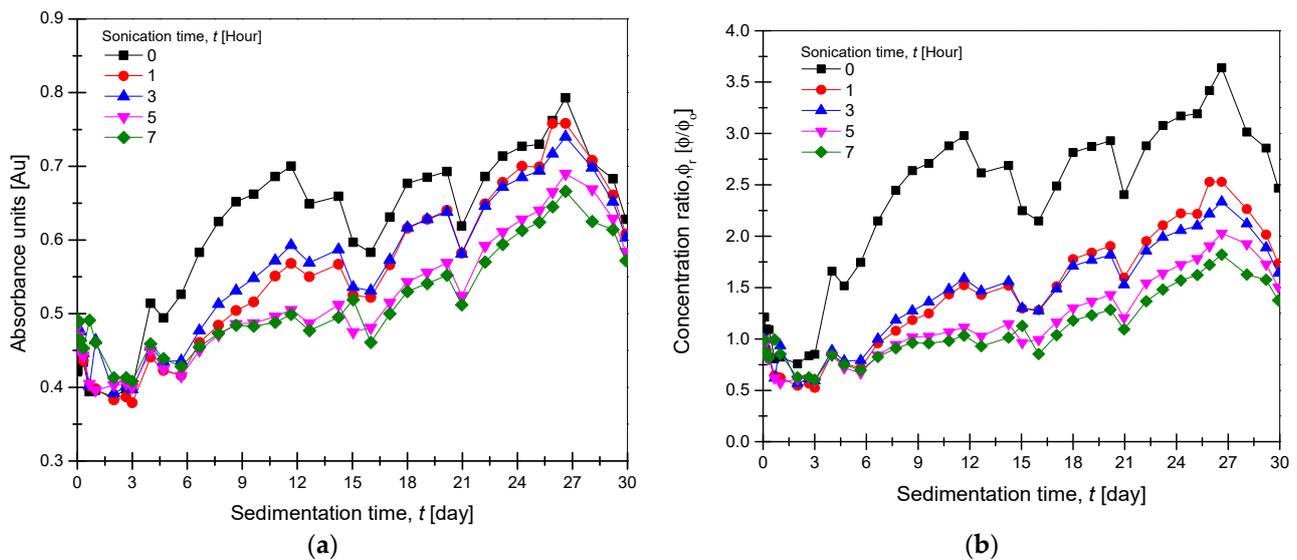
Figure 8. UV–Vis evaluation of SiO$_2$/PVE nanolubricants for 30 days at a 1.00% volume concentration with different sonication times: (**a**) absorbance value; (**b**) concentration ratio.

Figure 9a,b show the absorbance and the concentration ratio, respectively, of hybrid nanolubricants that have been ultrasonically treated for 1 to 7 h. A 0 h sample for baseline reference was plotted in the graph. The absorbance values for the samples with the sonication homogenisation process started between 2.396 and 2.506, while the sample without sonication started at 2.008. Both the absorbance and concentration ratio values declined with time at an almost constant rate for the first seven days. The concentration ratio for all samples was more than 70% after 7 days. The sedimentation rate then began to change, with the 7 h sample being the slowest and the 0 h and 1 h samples being the fastest. For the 5 h sample, the time between days 9 and 20 showed the quickest sedimentation rate before it reached a 0.2 concentration ratio on the 30th day. According to these results, the ultrasonication technique increases the absorbance value. With increasing sonication time, the absorbance values of all samples increased. The ultrasonication process breaks the nanoparticle aggregations down to a smaller size, making them disperse more uniformly. The uniform orientation of the nanoparticles can absorb more light energy that passes through them, causing the UV–Vis spectrophotometer measurement to return a higher absorbance value. Smaller nanoparticle aggregations also help the nanoparticles sustain a longer period in colloidal solution. The more negligible gravitational effect on the nanoparticles creates a slower falling rate to a lower level, which creates better stability. The presence of TiO$_2$ nanoparticles in hybrid nanolubricants also increased the stability of the SiO$_2$ nanoparticles. According to Kumar et al. [55], SiO$_2$ nanoparticles will have a homoagglomeration situation that creates nanoclusters in mono-nanolubricants. However, when other nanoparticles such as TiO$_2$ are dispersed together, the tendency for SiO$_2$ is to reduce the homoagglomeration. Another advantage of having hybrid nanolubricants with SiO$_2$ is that it enables the measurement of nanolubricants' stability by UV–Vis, while also returning the rational trend of the sedimentation process.
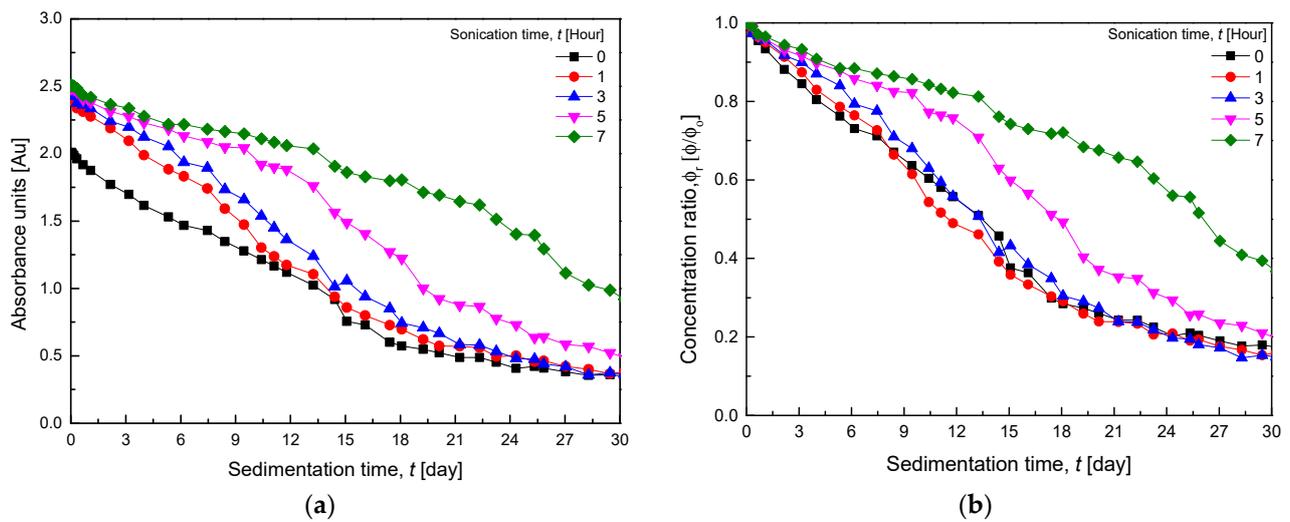
Figure 9. UV–Vis evaluation of SiO$_2$-TiO$_2$/PVE nanolubricants for 30 days at a 0.01% volume concentration with different sonication times: (**a**) absorbance value; (**b**) concentration ratio.

3.3. Zeta Potential Analysis

Stability tests such as the zeta potential and Zetasizer tests were conducted to confirm the stability observations made by visual sedimentation and UV–Vis evaluation results. The nanolubricant samples with different sonication times were tested, and the zeta potential results are presented in Figure 10a. The tests were undertaken within 8 h of the nanolubricants' preparation. It can be seen from the figure that almost all samples with absolute zeta potentials greater than 60 mV demonstrated excellent stability. These results were compared to the categorisation of stability proposed by Lee et al. [56]. According to the stabilisation hypothesis, a high absolute value of zeta potential indicates that the electrostatic repulsive forces between the nanoparticles are notably strong, indicating a stable suspension [53]. However, only the TiO$_2$/PVE nanolubricants with 0 and 1 h sonication times measured zeta potentials lower than 60 mV, which can still be considered to represent good stability. Measurement of zeta potential for the 3 and 5 h TiO$_2$/PVE nanolubricants showed a linear relationship between zeta potential and sonication time. The increase in the sonication period over 5 h did not show any improved stability. The outcomes confirmed the evaluation results from UV–Vis, which displayed a similar trend. The zeta potential value for the hybrid nanolubricants also showed excellent stability for all samples, although their values were slightly higher due to the sonication period. The 7 h sample showed the highest value of 105.3 mV, while the 0 h sample was the lowest at 78 mV. The zeta potential trend for the SiO$_2$/PVE nanolubricants was slightly different. The zeta potential for the 0 h sample was 128.5 mV, while it was 72.5 mV for the 3 h sample and 224.2 mV for the 7 h sample. All of the SiO$_2$/PVE nanolubricant samples showed excellent stability, i.e., above 60 mV; however, there was no evidence of a trend with increasing sonication time.
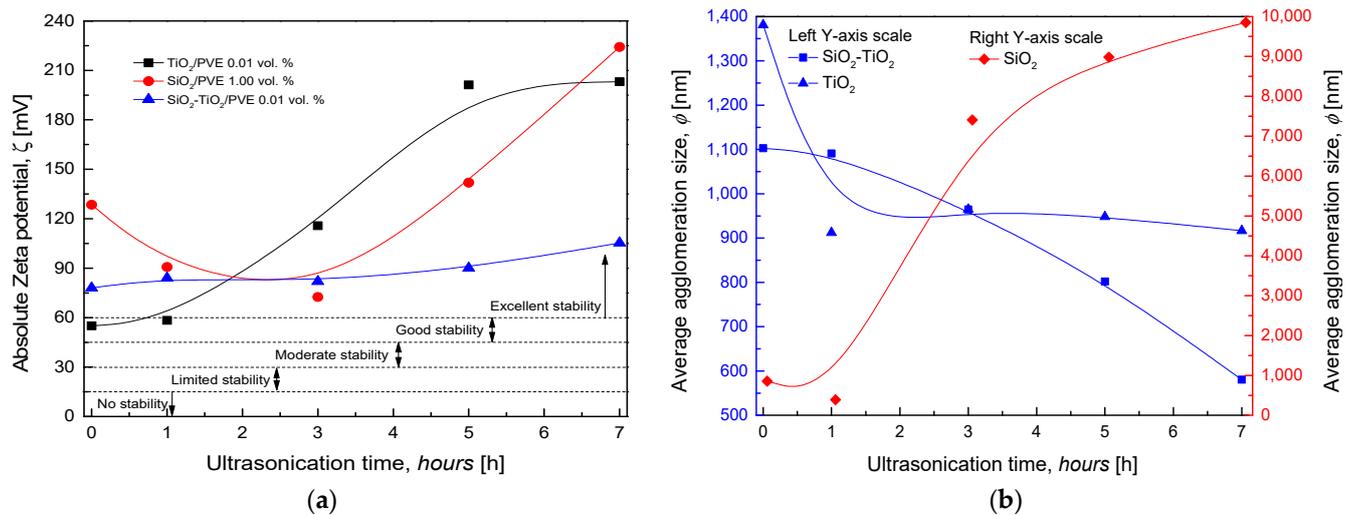
Figure 10. Zeta measurement versus ultrasonication time: (**a**) absolute zeta potential; (**b**) average agglomeration size.

The results from the Zetasizer testing are presented in Figure 10b, which shows exciting outcomes for all of the nanolubricants presented in this paper. The average agglomeration size for the mono-TiO_2/PVE and hybrid nanolubricants fell between 580 nm and 1380 nm for all samples homogenised by ultrasonication between 0 and 7 h. For the mono-SiO_2/PVE nanolubricants, there was a significant gap in the agglomeration size between the different sonication times, where the smallest was 389 nm while the highest was 9852 nm. The size of the TiO_2 caused the average agglomeration to decrease from 0 h to 1 h. This trend changed with the increase in sonication time, where the agglomeration size did not show much difference. The direction of the hybrid nanolubricants' Zetasizer results indicated a more significant influence of the ultrasonication process on the particle agglomeration size. From 0 h to 7 h, the agglomeration size dropped at an almost constant rate, starting at 1102 nm and ending at 580 nm. The 7 h hybrid zeta size was the smallest particle size measured in this paper. Both trends' results confirmed that the ultrasonication process broke down agglomerations and reduced their size to smaller units when the ultrasonication time increased. In contrast, the average agglomeration size for SiO_2/PVE was reduced from 856 nm to 389 nm from 0 h to 1 h of sonication time. However, the reducing trend came to a halt when the size increased to 7405 nm for 3 h. This trend increased continuously for the remaining samples, but at a slower rate. The trend showed that for SiO_2/PVE mono-nanolubricants, ultrasonication for more than one hour enhanced the particle agglomeration size. When the sonication time was more than one hour, the particle agglomeration took place, and the measurement showed that the size was much bigger compared to the original size without sonication. The optimal sonication period falls between one and three hours. This trend was aligned with other stability observations and measurements for the SiO_2 nanolubricant. As discussed previously, the increase in size due to particle agglomeration makes the mass heavier, and the heavier particles are more influenced by the gravitational effect, affecting their stability.

4. Conclusions

The present paper focuses on the dispersion of mono- and hybrid nanolubricants of TiO_2 and SiO_2 in a PVE base. The nanolubricants were observed, measured, and evaluated to determine their stability conditions. Unstable nanolubricants tend to agglomerate, which reduces their thermal conductivity and increases particle clogging in the VCR systems. Several conclusions can be drawn from the results obtained from our experimental work:

1. Dispersion of TiO_2 in PVE nanolubricant works well with magnetic stirring and a 7 h ultrasonication in a bath homogeniser. A concentration ratio of more than 95% was measured for this nanolubricant on the 30th day after preparation.
2. UV–Vis spectrophotometer measurement and photo-capturing of visual sedimentation observation can be used to evaluate the stability of mono- and hybrid nanolubricants. However, for mono-SiO_2/PVE nanolubricants, only the visual sedimentation method is reliable to measure its stability.
3. The stability of mono-SiO_2/PVE nanolubricants is improved when combining the nanoparticles with TiO_2 in a hybrid nanolubricant. UV–Vis measurement of the hybrid nanolubricants showed acceptable values and improved SiO_2/PVE nanolubricant stability.
4. Zeta potential and Zetasizer tests provide aligned results, confirming the UV–Vis and visual observation evaluation results. This also affirms that the UV–Vis spectrophotometer is reliable enough to measure the stability of nanolubricants.

The addition of TiO_2 and SiO_2 nanoparticles in a PVE-based nanolubricant can aid in thermal conductivity and heat transfer. Therefore, for optimal performance in VCR systems, 0.01% TiO_2/PVE, 1.00% SiO_2/PVE, and 0.01% TiO_2-SiO_2 nanolubricants with 7 h of sonication time are recommended. By using TiO_2 and SiO_2 nanolubricants with an appropriate volume concentration, providing a better potential for increasing system performance, we can subsequently increase the efficiency of the VCR system.

References

1. Masuda, H.; Ebata, A.; Teramae, K.; Hishinuma, N. Alteration of thermal conductivity and viscosity of liquid by dispersing ultra-fine particles. Dispersion of Al_2O_3, SiO_2 and TiO_2 ultra-fine particles. *Netsu Bussei* **1993**, *7*, 227–233. [CrossRef]
2. Anitha, S.; Thomas, T.; Parthiban, V.; Pichumani, M. What dominates heat transfer performance of hybrid nanofluid in single pass shell and tube heat exchanger? *Adv. Powder Technol.* **2019**, *30*, 3107–3117. [CrossRef]
3. Nabil, M.F.; Azmi, W.H.; Hamid, K.A.; Mamat, R. Experimental investigation of heat transfer and friction factor of TiO_2-SiO_2 nanofluids in water:ethylene glycol mixture. *Int. J. Heat Mass Transf.* **2018**, *124*, 1361–1369. [CrossRef]
4. Sharif, M.Z.; Azmi, W.H.; Redhwan, A.A.M.; Mamat, R. Investigation of thermal conductivity and viscosity of Al_2O_3/PAG nanolubricant for application in automotive air conditioning system. *Int. J. Refrig.* **2016**, *70*, 93–102. [CrossRef]
5. Nair, V.; Tailor, P.R.; Parekh, A.D. Nanorefrigerants: A comprehensive review on its past, present and future. *Int. J. Refrig.* **2016**, *67*, 290–307. [CrossRef]
6. Redhwan, A.A.M.; Azmi, W.H.; Sharif, M.Z.; Mamat, R. Development of nanorefrigerants for various types of refrigerant based: A comprehensive review on performance. *Int. Commun. Heat Mass Transf.* **2016**, *76*, 285–293. [CrossRef]
7. Sharif, M.Z.; Azmi, W.H.; Mamat, R.; Shaiful, A.I.M. Mechanism for improvement in refrigeration system performance by using nanorefrigerants and nanolubricants—A review. *Int. Commun. Heat Mass Transf.* **2018**, *92*, 56–63. [CrossRef]

8. Wang, R.; Hao, B.; Xie, G.; Li, H. A refrigerating-system using HFC134A and mineral lubricant appended with N-TIO₂(R) as working fluids. In Proceedings of the 4th International Symposium On Heating, Ventilating and Air Conditioning, Beijing, China, 11 September 2003; pp. 888–892.

9. Bi, S.; Shi, L.; Zhang, L. Application of nanoparticles in domestic refrigerators. *Appl. Therm. Eng.* **2008**, *28*, 1834–1843. [CrossRef]

10. Adelekan, D.S.; Ohunakin, O.S.; Babarinde, T.O.; Odunfa, M.K.; Leramo, R.O.; Oyedepo, S.O.; Badejo, D.C. Experimental performance of LPG refrigerant charges with varied concentration of TiO₂ nano-lubricants in a domestic refrigerator. *Case Stud. Therm. Eng.* **2017**, *9*, 55–61. [CrossRef]

11. Ohunakin, O.S.; Adelekan, D.S.; Gill, J.; Atayero, A.A.; Atiba, O.E.; Okokpujie, I.P.; Abam, F.I. Performance of a hydrocarbon driven domestic refrigerator based on varying concentration of SiO₂ nano-lubricant. *Int. J. Refrig.* **2018**, *94*, 59–70. [CrossRef]

12. Kumar, R.S.; Sharma, T. Stability and rheological properties of nanofluids stabilized by SiO₂ nanoparticles and SiO₂-TiO₂ nanocomposites for oilfield applications. *Colloids Surf. a-Physicochem. Eng. Asp.* **2018**, *539*, 171–183. [CrossRef]

13. Marcucci Pico, D.F.; da Silva, L.R.R.; Schneider, P.S.; Bandarra Filho, E.P. Performance evaluation of diamond nanolubricants applied to a refrigeration system. *Int. J. Refrig.* **2019**, *100*, 104–112. [CrossRef]

14. Marcucci Pico, D.F.; da Silva, L.R.R.; Hernandez Mendoza, O.S.; Bandarra Filho, E.P. Experimental study on thermal and tribological performance of diamond nanolubricants applied to a refrigeration system using R32. *Int. J. Heat Mass Transf.* **2020**, *152*, 119493. [CrossRef]

15. Zawawi, N.N.M.; Azmi, W.H.; Redhwan, A.A.M.; Sharif, M.Z.; Sharma, K.V. Thermo-physical properties of Al₂O₃-SiO₂/PAG composite nanolubricant for refrigeration system. *Int. J. Refrig.* **2017**, *80*, 1–10. [CrossRef]

16. Azmi, W.H.; Sharif, M.Z.; Yusof, T.M.; Mamat, R.; Redhwan, A.A.M. Potential of nanorefrigerant and nanolubricant on energy saving in refrigeration system—A review. *Renew. Sustain. Energy Rev.* **2017**, *69*, 415–428. [CrossRef]

17. Qiang, A.H.; Zhao, L.M.; Xu, C.J.; Zhou, M. Effect of dispersant on the colloidal stability of nano-sized CuO suspension. *J. Dispers. Sci. Technol.* **2007**, *28*, 1004–1007. [CrossRef]

18. Cacua, K.; Buitrago-Sierra, R.; Herrera, B.; Chejne, F.; Pabón, E. Influence of different parameters and their coupled effects on the stability of alumina nanofluids by a fractional factorial design approach. *Adv. Powder Technol.* **2017**, *28*, 2581–2588. [CrossRef]

19. Subramani, N.; Prakash, M.J. Experimental studies on a vapour compression system using nanorefrigerants. *Int. J. Eng. Sci. Technol.* **2012**, *3*, 95–102. [CrossRef]

20. Sanukrishna, S.S.; Vishnu, A.S.; Jose, M. Nanorefrigerants for energy efficient refrigeration systems. *J. Mech. Sci. Technol.* **2017**, *31*, 3993–4001. [CrossRef]

21. Lou, J.; Zhang, H.; Wang, R. Experimental investigation of graphite nanolubricant used in a domestic refrigerator. *Adv. Mech. Eng.* **2015**, *7*, 1–9. [CrossRef]

22. Gill, J.; Singh, J.; Ohunakin, O.S.; Adelekan, D.S. Energetic and exergetic analysis of a domestic refrigerator system with LPG as a replacement for R134a refrigerant, using POE lubricant and mineral oil based TiO₂-, SiO₂- and Al₂O₃-lubricants. *Int. J. Refrig.* **2018**, *91*, 122–135. [CrossRef]

23. Saravanan, K.; Vijayan, R. First law and Second law analysis of Al₂O₃/TiO₂ nano composite lubricant in domestic refrigerator at different evaporator temperature. *Mater. Res. Express.* **2018**, *5*, 10. [CrossRef]

24. Sezer, N.; Atieh, M.A.; Koc, M. A comprehensive review on synthesis, stability, thermophysical properties, and characterization of nanofluids. *Powder Technol.* **2019**, *344*, 404–431. [CrossRef]

25. Gallego, A.; Cacua, K.; Herrera, B.; Cabaleiro, D.; Piñeiro, M.M.; Lugo, L. Experimental evaluation of the effect in the stability and thermophysical properties of water-Al₂O₃ based nanofluids using SDBS as dispersant agent. *Adv. Powder Technol.* **2020**, *31*, 560–570. [CrossRef]

26. Sadeghy, R.; Haghshenasfard, M.; Etemad, S.G.; Keshavarzi, E. Investigation of alumina nanofluid stability using experimental and modified population balance methods. *Adv. Powder Technol.* **2016**, *27*, 2186–2195. [CrossRef]

27. Che Sidik, N.A.; Mahmud Jamil, M.; Aziz Japar, W.M.A.; Muhammad Adamu, I. A review on preparation methods, stability and applications of hybrid nanofluids. *Renew. Sustain. Energy Rev.* **2017**, *80*, 1112–1122. [CrossRef]

28. Jalili, M.M.; Davoudi, K.; Zafarmand Sedigh, E.; Farrokhpay, S. Surface treatment of TiO₂ nanoparticles to improve dispersion in non-polar solvents. *Adv. Powder Technol.* **2016**, *27*, 2168–2174. [CrossRef]

29. Yu, W.; Xie, H. A review on nanofluids: Preparation, stability mechanisms, and applications. *J. Nanomater.* **2012**, *2012*, 1–17. [CrossRef]

30. Zapata-Hernandez, C.; Durango-Giraldo, G.; López, D.; Buitrago-Sierra, R.; Cacua, K. Surfactants versus surface functionalization to improve the stability of graphene nanofluids. *J. Dispers. Sci. Technol.* **2021**, *43*, 1717–1724. [CrossRef]

31. Ouikhalfan, M.; Labihi, A.; Belaqziz, M.; Chehouani, H.; Benhamou, B.; Sarı, A.; Belfkira, A. Stability and thermal conductivity enhancement of aqueous nanofluid based on surfactant-modified TiO₂. *J. Dispers. Sci. Technol.* **2020**, *41*, 374–382. [CrossRef]

32. Chen, Y.; Renner, P.; Liang, H. Dispersion of nanoparticles in lubricating oil: A critical review. *Lubricants* **2019**, *7*, 7. [CrossRef]

33. Ahmed, M.S.; Elsaid, A.M. Effect of hybrid and single nanofluids on the performance characteristics of chilled water air conditioning system. *Appl. Therm. Eng.* **2019**, *163*, 114398. [CrossRef]

34. Zawawi, N.N.M.; Azmi, W.H.; Sharif, M.Z.; Najafi, G. Experimental investigation on stability and thermo-physical properties of Al₂O₃-SiO₂/PAG nanolubricants with different nanoparticle ratios. *J. Therm. Anal. Calorim.* **2019**, *135*, 1243–1255. [CrossRef]

35. Leong, K.Y.; Ku Ahmad, K.Z.; Ong, H.C.; Ghazali, M.J.; Baharum, A. Synthesis and thermal conductivity characteristic of hybrid nanofluids—A review. *Renew. Sustain. Energy Rev.* **2017**, *75*, 868–878. [CrossRef]

36. Redhwan, A.A.M.; Azmi, W.H.; Sharif, M.Z.; Mamat, R.; Zawawi, N.N.M. Comparative study of thermo-physical properties of SiO$_2$ and Al$_2$O$_3$ nanoparticles dispersed in PAG lubricant. *Appl. Therm. Eng.* **2017**, *116*, 823–832. [CrossRef]

37. Motozawa, M.; Makida, N.; Fukuta, M. Experimental study on physical properties of CuO-PVE nano-oil and its mixture with refrigerant. In Proceedings of the 24th International Compressor Engineering Conference, West Lafayette, IN, USA, 9–12 July 2018; pp. 1–10.

38. Karnaz, J.; Seeton, C. Evaluation of lubricant properties and refrigerant interaction. In Proceedings of the 24th International Compressor Engineering Conference, West Lafayette, IN, USA, 9–12 July 2018; pp. 1–10.

39. Idemitsu Kosan, C.L. Daphne Hermetic Oil FVC68D. In *Material Safety Data Sheet*; Idemitsu Kosan Co., Ltd.: Tokyo, Japan, 2010; pp. 1–5.

40. Hongwu International, G.L. Anatase Nano TiO2 Titanium Dioxide Powders. Available online: www.hwnanomaterial.com/anatase-nano-tio2-titanium-dioxide-powders_p49.html (accessed on 25 September 2021).

41. Beijing Deke Daojin, S.A.T.C.L. Nano Silica. Available online: www.dknano.com/Ecplb.asp?Fid=1177&ClassId=1190&NewsId=2993 (accessed on 25 September 2021).

42. Zawawi, N.N.M.; Azmi, W.H.; Ghazali, M.F.; Ali, H.M. Performance of Air-Conditioning System with Different Nanoparticle Composition Ratio of Hybrid Nanolubricant. *Micromachines* **2022**, *13*, 1871. [CrossRef]

43. Zawawi, N.N.M.; Azmi, W.H.; Redhwan, A.A.M.; Ramadhan, A.I.; Ali, H.M. Optimization of air conditioning performance with Al$_2$O$_3$-SiO$_2$/PAG composite nanolubricants using the response surface method. *Lubricants* **2022**, *10*, 243. [CrossRef]

44. Zawawi, N.N.M.; Azmi, W.H.; Redhwan, A.A.M.; Sharif, M.Z.; Samykano, M. Experimental investigation on thermo-physical properties of metal oxide composite nanolubricants. *Int. J. Refrig.* **2018**, *89*, 11–21. [CrossRef]

45. Urmi, W.; Rahman, M.M.; Hamzah, W.A.W. An experimental investigation on the thermophysical properties of 40% ethylene glycol based TiO$_2$-Al$_2$O$_3$ hybrid nanofluids. *Int. Commun. Heat Mass Transf.* **2020**, *116*, 104663. [CrossRef]

46. Beer, A.; Beer, P. Determination of the absorption of red light in colored liquids. *Ann. Der Phys. Und Chem.* **1852**, *86*, 78–88. [CrossRef]

47. Selvamani, V. Stability Studies on Nanomaterials Used in Drugs. In *Characterization and Biology of Nanomaterials for Drug Delivery*; Elsevier Inc.: Amsterdam, Netherlands, 2018; pp. 425–444. [CrossRef]

48. Suzuki, Y.; Mizuhata, M. Predictive zeta potential measurement method applicable to nonaqueous solvents in high-concentration dispersion systems for the system of LiClO$_4$–propylene carbonate solution and LiCoO$_2$ powder sheet. *Electrochemistry* **2022**, *90*, 103001. [CrossRef]

49. Lambert, J.H. Photometry: Or on the Measure and Gradations of Light, Colors, and Shade. 1760. *Transl. Lat. By David L. DiLaura* **2001**, *22*, 1760.

50. Lin, L.; Peng, H.; Ding, G. Dispersion stability of multi-walled carbon nanotubes in refrigerant with addition of surfactant. *Appl. Therm. Eng.* **2015**, *91*, 163–171. [CrossRef]

51. Lin, L.; Peng, H.; Chang, Z.; Ding, G. Experimental research on degradation of nanolubricant–refrigerant mixture during continuous alternation processes of condensation and evaporation. *Int. J. Refrig.* **2017**, *76*, 97–108. [CrossRef]

52. Redhwan, A.A.M.; Azmi, W.H.; Sharif, M.Z.; Mamat, R.; Samykano, M.; Najafi, G. Performance improvement in mobile air conditioning system using Al$_2$O$_3$/PAG nanolubricant. *J. Therm. Anal. Calorim.* **2019**, *135*, 1299–1310. [CrossRef]

53. Ghadimi, A.; Saidur, R.; Metselaar, H.S.C. A review of nanofluid stability properties and characterization in stationary conditions. *Int. J. Heat Mass Transf.* **2011**, *54*, 4051–4068. [CrossRef]

54. Sharif, M.Z.; Azmi, W.H.; Redhwan, A.A.M.; Mamat, R.; Najafi, G. Energy saving in automotive air conditioning system performance using SiO$_2$/PAG nanolubricants. *J. Therm. Anal. Calor.* **2019**, *135*, 1285–1297. [CrossRef]

55. Kumar, R.S.; Narukulla, R.; Sharma, T. Comparative Effectiveness of Thermal Stability and Rheological Properties of Nanofluid of SiO$_2$-TiO$_2$ Nanocomposites for Oil Field Applications. *Ind. Eng. Chem. Res.* **2020**, *59*, 15768–15783. [CrossRef]

56. Lee, J.H.; Hwang, K.S.; Jang, S.P.; Lee, B.H.; Kim, J.H.; Choi, S.U.S.; Choi, C.J. Effective viscosities and thermal conductivities of aqueous nanofluids containing low volume concentrations of Al$_2$O$_3$ nanoparticles. *Int. J. Heat Mass Transf.* **2008**, *51*, 2651–2656. [CrossRef]