The stability of TiO$_2$/POE nanolubricant for automotive air-conditioning system of hybrid electric vehicles

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Abstract. Nanolubricant are containing nanoparticles that are mixed with the base lubricant. Nanoparticle consists of ultra-fine size of particles from 1 to 100 nm. It was widely used as additional material to enhance properties of lubricant. The thermo-physical properties of the nanolubricant are improved and thus be able to improve the performance of vapour compression refrigeration system (VCRS) and automotive air-conditioning (AAC) system. The stability condition is one of the priority in formulation of nanolubricant for new application in AAC system of hybrid electric vehicles (HEV). The main objective of this study is to investigate the stability of TiO$_2$ nanoparticles dispersed in Polyol-Ester (POE) lubricant. The TiO$_2$/POE nanolubricant was prepared at volume concentration of 0.01 to 0.1% using the two-step method without any surfactant. The stability investigations were conducted by using visual sedimentation observation, micrograph observation, UV-Vis Spectrophotometer measurement and zeta potential measurement. The findings by visual sedimentation observation showed the best stability condition for more than 14 days at 0.01% and 0.03% volume concentration. Meanwhile the optimum sonication time is observed at 5 hours by visual and supported by UV-Vis evaluation. Further, the concentration ratio from UV-Vis evaluation was recorded above 95% for 5 hours sonication time and more than 30 days observation. Finally, the Zeta potential for the present nanolubricant was measured with 81.1 mV and obtained within the range of very good stability condition. Hence, this can confirm a good stability condition for the present TiO$_2$/POE nanolubricant. Further investigation is required for the properties evaluation and performance of the nanolubricant in AAC system of HEV.

1. Introduction
Nanoparticle was widely used as value added in producing new materials. Nanoparticles are also increasingly widespread in the production of enhanced material properties. Nanoparticle is a kind of material that has a very small and fine particle size of less than 100 nm. It has a variety of properties that can be applied to the production of materials to be used on various applications. Dispersion of nanoparticle is used in sectors such as biomedical, health care, food agriculture, industrial, electronics,
environment, renewable energy and textile [1, 2]. Application of nanoparticle in liquid can be divided into two types that were commonly used in industry. There are nanolubricant and nanofluid and others type is nanorefrigerant in application of refrigerator or air-conditioning system. Choi et al. [3] has applied the first concept of nanoparticles in a base fluid called nanofluids. Thermo-physical properties of the base fluid can be increased and it was proven by using this method.

The element of thermo-physical properties like thermal conductivity, viscosity, density and stability have been one of the main criteria to investigate since many years ago by many researchers [4-8]. Nanolubricant stability is one of the first elements need to be conducted before proceed to the next step. The stability investigation also has been done by the previous researches [9-11]. The application of nanoparticles in lubricants is widely been used in the automotive industry to improve the AAC system performance. As technology rapidly developed, nanolubricant technology has evolved from time to time. The first generation of nanolubricant was more focused on one type of nanoparticle which is mixed into the base lubricant. Sharif et al. [12, 13] and Redhwan et al. [14] investigated the effect of Al2O3 and SiO2 nanoparticles additives into PAG lubricant. While Krishnan et al. [15] and Nabil et al. [16] reviewed that nanoparticles can enhance the performance in vapour compression refrigeration system.

Operation of AAC system is one of the most significant factors affecting real-world fuel consumption [17]. Fuel consumption is associated to the AAC system by up to 27% [18]. Dahlan et al. [19] have performed the study about performance of electric compressor in non-electric vehicle. This researcher also give opinion that the DC compressor has high potential to be implemented to the conventional non-electric vehicle to have lower fuel consumption because of lower load with better performance. Other researcher conclude that using the direct current compressor has high possibility in reducing the load of engine system and result the higher coefficient of performance and lowering the fuel consumption. The result shows about 15% to 54% increment of electrically driven compressor (EDC) compressor performance comparing with belt-driven compressor. It also cause the fuel reduction percentage is about 5% to 14% [20]. The novelty of the SiO2/PAG nanolubricant in term of energy saving have been proven by the findings of the compressor work reduced up to 16.5% and the reduction in the compressor directly associated with the energy saving characteristic of the vapour compression system [21].

It is essential to find and innovative AAC solution to HEVs or EVs [22]. Due to that, many studies and approaches have been carried out to find out how to improve and enhance the performance and affect the energy-saving from the AAC system especially in new technology of HEV. In this present study, this nanolubricant will be use in hybrid electric vehicle (HEV) air-conditioning system. The compressor in AAC system for HEV is the most different component compared to conventional AAC system. Common vehicle use belting driven compressor and HEV used electrically driven compressor (EDC). The lubricant inside the compressor is also different in terms of the properties. PAG lubricant is primarily used in common vehicle AAC system while POE lubricant commonly is used in HEV AAC system. Therefore, the goal of this study is to investigate the stability of the TiO2/POE nanolubricant. An experimental study will be conducting through visual sedimentation observation, UV-Vis Spectrophotometer and zeta potential to find the best processing concentration and sonicaiton time of TiO2/POE nanolubricant. After that, HEV AAC system performance can be proceeded for further investigations.

2. Methodology

2.1. Material properties
In producing a sample of the nanolubricant, it involved two main types of materials namely TiO2 nanoparticle and lubricant base type Polyol-Ester (POE) RL68H. This TiO2 nanoparticle will be dispersed in the base lubricant of POE RL68H. The TiO2 nanoparticle purchased from US Research Nanomaterials, Inc. The size is 50 nm with a purity of 99%. POE has been widely and successfully used with electric compressors for over 20 years and its good dielectric properties make it the popular choice for electric compressors in hybrid cars and other vehicles with electric compressors. The details properties of nanoparticle are given in table 1 and the properties of Polyol-Ester (POE) RL68H are
presented in table 2. The nanoparticle size characterization of the TiO$_2$/POE nanolubricant by field scanning electron microscope (FESEM) technique carried out using JEOL JSM 7800F machine. The FESEM image for nanoparticle is shown in figure 1.

| Table 1. Properties of TiO$_2$ nanoparticle [10, 23]. |
|---------------------------------------------------------|
| Properties                                             | TiO$_2$ |
| Thermal Conductivity (W m$^{-1}$ K$^{-1}$)              | 8.4     |
| Specific heat/J kg$^{-1}$ K$^{-1}$                      | 692     |
| Density, kg.m$^{-3}$ @ 293 K                            | 4230    |
| Molecular mass, g mol$^{-1}$                            | 79.86   |
| Average particle diameter, nm                           | 50      |

| Table 2. Properties of POE RL68H lubricant [24].       |
|---------------------------------------------------------|
| Properties                                             | POE RL68H |
| Viscosity @ 40°C (cSt)                                  | 66.6      |
| Viscosity @ 100°C (cSt)                                 | 9.4       |
| Pour Point (+C)                                         | -39       |
| Density @ 20°C (g/ml)                                   | 0.977     |
| Flash Point COC (+C)                                    | 270       |

![Figure 1. TEM Image for TiO$_2$ nanoparticles at 100 nm scale [10, 23].](image)

2.2. Preparation of TiO$_2$/POE nanolubricants

The process of two step-method have been used in preparing the nanolubricant as recommended [25]. It also been used by the previous studies [26, 27]. TiO$_2$ nanoparticle and POE base lubricant have been mixed. The preparation of the nanolubricant starts by measuring the mass of TiO$_2$ nanoparticles. Equation (1) [26, 28] has been used to determine the volume concentration of the nanolubricant required.

\[
\phi = \frac{m_p/\rho_p}{m_p/\rho_p + m_L/\rho_L} \times 100
\] (1)

The nanoparticle was filtered with strainer in the process of weighing the nanoparticle. Then, the nanoparticle dispersed in POE and stirred using magnetic stirrer about half an hour and undergo with sonication. The sonication process using the ultrasonic bath Fisherbrand (model: FB15015) to enhance the stability. This nanolubricant was prepared at a volume concentration of 0.01, 0.03, 0.05, 0.07 and 0.1%. The nanolubricant was first prepared at the highest concentration followed to the lower concentration.
2.3. The stability of nanolubricant

The stability studies need to be conducted using qualitative and quantitative experiments. Qualitative experiment involved visual observation of sedimentation. This observation was carried out at least for 14 days [23, 26]. The stability of the nanolubricant considered stable when the concentration is constant [29]. Then, the quantitative experiments involved the UV-Vis Spectrophotometer measurement and zeta potential measurement was conducted. The UV–Vis was used to determine the peak absorption wavelength and absorbance value of the sample by comparing intensity level with the base lubricant and zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the particles [30]. The UV-Vis measurement was conducted for at least 14 days (340 hours) by varying the sonication time. The wavelength of the UV-Vis Spectrophotometer is set at 530 nm after the nanolubricant was scanned to determine the peak absorption wavelength for 0.01% of concentration. The stability evaluation by UV-Vis was also used by previous studies by Sharif et al. [21] and Yu & Zie [25]. After that, the measurement of zeta potential was conducted using Anton-Paar Litesizer 500 to support and prove the stability of the nanolubricant.

3. Results and discussion

3.1. Analysis method with UV-Vis Spectrophotometer

The observation of absorbance for volume concentration from 0.01 to 0.1% is shown in figure 2. The linear relationship between absorbance, $A$ and concentration, $\phi$ was found and proven to follow the linear relation of the Beer-Lambert law. Beer-Lambert law is about a linear relationship between the absorbance intensity and the nanolubricant concentration [21].

![Figure 2. UV-Vis Spectrophotometer linear relation graph between absorbance and TiO$_2$/POE nanolubricant concentration.](image)

Volume concentration of 0.01% of the nanolubricant for five different sonication hours was demonstrated in figure 3. The ideal absorbance ratio is one (100%) which present the ideal stability of the nanolubricant [31]. From the findings, all concentrations ranged from 0 to 7 hours showed that it started to decrease after 24 hours. It showed a downward trend of 0 hour sonication, and continue up to 15 days. Meanwhile, after 2 days (48 hours), concentration of 1, 3, 5 and 7 hours remain stable until 31 days (744 hours). The concentration ratio for 1, 3, 5 and 7 hours were kept above 95% after 30 days although its decrease a little bit day by day. From this figure, it was found that 5 hours sonication time
indicated the best absorbance ratio compared to others sonication time. Therefore, to produce this TiO$_2$/POE nanolubricant, the 5 hours sonication time was the best selection.

![Figure 3](image1.png)

**Figure 3.** The concentration ratio of TiO$_2$/POE for different sonication time as a function of time.

### 3.2. Concentration ratio comparison with literature

The comparison of the current study among the best nanolubricant stability from previous study showed in figure 4 [21, 29]. SiO$_2$/PAG nanolubricant gave the best absorbance ratio about 70% in 2 weeks time with the 2 hours of sonication time and 0.2% concentration [29] and Al$_2$O$_3$/PAG nanolubricant give the best absorbance ratio about 90% also in 2 weeks time with 1.5 hours of sonication time with 0.2% of concentration [21]. Based on this comparison, it can be concluded that the stability for the TiO$_2$/POE nanolubricant shows a better and stable absorbance ratio in same range of 2 weeks time.

![Figure 4](image2.png)

**Figure 4.** Comparison of concentration ratio with sedimentation ratio with literature.
3.3. Zeta Potential evaluation
Zeta potential is another quantitative experiment to evaluate and support the stability of the nanolubricant. It validate the quality of nanofluid or nanolubricant stability through a study of its electrophoretic behaviour [25]. In this case, TiO₂/POE nanolubricant has been tested using the Anton-Paar Litesizer 500. The higher of absolute value, the better dispersion of the particles into the base lubricant shows the better stability [21]. Table 3 show the zeta potential and the classification of stability.

Table 3. Zeta potential and classification stability [32]

| Zeta potential (mV) | Stability                      |
|---------------------|--------------------------------|
| 0                   | Little or no stability         |
| 15                  | Some stability but settling lightly |
| 30                  | Moderate stability             |
| 45                  | Good stability, possible settling |
| 60                  | Very good stability, little settling likely |

The result of zeta potential measurement for TiO₂/POE nanolubricant is 81.1 mV. The result has then been compared with the classification of nanofluid stability based on the zeta potential of very good stability as shown in figure 5. The absolute value above 60 mV is desirable for very good stability. It proved that the TiO₂/POE is beyond the stable limit of 60 mV. From this finding, it can be concluded that the stability of this TiO₂/POE nanolubricant confirmed in the rate of very good stability.

3.4. Visual observation and the effect
The images of TiO₂/POE nanolubricant for a volume concentration of 0.01% with different sonication time 0, 1, 3, 5 and 7 hours are shown in figure 6 and the images of TiO₂/POE nanolubricant for a volume concentration of 0.01, 0.03, 0.05, 0.07 and 0.1% with 3 hours sonication time are shown in figure 7. These images were taken after preparation and continue every day until at least 14 days or as long as it can hold to see the sedimentation and deposition of the nanoparticle in the liquid. From figure 6, no sedimentation of particles observed after the nanolubricant is prepared. The sedimentation of particles started after a day for 0 hour and others by day 7 afterward but in minimum sedimentation. After 14 days, the sedimentation can be seen especially for 0 and 7 hours compared to 3 and 5 hours which are more stable with a fewer sedimentation. Figure 7 also shows the same trend as figure 6 but this time,
The concentration of 0.05, 0.07 and 0.1 clearly can be seen the sediment after 3 days. Compared to 0.01 and 0.03, the nanolubricant are still in the stable condition with very small sediment.

Figure 6. Sedimentation observation of TiO$_2$/POE nanolubricant with different sonication time.

Figure 7. Sedimentation observation of TiO$_2$/POE nanolubricant with different concentration.
4. Conclusion

TiO$_2$ was successfully dispersed into the POE lubricant which normally utilize in the refrigeration system by using two-steps method without any surface stabilizer or surfactants. The optimum sonication time process is 3 hours with 0.01% of concentration was confirmed by using the UV-Vis spectrophotometer analysis. It was done by the evaluation of various concentration and sonication time with both qualitative and quantitative method involving visual observation and UV-Vis spectrophotometer analysis. From the visual observation of the sedimentation, it can be concluded that this nanolubricant was in stable condition even after 14 days even some of the mixing show drastically occurred the sediment. It was shown that the peak absorbance of the TiO$_2$/POE nanolubricant lies at 530 nm wavelengths. After 14 weeks, the result from the UV-Vis showing that the relative concentration of these nanolubricant was maintained at over 95% compared to the initial concentration. Supported by Zeta Potential finding which is 81.1 mV, it has clearly shown that TiO$_2$/POE nanolubricant was in a very good stable condition after 14 weeks.

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