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Rheological Properties of TiO_2/POE Nanolubricant for Automotive Air-Conditioning System

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ABSTRACT

The enhancement of nanolubricant rheological properties can improve the performance of automotive air-conditioning systems. The rheological properties of the TiO_2/POE nanolubricant were investigated in this study at 0.01 to 0.1% volume concentrations and temperatures ranging from 0 to 100°C. TiO_2 nanoparticles were dispersed in the base lubricant of Polyol-ester (POE RL68H) lubricant in two steps. The dynamic viscosity was measured with an Anton-Paar Rotational Rheometer. According to the findings, the TiO_2/POE nanolubricant behaved as Newtonian fluids at all volume concentrations and temperatures. The dynamic viscosity increment of nanolubricants up to 1.75% only occurred for 0.1% volume concentration and temperature of 90 to 100°C. Meanwhile, when compared to POE lubricant, nanolubricants with volume concentrations of 0.01 and 0.05% showed a decrement trend in dynamic viscosity of up to 1.8%. Finally, the TiO_2/POE nanolubricant improved the rheological properties of the POE lubricant for use in automotive air-conditioning systems.

1. Introduction

Lubrication is the best method of reducing friction and applying for mechanical movement systems. Lubrication technology is always in high demand. As a result, various methods have been developed to improve the capability of lubricant for various applications. One of method is the use of nanoparticles in lubricants. Nanolubricant can improve the energy conservation.

According to the literature, almost 30% of energy is lost because of friction and wear [1]. Nanolubricants are colloidal suspensions in which nanosized particles are dispersed in the base oils.

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Basically, there are three major components in preparation of nanolubricants. The first component is base oils. The base oils are classified into three types of oils namely mineral oils, synthetic oils and vegetable oils. The second component is additives. The additives can be classified into two types namely nano additives and chemical additives. Nano additives are nanoparticles, whereas chemical additives are antioxidants, AW, EP, PPD corrosion inhibitors, and others. Nanoparticle dispersion as nano additives has been widely used in a variety of industries including biomedical, health care, food agriculture, industrial, electronics, environment, renewable energy, and textile [2-6].

Before proceeding to the next step of property evaluation, the stability of the nanolubricant must be considered. Previous researchers conducted a stability investigation as well [7-10]. The thermo-physical properties or rheological properties of nanolubricants are then investigated for the best stability condition. Many researchers studied thermo-physical properties such as thermal conductivity, rheology, viscosity, and density [11-16]. The performance of air-conditioning system is one of major concern in automotive system as reviewed by Zhang *et al.,* [17] and Datta *et al.,* [18]. One of the most effective methods for improving the performance of an automotive air-conditioning (AAC) system is to disperse nanoparticles in base lubricants. The nanolubricants can be used in the automotive industry to improve the performance of the air-conditioning system. The first nanolubricant generation concentrated on monotype nanoparticles dispersed in the base lubricant. Sharif *et al.,* [19] investigated the effect of adding Al2O3 nanoparticles to PAG lubricants. While Krishnan *et al.,* [20] examined the use of nanoparticles in a vapour compression refrigeration system.

The fuel consumption is important and significant factor in the operation of AAC system [21]. The fuel consumption of vehicles was increased up to 27% with the use of the AAC system [22]. However, for the case of hybrid electrical vehicles (HEV) or commonly known as hybrid cars, it is not only affecting the fuel consumption but also the energy consumption from the battery itself. A study on the performance of an electric compressor in a non-electric vehicle was carried out by Dahlan *et al.,* [23]. They discovered that a direct current (DC) compressor can be used in a conventional non-electric vehicle with lower fuel consumption. As a result, the use of an electric driven compressor (EDC) outperforms a conventional car. When compared to a belt-driven compressor, the EDC improves performance by 15 to 54%. In addition, this also can cause the fuel reduction percentage between 5 to 14% [24]. The energy saving for AC compressor with nanolubricant was investigated by Sharif *et al.,* [25]. The SiO2/PAG nanolubricant was reduced the compressor work for up to 16.5%.

The improvement in performance and energy saving of AAC systems are related to the characteristics or properties of nanolubricants. The viscosity effect and rheological properties are vital to be investigated. The majority of research findings demonstrated the increment of viscosity with increasing the volume concentration, while decrement of viscosity with increasing temperature. Table 1 presented previous research on the rheological properties of nanolubricants.

As a result, finding and innovating AAC solutions for HEVs or EVs is critical [29]. The demand for new technology in HEVs has prompted many researchers to improve the performance and energy-saving capabilities of the AAC system. TiO_2/POE nanolubricant will be used in the air-conditioning system of a hybrid electric vehicle (HEV) in this paper. For AAC, common vehicles use a belt-driven compressor, whereas HEVs use an electric-driven compressor (EDC). Because HEVs require a different type of compressor, they require a different base lubricant. PAG lubricant is primarily used in common AAC systems, whereas POE lubricant is primarily used in HEV systems. As a result, the goal of this research is to determine the stability and rheological properties of the TiO_2/POE nanolubricant for use in the HEV AAC system.

Table 1
Summarizes previous research on the rheological properties of nanolubricants

Nanolubricants	Summary of finding
TiO_2 nanoparticles in raw mineral oils as a lubricant additive [26]	The addition of nanoparticles to mineral oil increased its viscosity. The friction coefficient decreases as the volume fraction of the nanoparticle additive increases. The authors proposed 0.01% as the optimal volume concentration for optimal performance.
Al_2O_3/PAG nanolubricant [19]	The results showed that increasing the volume concentration increased viscosity while increasing the temperature decreased viscosity. The authors suggested using Al_2O_3/PAG nanolubricants with a volume concentration of less than 0.3% for use in automobile air conditioning systems.
Nanoparticles of SiO_2 and Al_2O_3 dispersed in PAG lubricant [27]	SiO_2 nanolubricants have a viscosity that increases with volume concentration but decreases with temperature. The authors advocated for the use of SiO_2 nanolubricants with a volume concentration of less than 1.0% in automobile air conditioning systems.
Al_2O_3/POE and ZnO/POE nanolubricants [28]	With increasing nanoparticle mass fraction, the liquid viscosity, density, and thermal conductivity increased. As the temperature rose, the viscosity and density decreased.

2. Methodology

2.1 The Properties of Material

TiO_2 nanoparticles and the lubricant-based type Polyol-Ester (POE) RL68H were used in the preparation of nanolubricants. HWNANO was used to obtain the TiO_2 nanoparticles (Hongwu International Group Ltd). The size is 50 nm, and the purity is 99.9%. POE lubricants are widely used in refrigerators, commercial air-conditioning systems, hybrid cars, and other vehicles with electrically powered compressors (EDC). The TiO_2 nanoparticles were dispersed in the POE RL68H base lubricant. Table 2 lists the nanoparticle's specific properties. Table 3 shows the properties of the Polyol-Ester (POE) RL68H. Transmission Electron Microscopy (TEM) was used to characterize the TiO_2/POE nanolubricant. Figure 1 shows a TEM image of a nanolubricant. By examining the particle distribution in the TEM image, it was clear that the size of TiO_2 nanoparticles is uniform and irregular in shape. While suspended in POE lubricants, the nanoparticles demonstrated good dispersion and less agglomeration.

Table 2
Properties of TiO_2 nanoparticle [8, 30]

Properties	Unit	TiO_2
Thermal Conductivity	$W\ m^{-1}\ K^{-1}$	8.4
Specific heat	$J\ kg^{-1}\ K^{-1}$	692
Density (at 293 K)	$kg.m^{-3}$	4230
Mass of molecular	$g\ mol^{-1}$	79.86
Average particle diameter	nm	50

Table 3
POE RL68H lubricant properties [31]

Properties	Unit	POE RL68H
Viscosity (at 40°C)	cSt	66.6
Viscosity (at 100°C)	cSt	9.4
Pour Point	°C	-39
Density (at 20°C)	g/ml	0.977
Flash Point COC	°C	270

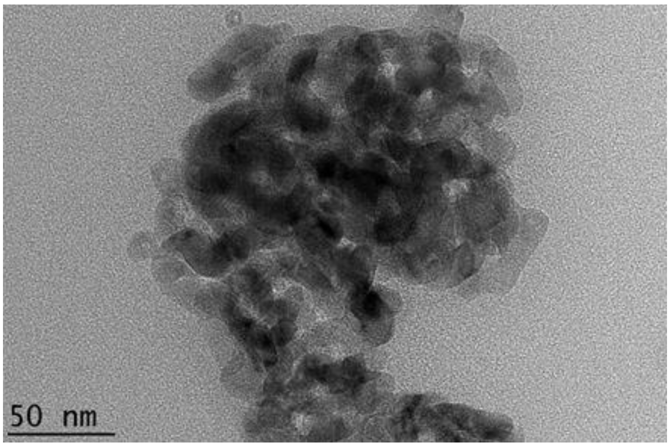

Fig. 1. TEM Image for TiO_2/POE nanolubricant at 50 nm

2.2 TiO_2/POE Nanolubricant Preparation

In order to make the nanolubricant, a two-step technique was used [32]. It was also used in previous studies [33, 34]. TiO_2 nanoparticles and POE base lubricant were combined. The mass of TiO_2 nanoparticles was measured to begin the preparation of the nanolubricant. The volume concentration of the nanolubricant was calculated using Eq. (1) [33, 35].

$$\emptyset = \frac{m_p/\rho_p}{m_p/\rho_p + m_L/\rho_L} \times 100 \tag{1}$$

As shown in Figure 2, the nanoparticle was filtered with a strainer during the weighing process. Before being dispersed in the POE lubricant, the strainer was used in the nanolubricant preparation process to reduce the agglomeration size. The nanoparticles were then dispersed in POE lubricants and stirred for 30 minutes with a magnetic stirrer before being sonicated. To improve the stability of the nanolubricant, the sonication process used an ultrasonic bath with ultrasonic pulses of 100W and 36 (+/- 3) kHz. The TiO_2/POE nanolubricant in this study was prepared at volume concentrations of 0.01, 0.03, 0.05, 0.07, and 0.1%. The nanolubricant was created by reducing the concentration from the highest to the lowest.

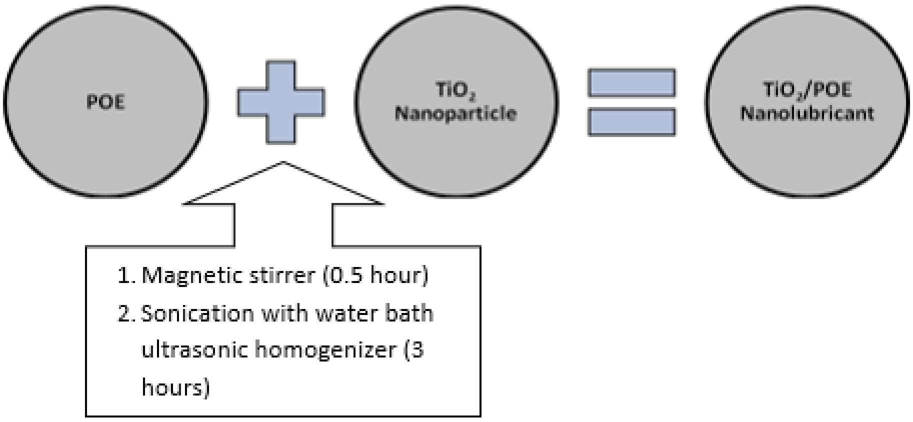

Fig. 2. Two step method process in preparing the nanolubricant

2.3 The Nanolubricant Stability

Quantitative and qualitative methods were used to test the stability of nanolubricant. Visual observation of sedimentation was utilized as a qualitative method. This study lasted a minimum of 14 days and a maximum of 60 days [30, 33, 36]. The nanolubricant is said to be stable when the concentration ratio remains constant over time [37]. Then, as illustrated in Figure 3, the quantitative approach used an Ultraviolet-Visible (UV-Vis) spectrophotometer. By comparing the intensity level with the base lubricants, the UV–Vis was utilized to calculate the sample's peak absorption wavelength and absorbance value [38]. By adjusting the sonication period, the UV-Vis measurement was carried out for at least 14 days (340 hours). The UV-Vis spectrophotometer's peak wavelength was discovered to be 530 nm. The peak absorption wavelength of the TiO_2/POE nanolubricant was determined by scanning the absorbance of the TiO_2/POE nanolubricant with a variety of wavelengths at a constant 0.01% volume concentration [36]. Previous research had also employed UV-Vis to assess stability such as Sharif *et al.,* [25] and Yu & Zie [32].

Fig. 3. UV-Vis Spectrophotometer

2.4 Dynamic Viscosity Measurements

The TiO_2/POE nanolubricant's dynamic viscosity was measured using the Anton-Paar Rotational Rheolab QC, as shown in Figure 4, at varied temperatures between 30 and 100 °C and different volume concentrations. The data was collected in the range of 0 to 1.0 mPa.s and a torque range of 10 to 100%. The torque notion was used in the rotational viscometer. To rotate the liquid, torque was necessary, which was a component of the liquid's viscosity. It will cause the liquid's viscous drag against the spindle. Depending on the viscosity of the nanolubricant, changing speeds of the spindle will cause varied shear stress, shear rate, and torque as the temperature rises. The rotational rheometer can measure the viscosity of liquid samples with an accuracy of 0.1 mPas in the range of 1 to 10^9 mPas, as well as accurate temperature control in the range of 0 °C to 180°C with an accuracy of 0.1°C. The DIN 54453 double gap measuring systems and a viscosity of less than 100 mPa.s for low viscosity samples.

Fig. 4. Anton-Paar Rotational Rheometer Rheolab QC Rheometer

3. Results and Discussion

3.1 Nanolubricant Stability Tests

Figure 5 presented the absorbance for volume concentrations ranging from 0.01 to 0.1%. The linear relationship between absorbance, *A*, and concentration, ϕ, was discovered and proved to obey the Beer-Lambert law's linear relationship. The Beer-Lambert law states that the absorbance intensity and nanolubricant concentration have a linear relationship [25, 36].

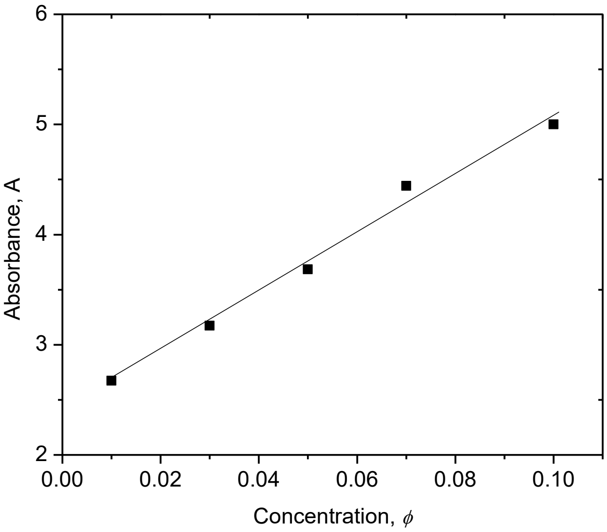

Fig. 5. Linear relation between absorbance and concentration of TiO_2/POE nanolubricant

Figure 6 shows the TiO_2/POE nanolubricant concentration ratio at 0.01% volume concentration and various sonication hours. The optimal absorbance ratio is one (100%), indicating that the nanolubricant is stable [39]. From the findings, the concentration ratio started to decrease within 24 hours for all sample for sonication time from 0 to 7 hours. The concentration ratio for reference sample at 0 hour decreased significantly and reached 0.55 ratio on 60 days observation. Meanwhile, concentration ratios for sonication time of 1, 3, 5 and 7 hours were remained stable above 0.9 (90%) on 60 days evaluation. This condition was confirmed the effectiveness of using ultrasonic bath to improve the stability of nanolubricant.

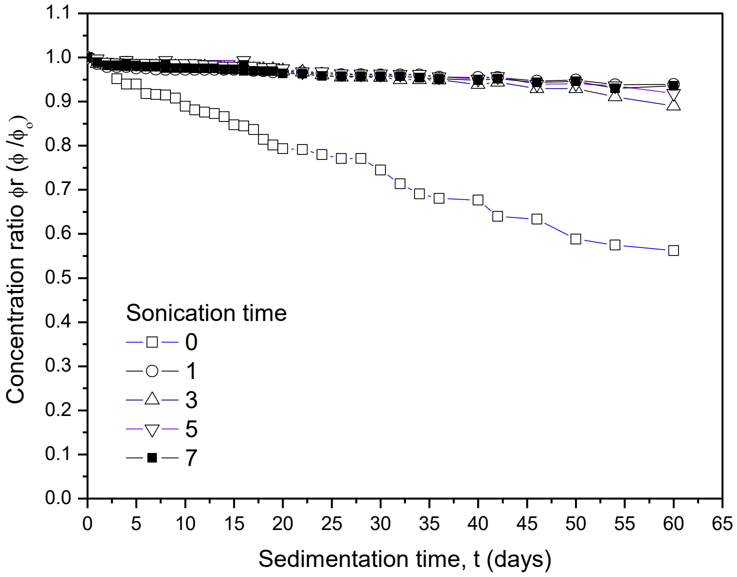

Fig. 6. The concentration ratio of TiO_2/POE nanolubricant at different sonication time

3.2 Dynamic Viscosity of Nanolubricant

3.2.1 Dynamic viscosity against rotational speed

Figure 7 depicts the pure POE lubricant viscosity against rotational speed. While Figure 8 depicts the viscosity TiO_2/POE nanolubricant against rotational speed at 0.01% volume concentration. It can be seen that the dynamic viscosity of pure POE lubricant and TiO_2/POE nanolubricant remains constant with rotational speed at different temperatures. It can be concluded that the pure POE lubricant and TiO_2/POE nanolubricant behaved as Newtonian fluid at all volume concentration and temperatures.

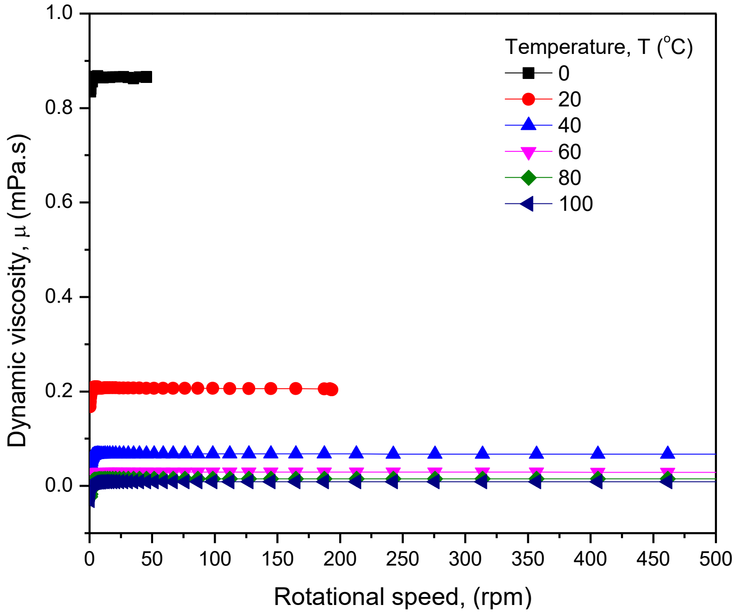

Fig. 7. Pure POE lubricant viscosity against rotational speed

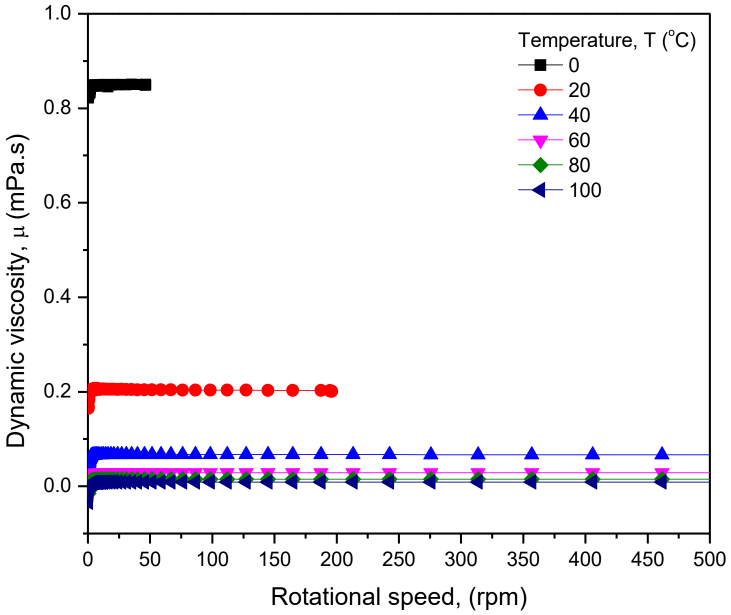

Fig. 8. The viscosity of TiO_2/POE nanolubricant against rotational speed at 0.01% volume concentration

3.2.2 Dynamic viscosity against shear strain rate

Figure 9 depicts the shear stress against shear strain for pure POE lubricant. While Figure 10 presents the shear stress against shear strain for TiO_2/POE nanolubricant at 0.01% volume concentration. It can be observed that the shear stress is directly proportional with the shear strain for different temperatures and applicable for both pure POE lubricant and TiO_2/POE nanolubricant. It may also be deduced that at all volume concentrations and temperatures, pure POE lubricant and TiO_2/POE nanolubricant behave as Newtonian fluids.

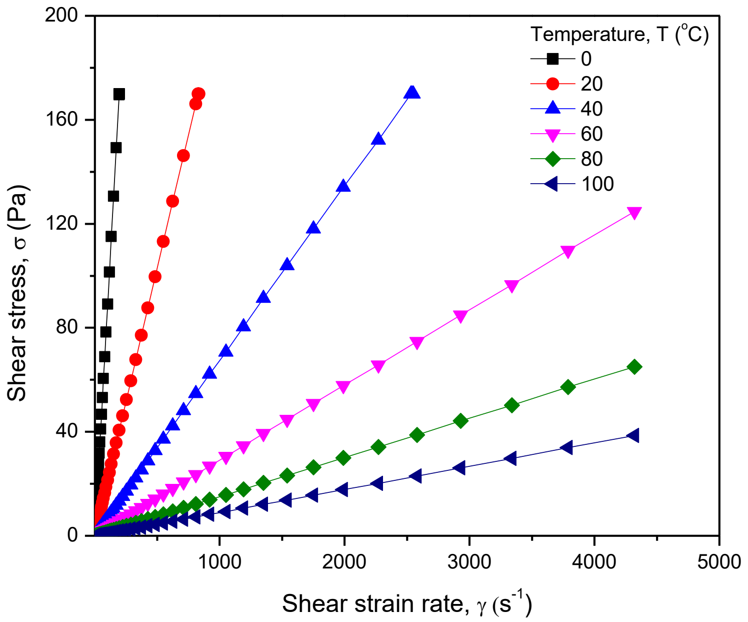

Fig. 9. The pure POE lubricant viscosity against rotational speed

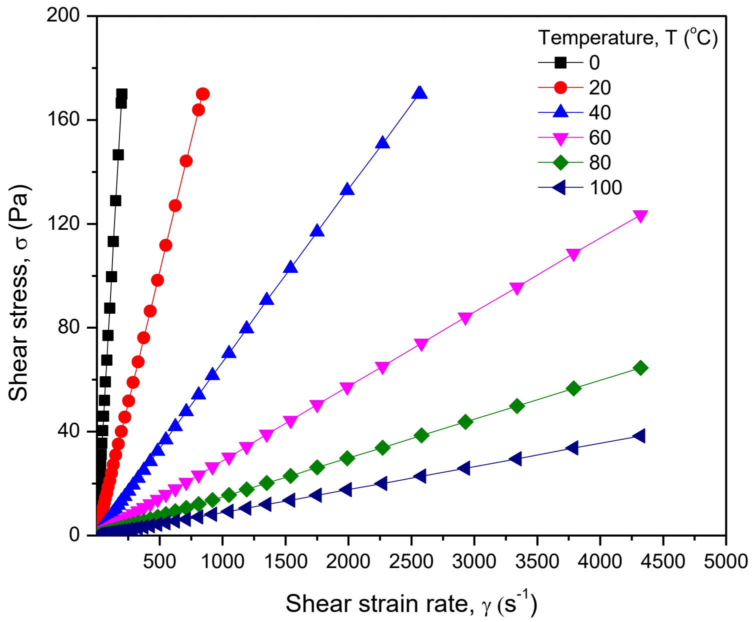

Fig. 10. The 0.01 concentration of TiO_2/POE nanolubricant shear stress against shear strain rate

3.2.3 Dynamic viscosity against temperature

Figure 11 depicts the fluctuation in dynamic viscosity for the TiO_2/POE nanolubricant at varied temperatures and volume concentrations. The graph shows that the nanolubricant's dynamic viscosity increased significantly with volume concentration. For 0.1% volume concentration, the increase in dynamic viscosity was only seen at temperatures between 40 and 100°C. Van der Waals interactions between molecules and liquids are one of the various physical mechanisms that cause the increase in dynamic viscosity [40, 41]. In another study, Afrand *et al.,* [42] according to the study, enhancing the connections between nanoparticles and engine oil molecules can increase viscosity.

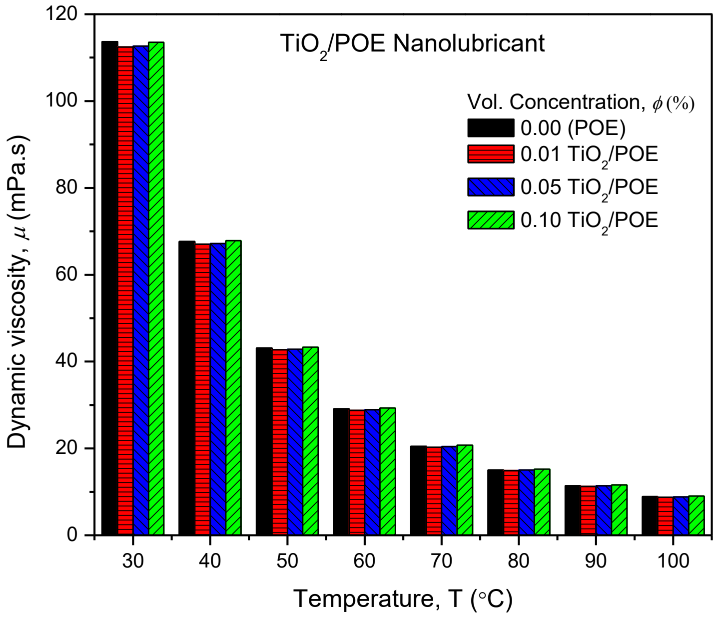

Fig. 11. TiO_2/POE nanolubricant dynamic viscosity against temperature

Figure 12 depicts the TiO_2/POE nanolubricant dynamic viscosity increment as a function of temperature. The highest dynamic viscosity increment was observed up to only 1.75% and occurred at 0.1% volume concentration and temperatures ranging from 90 to 100°C. It also agreed well with the data by Zawawi *et al.,* [7, 13, 33]. Interestingly, the dynamic viscosity showed the decrement trend up to 1.8% for 0.01% and 0.05% volume concentration at temperature 0 to 100 °C compared to pure POE. However, the reduction trend with viscosity of nanolubricants is not common in the literatures. This showed that the nanoparticles did not affect the lubricant in term of the Van der Waals forces but it gives much better and smoother interactions between the nanoparticles and the lubricant compared to pure POE lubricant. The decrement effect of dynamic viscosity means it will decrease the work load of the EDC hence better performance.

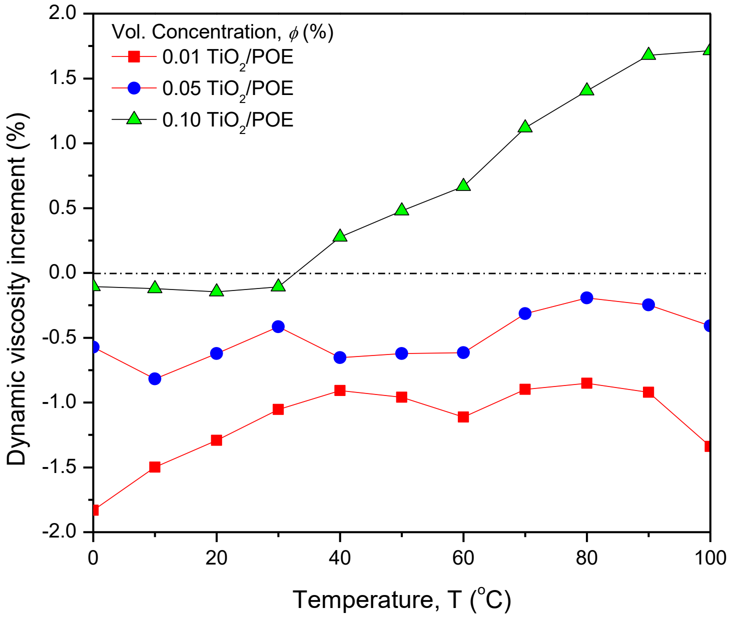

Fig. 12. TiO_2/POE nanolubricant dynamic viscosity increment against temperature

4. Conclusions

In this paper, TiO_2 nanoparticles were dispersed into POE lubricant using a two-step method without the use of any surface stabilizer or surfactant for use in AAC and refrigeration systems. The TiO_2/POE nanolubricant was observed in excellent stability condition for up to 60 days. The both pure POE lubricant and TiO_2/POE nanolubricant behave as Newtonian fluids for all volume concentrations and temperatures. At certain operating temperatures, the TiO_2/POE nanolubricant demonstrated lower dynamic viscosity than pure POE lubricant for less than 0.1% volume concentrations. For 0.1% volume concentration, the increase in dynamic viscosity was only observed at temperatures ranging from 40 to 100°C. It can be concluded that the TiO_2/POE nanolubricant outperformed the pure POE lubricant in terms of rheological properties. To extend the current work, additional research on the performance of AAC systems in HEVs using the current TiO_2/POE nanolubricant is required.

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