Evaluation of TiO$_2$ nanoparticles as viscosity modifier in palm oil bio-lubricant

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Abstract. TiO$_2$ nanoparticles is one of the most studied nanomaterials as an additive in oil lubricant due to its outstanding chemical and physical properties as well as low toxicity. This study aims to investigate the effect of TiO$_2$ nanoparticles, as additive in renewable palm oil lubricant on the change of viscosity. Viscosity is one of the most vital physical parameters for assessing the performance of lubricant oil. The method for preparation of all samples involved adding of TiO$_2$ nanoparticles at concentrations of 0, 0.5 and 1.0 weight percentage in lubricants, followed by mixing using ultrasonication method for 30 minutes. Investigation on the viscosity showed that the viscosity of palm oil bio-lubricants is comparable to SAE 0W20 grade lubricant. The viscosity index tends to increase with the concentration of TiO$_2$ additive.

1. Introduction

In it commonly known that the main sources of wear and friction are owing to energy losses during high friction and failure in machinery engines, bearings and gears [1-3]. Friction is the main cause of energy loss in engine which covers approximately 15% from the total energy losses in engine [4]. The value relies on the energy used to overcome the brake interaction, tyres rolling resistance, transmission systems and the rubbing of parts in the engine.

While many other countries used vegetable oil such as corn, canola and rapeseed as bio-lubricant oils, Malaysia also is seen to have started the work on using palm oil as bio-lubricant oil to promote our own homegrown resource. Palm oil is a sustainable option compared to the conventional petroleum-based lubricants. Studies carried out by Masjuki et al. revealed that chemically modified palm oil (CMPO) exhibits better performance compared to mineral oil in reducing friction with the addition of nanoadditives [5]. On the other hand, S.Syahrullail et al. reported that palm oil has a comparable tribological performance to paraffinic mineral oil to reduce the extrusion load [6].

Several types of nanoparticles have been used as additive to improve lubrication properties of bio-lubricant such as metal, metal oxide, carbon, carbonate, borate and organic materials [7-16]. The additives have been reported to act as an anti-friction and wear reducer. The performances of nanoparticles such as TiO$_2$, ZnO, CuO and SiO$_2$ as additives also have been investigated in numbers of works [8, 10, 17-23]. It was found that friction and wear reduction behaviour strongly relies on the characteristics of the additives such as size, morphology, hardness and concentration [8, 24, 25]. The size of particles used as additive is usually in the range of 2 to 120 nm [8, 12, 26-28]. Previous works also exposed that the smaller size of nanoparticles are more likely to interrelate with the surfaces forming thin film on the lubricating surface and behave as a protective film to reduce friction [28].
However, one of the most challenging issues when using nanoparticles as an additive, is the existence of attractive force between particles that promotes aggregation due to its high surface area [20]. This phenomenon limits the tribological performance of the nanoparticles as additives.

TiO2 nanoparticles are one of the well-known nanoadditives for synthetic lubricant. It was used as an additive due to its low toxicity, anti-oxidant features and non-volatility behaviours [29-31]. Numerous works have also reported the excellent performance of TiO2 as an additive in lubricant oil. Nevertheless, most of the works were carried out with conventional synthetic oil. This work will provide initial information on the variation of viscosity with the addition of TiO2 nanoparticles as additive in palm oil bio-lubricant. This paper will discuss how the viscosity of palm oil bio-lubricant changes with the addition of TiO2 nanoparticles as additive. It is well recognized that viscosity is one of the most critical physicochemical properties as a lubricant oil.

2. Experimental

2.1. Materials

In this study, palm oil and synthetic oil (SAE 10W-40) were selected as the base oil. Synthetic oil is used as comparison to investigate the performance of palm oil lubricant. The effect of adding nanoparticles additives at different concentrations in palm oil and synthetic oil were investigated. The physicochemical properties of TiO2 nanoparticles are shown in Table 1. Titanium oxide (TiO2) nanoparticles with average size of 21 nm with purity level of 99.5% were purchased from Sigma Aldrich.

| Parameter      | Value      |
|----------------|------------|
| Colour         | White      |
| Purity         | 99.5%      |
| SSA            | 289 m2/s   |
| Diameter       | 21 nm      |
| Morphology     | Nearly spherical |

2.2. Preparation of lubricant samples

TiO2 nanoparticles powder were added into the lubricant oils at different concentrations, range between zero to one weight percentage (wt%). The required quantity of nanoparticles powder is accurately weighted using a precision balance and mixed directly with the base oil. Surfactant ethylene glycol (EG) was then added into the lubricant. EG was used to disperse the nanoparticles in the base oil to avoid agglomeration and precipitation of the TiO2 nanoparticles. The nanoparticles additive was mixed in the lubricating oil using ultrasonication method. The time of agitation was fixed at 30 minutes. Table 2 summarises the lubricant blends with its weight ratio percentage.

| Blend | Type of base oil | TiO2 (wt%) |
|-------|------------------|------------|
| SO    | Synthetic oil    | 0.0        |
| SO1   | Synthetic oil    | 0.5        |
| SO2   | Synthetic oil    | 1.0        |
| PO    | Palm oil         | 0.0        |
| PO1   | Palm oil         | 0.5        |
| PO2   | Palm oil         | 1.0        |

2.3. Characterisation of the lubricants

The viscosity of all lubricant samples at 40°C and 100°C was measured using Kinematic Viscometer model Canon CT-500. Kinematic viscosity is expressed in centistokes (cSt) by multiplying the efflux time and viscometer constant. It is mathematically calculated using Eq. 1.
\[ v = C t \]  

where

\( v = \) kinematic viscosity, mm\(^2\)/s
\( C = \) viscometer constant, mm\(^2\)/s
\( t = \) flow time, s

3. Results and Discussion

The viscosity of the samples was measured at temperature of 40°C and 100 °C for three concentrations of TiO\(_2\) at 0, 0.5 and 1.0 wt%. The kinematic viscosity (VI) of the lubricant samples was then analysed according to the ASTM D445 and ASTM D2272 standard. Table 3 shown the recorded kinematic viscosity and their viscosity index (VI). The properties of some of the SAE grade lubricants are listed in Table 4 as a comparison [32]. The kinematic values are illustrated in Figure 1. Kinematic viscosity of all bio-lubricant samples (PO, PO1 and PO2) conforms to viscosity class of SAE 0W20 lubricant which indicate that the synthetic oil SAE 0W20 is a low-viscosity type of lubricant from group IV.

| Type of Lubricant | Viscosity at 100 °C (cSt) | Viscosity at 40 °C (cSt) | Viscosity Index |
|------------------|--------------------------|--------------------------|----------------|
| SO               | 19.11                    | 112.11                   | 192.31         |
| SO1              | 19.33                    | 112.93                   | 193.52         |
| SO2              | 20.44                    | 113.20                   | 206.04         |
| PO               | 10.32                    | 49.32                    | 204.30         |
| PO1              | 10.40                    | 49.72                    | 204.43         |
| PO2              | 10.74                    | 50.05                    | 212.31         |

Table 4. Properties of typical SAE lubricant [32]

| SAE grade | Viscosity (cSt) |
|-----------|-----------------|
|           | 40°C | 100°C |
| 0W20      | 45    | 9     |
| 5W30      | 65    | 13    |
| 10W40     | 100   | 18    |
| 40        | 160   | 18    |
| 50        | 200   | 19    |
Figure 1. Variation of kinematic viscosity with temperature of SAE grade lubricants and bio-lubricant samples.

To further investigate the changes of kinematic viscosity of lubricant samples, the recorded values in Table 2 are presented in Figure 2(a and b). As can be seen in the figures, the value of kinematic viscosity increased for both synthetic and palm oil as the concentration of TiO2 nanoparticles rise. The viscosity of palm oil samples is approximately 50% lesser than the synthetic oil samples. Low viscosity of palm oil can minimize viscous friction [33]. Both synthetic and palm oil samples have the same trend of viscosity change with TiO2 concentration. The results indicate that TiO2 nanoparticles acted similarly in synthetic and palm oil lubricants. Especially at high temperature (Figure 2(b)), major increased of viscosity value can be observed at TiO2 concentration of 1.0 wt%. It can therefore say that at high temperature TiO2 effectively act as viscosity modifier in bio-lubricant samples.

Figure 2. Kinematic viscosity of synthetic and palm oil at temperature of (a) 40°C and (b) 100°C respectively.

The similar finding has also been reported by many other works of TiO2 in synthetic lubricant oil [34, 35]. However, the outcomes contradict with the earlier formulation developed by our group where the addition of TiO2 reduces viscosity kinematic at 100°C [36]. Looking at the point of rheology, when TiO2 nanoparticles were added to oil, it will act as obstacles that will disturb the oil flow thus increase the flow resistance like viscosity (Figure 3). In this work, ethylene glycol was added as a surfactant. It is widely known to enhance the dispersion of nanoparticles like TiO2 by limiting aggregation and sedimentation of the particles. Addition of ethylene glycol may has produced ethylene glycol surface
modified TiO$_2$ nanoparticles that are well dispersed in the lubricant oil samples as illustrates in Figure 4[37]. As the number of TiO$_2$ nanoparticles increased in the oil, there were more flow resistance in the oil and therefore increase the viscosity of the TiO$_2$ lubricant oil samples.

![Figure 3. Schematic of lubricant oil flow with particle.](image)

Figure 3. Schematic of lubricant oil flow with particle.

![Figure 4. Schematic of TiO$_2$ dispersion in lubricant oil with and without surfactant ethylene glycol.](image)

Figure 4. Schematic of TiO$_2$ dispersion in lubricant oil with and without surfactant ethylene glycol.

The viscosity index (VI) against the concentration of TiO$_2$ is depicted in Figure 5. Higher viscosity index (VI) promotes a more stable viscosity across a range of temperatures (independent to temperature). An apparent change in the values of VI can be observed with the addition of 1.0% of TiO$_2$ by 4.1% and 7.3% for palm oil and synthetic lubricant samples, respectively. Lubricant samples with 0.5 wt% TiO$_2$ nanoparticles seem not to influence the VI for all lubricant samples. This confirms that the TiO$_2$ additive has successfully improved the stability of lubricant samples.

On the other hand, it can also be seen that the VI of palm oil is 5.9% higher as compared to the synthetic oil. It indicates that palm oil lubricant with 1.0% TiO$_2$ will be able to provide good resistance to thinning of lubricant film for better fuel consumption in engine [33]. High VI of palm oil lubricants may attributed to the fact that the molecular weight of bio-lubricant is more stable than synthetic oil. This property makes the palm oil suitable for high-temperature applications, typically 250°C and above [38].
4. Conclusion
The current work investigates the viscosity change of palm oil bio-lubricant with the addition of TiO$_2$ nanoparticles as an additive. The experimental results show that palm oil bio-lubricant samples with and without TiO$_2$ additive exhibit comparable viscosity value to the SAE 0W20 grade at both temperature of 40°C and 60°C. Addition of TiO$_2$ as an additive in palm oil indicates improvement of the viscosity index of the bio-lubricant which may correlates to the well dispersion of TiO$_2$ with ethylene glycol. The viscosity index of palm oil bio-lubricant was increased by 4.1% using TiO$_2$ as an additive.

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