Preparation and dispersion stability of graphite nanoparticles in palm oil

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1.0 INTRODUCTION

The advent of nanotechnology has allowed the synthesis of nanomaterial in various fields, including optic and optoelectronics (Reddy et al., 2008), photocatalysis (Reddy et al., 2014), electrical and sensor devices (Zhang et al., 2007), biomedical applications (Gupta and Gupta, 2005), and so on due to their excellent chemical, thermal and mechanical properties. Recently, significant interest has been directed towards the synthesis of nanoparticles in base fluid/lubricant, since it can provide useful advantages in terms of heat transfer performance (Sheikholeslami, 2018a, 2018b, 2018c) and tribological performance (Ahmadi et al., 2013; Gulzar et al., 2015; Peña-parás et al., 2014; Xie et al., 2016). Despite the tribological performance advantages of using nanolubricants, it is still challenging to produce homogenous and long-term stability of nanolubricants without agglomeration. Previous research found that the...
agglomeration of nanoparticles affected the tribological performance of the nanolubricant. It is therefore important to improve the dispersion stability of nanolubricant to provide a suspension without agglomeration and have a long-term stability, in order for it to be used in actual future applications. Nevertheless, until recently, limited academic attention has been paid on the effects of dispersion stability from different preparation techniques.

Some methods, including physical (one-step and two-step methods) (Zin et al., 2015) and chemical treatments (use of surfactant, surface modification, and pH control) (Afifah et al., 2016; Zhu et al., 2010; Lou et al., 2015), can be used to provide a stable suspension. For physical treatment, generally the two-step method is the most widely used by previous researchers to prepare a suspension; since it is the most economical method for large scale production. The selection of a preparation method is important to provide an established stability of suspension. The present research will only focus on the physical treatment. Dispersion stability of nanolubricants can be determined through various methods: by sedimentation method (Peng et al., 2010), by UV-vis spectrophotometer (Vakili-Nezhaad and Dorany, 2009), by dynamic light scattering (Lou et al., 2015), by zeta potential analysis (Sabareesh et al., 2012), by electron microscopy (Lee and Rhee, 2014) and by optical microscope (Azman et al., 2016). It is important to evaluate the aggregate state of nanoparticles and sedimentation characteristics in nanolubricants. Amongst others, sedimentation method and observation through optical microscope are requiring relatively simple process and cost-effective method.

Graphite, a lamellar solid nanoparticle, has gained popularity for the last two decades as solid lubricants and as additives in lubricant. Graphite has an excellent lubrication characteristic when used as solid lubricants in hot and cold forming operations (Podgornik et al., 2015). It also widely used as electrode and heating elements for industrial blast furnace since it has high thermal conductivity and high in-plane electrical (Wang et al., 2012). Previous work has shown that graphite also improves the tribological performance of lubricant (Choi et al., 2011; Huang et al., 2006; Lee et al., 2009; Su et al., 2015). It is well known that graphite nanoparticles were effective in improving the tribological performance of the lubricant due to their layered and crystal structure with strong interlayer covalent bonds and the molecular layers are relatively far apart due to the weak van der Waals force (Srinivas et al., 2017; Yan et al., 2014).

The aim of this study is therefore to evaluate the effects of different preparation techniques on the dispersion stability of graphite (CG) nanoparticles in the palm kernel oil (PKO) based lubricant. To achieve the aim of this research, three different two-step methods were considered, including magnetic stirrer, overhead stirrer and high-shear homogeniser. The dispersion stability of the nanolubricants was measured by sedimentation photographs and optical microscope. The effects of different mixing methods on viscosity and tribological performance of nanolubricants also were evaluated using rotary viscometer and four ball tribotester, respectively.

2.0 EXPERIMENTAL PROCEDURE

2.1 Materials
Refined, bleached and deodorized palm kernel oil (PKO), with a density of 0.90 g/cm3, was used as the based lubricant. Graphite (CG) nanopowder, with 99.5% purity, from MK Impex Corp, Canada, was used for the dispersion in this study. The average nanoparticle size was 50 nm with a density of 2.26 g/cm3. The transmission electron micrograph (TEM) of graphite nanopowder with sheet morphology is shown in Figure 1.
2.2 Preparation methods of nanolubricant

The nanolubricants were prepared by dispersing CG nanoparticles in PKO by a two-step method. In order to study the effects of the nanolubricant’s dispersion method, CG nanoparticles, with a concentration of 0.05 wt%, are dispersed in PKO via three different two-step methods (magnetic stirrer, overhead stirrer and high-shear homogeniser). The details of these preparation methods are summarized in Table 1.

<table>
<thead>
<tr>
<th>Two-step methods</th>
<th>Test condition</th>
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<tbody>
<tr>
<td>Magnetic stirrer (M1)</td>
<td>Speed (1200 rpm), duration (120 min)</td>
</tr>
<tr>
<td>Overhead stirrer (M2)</td>
<td>Speed (400 rpm), duration (120 min), power input (72W), frequency (50/60 Hz)</td>
</tr>
<tr>
<td>High-shear homogeniser (M3)</td>
<td>Speed (13000 rpm), duration (45 min), power input (800W), frequency (50/60 Hz)</td>
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</table>

2.3 Evaluation of dispersion stability

The effects of dispersion methods, on the stability of nanolubricants, are evaluated using sedimentation photographs and metallographic microscopy. After preparation of the nanolubricants, vials of 50 ml were filled with nanolubricant. Next, sedimentation photographs were taken over a period of time. For metallography microscopy, the present research uses an optical microscope instead of electron microscopy; since it can characterize the aggregate size of the suspension on a micrometer scale (Azman et al., 2016).

2.4 Viscosity analysis

In this research, the effects of dispersion methods on the viscosity of CG/PKO nanolubricants were evaluated. The kinematic viscosity of the tested nanolubricants were measured using rotary viscometer which is determined from the measurement of the torque required to rotate the spindle. The measured torque is used to calculate the viscosity of the nanolubricants, which is automatically displayed by the rotational viscometer. In this method, the tested nanolubricants is...
placed in a 200 ml beaker and the metal spindle is rotated at a fixed speed (rpm) and the torque is created. The temperature range are from 40°C to 100°C, where the beaker is heating using hot plate and the temperature is monitored through the digital thermometer. Then, the viscosity index (VI) of the lubricants was also determined to show the temperature dependence of a nanolubricants kinematic viscosity.

2.5 Tribological performance

The four ball tribotester was applied to evaluate the effects of dispersion methods on the tribological performance of CG/PKO nanolubricants. The experiment was carried out in accordance to ASTM D4172. The balls used were steel ball with 12.7 mm diameter which made AISI 52100 steel with 64-66 Rc hardness. Before each test, the balls were cleaned thoroughly with acetone and wiped with fresh lint free industrial wipe to remove any dirt and contaminants. One steel ball was placed into the collet and mounted on the motor spindle and make a point contact with three stationary steel balls immersed in 10 ml lubricant. The test was carried out under 392 N applied load at 1200 rpm sliding speed for an hour at 75°C temperature. After each test, the steel balls were cleaned with acetone and the wear scar diameter were measured using optical microscope. The coefficient of friction was taken directly from the electronic display.

3.0 RESULTS AND DISCUSSION

3.1 Dispersion stability of nanolubricants

Sedimentation photographs were taken over a period of time, then sedimentation ratio was calculated by dividing the height percentage of the sediment nanoparticles against the total suspension height. The larger sedimentation ratio indicated stable dispersion stability. Figure 2 shows the sedimentation ratio and sedimentation photographs of CG/PKO nanolubricants prepared by different dispersion methods. Figure 2 shows that the fastest sedimentation rate was in the nanolubricant prepared by magnetic stirrer; where a bigger separation layer of CG nanoparticles and PKO based lubricant can be seen. The sedimentation ratio was reduced to 70% after 360h preparation. Based on this figure, the stability of nanolubricants shows improvement after using the overhead stirrer and the high-shear homogeniser. It shows 90% of sedimentation ratio of nanolubricants prepared by high-shear homogeniser remained after 360h which improved by 13% and 20% compared to overhead stirrer and magnetic stirrer, respectively.

To further investigate the dispersion of CG in lubricant, metallographic micrographs were taken using an optical microscope. Figure 3 represents the threshold image of the metallographic micrographs. After preparation of the nanolubricant, a drop of each suspension was poured onto a glass slide, left to dry at room temperature, and observed with an optical microscope (Azman et al., 2016). It was observed that dispersing CG nanoparticles in lubricant using the magnetic stirrer (Figure 3a) had the highest level of agglomeration. Using the overhead stirrer was apparently more effective at breaking the agglomerate size of the particles than using the magnetic stirrer (see Figure 3b). Figure 3c shows that the high-shear homogeniser effectively diminished the agglomeration of CG nanoparticles. The high-shear homogeniser was therefore deemed to be the most effective two-step method of providing a more stable suspension than the other methods.

These results show that different dispersion methods affect the dispersion stability; which agrees well with the results of a study by Hwang et al. (2008). The authors confirm that the high-shear homogeniser was the most effective dispersion method of all to disperse nanoparticles in the base.
fluid. This is because the high-shear homogeniser was able to provide sufficient energy to break down the agglomerate nanoparticles using high shear force. For the present research, it was able to provide a shear rate of up to 40,000 s\(^{-1}\).

![Figure 2: Sedimentation ratio and sedimentation photographs of different dispersion methods (M1: magnetic stirrer; M2: overhead stirrer; M3: high-shear homogeniser).](image)

![Figure 3: Threshold image of metallographic micrographs of CG in lubricant under different dispersion methods of (a) magnetic stirrer; (b) overhead stirrer; (c) high-shear homogeniser.](image)

### 3.2 Effects of dispersion stability on viscosity of nanolubricants

Figure 4 shows the kinematic viscosity of CG/PKO nanolubricants of different dispersion methods with the temperature ranged from 40°C to 100°C. In general, it can be seen that the viscosity has the same trend, increase in temperature led to a decrease in the kinematic viscosity. The temperature effect on lubricant viscosity is due to the weakening of the inter-particle and inter-molecular adhesion forces (Kole and Dey, 2011). It can be seen that the viscosities of nanolubricants prepared by M1 and M3 are slightly higher than the nanolubricant prepared by M2 at temperatures of 40 - 60°C. However, the viscosities of nanolubricants prepared by M1 and M2 are significantly lower than the nanolubricant prepared by M3 at temperatures of 70 - 100°C. Overall, it is observed that the viscosity of nanolubricant prepared by M3 is the highest at temperatures of 40 - 100°C. The viscosity difference between the dispersion methods probably
due to dispersion stability of nanolubricants. Since the agglomeration of nanoparticles prepared by M1 and M2 were larger than that of M3 (as seen in Figure 3), it makes the nanoparticles easily settling down and sediment at the bottom of the beaker. Thus, this agglomeration has small effect on the flow of resistance as the viscometer spindle senses the resistance up to a certain level of suspension (Mahbubul et al., 2014).

Figure 4: Kinematic viscosity of CG/PKO nanolubricants of different dispersion methods (M1: magnetic stirrer; M2: overhead stirrer; M3: high-shear homogeniser) at various temperatures.

3.3 Effects of dispersion stability on friction and wear performance

The effects of the dispersion methods on the friction performance is presented in Figure 5. It shows that coefficient of friction (COF) of lubricant containing CG nanoparticles are lower than the base lubricant, indicating that the CG nanoparticles are potential additives in improving friction performance. Overall, it is clear that the addition of CG nanoparticles in base lubricant by different dispersion methods resulted in different friction performance. It can be seen that the COF was slightly reduced by 1.9% for nanolubricant prepared by magnetic stirrer (M1), and 2.1% for nanolubricant prepared by overhead stirrer (M2) compared to the base lubricant. It appeared that the COF decrease by 7.9% for nanolubricant prepared by high-shear homogeniser (M3), which shows the highest reduction in COF. The outstanding friction performance of nanolubricant prepared by high-shear homogeniser could be attributed to their excellent dispersion stability, as shown in Section 3.1. Better dispersion stability of nanolubricants make the nanoparticles easily enter the contact area, thereby reduce metal-to-metal contact. In contrast, the COF of nanolubricants shows increment after using the magnetic stirrer and the overhead stirrer. This phenomenon occurs due to the agglomeration of nanoparticles that can adversely affect the friction performance. This finding supported previous research by Moshkovith et al. (Moshkovith et al., 2007) which found that decreasing the agglomeration size, increases the probability of the nanoparticles to penetrate into the contact area, thus reduce friction. They reported that the size of agglomerate nanoparticles reduced after a long mixing time. Xie et al. (Xie et al., 2016) also reported that poor dispersion stability increases the tendency of nanoparticles to agglomerate, in turn, resulted in lesser friction performance.
Figure 6 shows the effects of the dispersion methods on the anti-wear performance. The results revealed that the wear scar diameter (WSD) were slightly increased by 5.5% and 5.3% compared to the base lubricant when the nanolubricants prepared by M1 and M2, respectively. A small reduction of WSD (2%) was obtained when the nanolubricants prepared by M3. These results revealed that dispersion stability of nanolubricants affect the anti-wear performance. This confirms previous findings in the literature (Gulzar et al., 2015) which indicated that agglomeration of nanoparticles will be resulted in lesser wear protection. Therefore, it can be concluded that tribological performance of nanolubricants dependent on the dispersion stability.

Figure 5: Effects of different dispersion methods (M1: magnetic stirrer; M2: overhead stirrer; M3: high-shear homogeniser) on coefficient of friction (COF).

Figure 6: Effects of different dispersion methods (M1: magnetic stirrer; M2: overhead stirrer; M3: high-shear homogeniser) on wear scar diameter (WSD).

4.0 CONCLUSION
The present research revealed that different dispersion methods displayed different dispersion stabilities of suspension. Among the two-step methods employed, the high-shear
homogeniser method was found to be the most effective at providing a stable suspension. Therefore, from this research, it was found that the dispersion stability of nanolubricants affects the viscosity and tribological performance. The dispersal mechanism of nanoparticles in a based lubricant additive requires further investigation.

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