DISPERSION STABILITY OF GRAPHENE IN BIO-BASED LUBRICANT AND ITS EFFECT ON TRIBOLOGICAL PROPERTIES

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DISPERSION STABILITY OF GRAPHENE IN BIO-BASED LUBRICANT AND ITS EFFECT ON TRIBOLOGICAL PROPERTIES

ABSTRACT

The upsurge in the usage of petroleum-based product nowadays have caused huge alarming concern to the society as they are non-renewable and harmful to the environment. Therefore, it is important to hunt for a suitable alternative such as bio-based lubricant. However, bio-based lubricant cannot perform well on its own, hence there is need for suitable additives to be introduced. Graphene is a promising additive due to its unique two-dimensional structure and remarkable properties. However, several reports have stated that graphene is unable to form a stable suspension in the lubricant. Hence this study was carried out to study the dispersibility of graphene in bio-based lubricant and how it will affect to its tribological performance as well as choosing a suitable surfactant to counter this low dispersibility. To achieve this, three bio-based polyol esters i.e., neopentyl glycol dioleate (NPG), trimethylol propane trioleate (TMP) and pentaerythritol tetraoleate (PE) were selected as base oil for graphene to be dispersed in. The graphene nanoparticles were added at various concentration (0.01 wt.%, 0.03 wt.%, 0.05 wt.%, 0.07 wt.% and 0.10 wt.%) into the base oils via magnetic stirrer. Three surfactant (ionic liquid, oleic acid and Triton X-100) were used to improve the dispersion stability of graphene. The dispersion stability of graphene was observed using sedimentation method and UV-Vis spectroscopy for over one month. Tribological behaviour of base oil with graphene before and after one month were tested using fourball tribotester whereas samples with surfactant were tested using high frequency reciprocating rig (HFRR). Worn surface from HFRR testing were observed under scanning electron microscope, energy-dispersive X-ray spectroscopy. Raman spectroscopy and optical surface analyser. In term of physical properties, no significant change is observed after the addition of graphene and surfactant. Varying suspension stability were observed in different base oil which indicated there is a matter of compatibility when selecting the base oil for graphene additive. Based on the tribological tests, graphene is more promising as an antiwear additive compared to its performance as a friction modifier. After one month, graphene sedimentation reduced its tribological performance and the more stable suspension retained its performance. Out of all surfactant, ionic liquid is the most promising surfactant as stable suspension is observed for over one-month. Synergistic behaviour of graphene and ionic liquid have been confirmed as this combination significantly improved its tribological performance.

Keywords: bio-based lubricant, graphene, dispersion stability, tribology

KESTABILAN DAYA SUSPENSI GRAFIN DALAM MINYAK PELINCIR BERASASKAN BIO DAN KESANNYA TERHADAP SIFAT-SIFAT TRIBOLOGI

ABSTRAK

Peningkatan penggunaan produk berasaskan petroleum pada masa kini telah menimbulkan kebimbangan besar kepada masyarakat kerana ia tidak boleh diperbaharui dan membahayakan alam sekitar. Oleh itu, ianya penting untuk mencari alternatif yang sesuai seperti pelincir berasaskan bio. Namun, pelincir berasaskan bio tidak dapat berfungsi dengan baik, oleh itu bahan tambahan yang sesuai perlu untuk diperkenalkan. Grafin adalah bahan tambahan yang berpotensi kerana struktur dua dimensinya yang unik dan sifatnya yang luar biasa. Walau bagaimanapun, beberapa laporan menyatakan bahawa grafin tidak dapat membentuk suspensi stabil dalam pelincir. Oleh itu, kajian ini dijalankan untuk mengkaji daya suspensi grafin dalam pelincir berasaskan bio dan bagaimana ia akan mempengaruhi prestasi tribologinya serta memilih surfaktan yang sesuai untuk mengatasi tahap suspensi rendah ini. Untuk mencapai ini, tiga ester poliol berasaskan bio iaitu neopentyl glycol dioleate (NPG), trimethylol propane trioleate (TMP) dan pentaerythritol tetraoleate (PE) dipilih sebagai minyak asas untuk grafin disebarkan. Grafin ditambahkan pada pelbagai kepekatan (0.01 % wt, 0.03% wt, 0.05% wt, 0.07% wt dan 0.10% wt) ke dalam minyak asas melalui pengaduk magnet. Tiga surfaktan (cecair ionik, asid oleik dan Triton X-100) digunakan untuk meningkatkan kestabilan penyebaran grafin. Kestabilan penyebaran grafin diperhatikan menggunakan kaedah pemendapan dan spektroskopi UV-Vis selama satu bulan. Tingkah laku tribologi minyak asas dengan grafin sebelum dan selepas satu bulan diuji menggunakan empat bola tribotester manakala sampel dengan surfaktan diuji menggunakan rig frekuensi tinggi (HFRR). Permukaan haus dari pengujian HFRR diperhatikan di bawah mikroskop elektron pengimbasan, spektroskopi sinar-X penyebaran tenaga, spektroskopi Raman dan penganalisis permukaan optik. Dari segi sifat fizikal, tidak ada perubahan yang ketara setelah penambahan grafin dan surfaktan. Kestabilan suspensi berubah-ubah diperhatikan pada minyak asas yang berbeza yang menunjukkan ada keserasian ketika memilih minyak asas untuk aditif grafin. Berdasarkan keputusan ujikaji tribologi, grafin lebih berpotensi sebagai bahan tambahan anti pakaian berbanding prestasinya sebagai pengubah geseran. Selepas satu bulan, pemendapan grafin mengurangkan prestasi tribologinya dan suspensi yang lebih stabil mengekalkan prestasinya. Daripada semua surfaktan, cecair ionik adalah surfaktan yang paling menjanjikan kerana suspensi yang stabil diperhatikan selama lebih dari satu bulan. Tingkah laku sinergistik grafin dan cecair ionik telah disahkan kerana kombinasi ini meningkatkan prestasi tribologinya dengan ketara.

Keywords: Pelincir berasaskan bio, grafin, kestabilan sebaran, tribologi

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LIST OF SYMBOLS AND ABBREVIATIONS

NPG	Neopentyl glycol
TMP	Trimethylol propane
PE	Pentaerythritol
HFRR	High frequency reciprocating rig
EDX	Energy-dispersive X-ray
SEM	Scanning electron microscopy
FESEM	Field emission scanning electron microscopy
UV-Vis	Ultraviolet–visible
FFO	Fully formulated oil
PAO	Poly-alpha-olefin
VI	Viscosity index
ZDDP	Zinc dithiophosphates
OCP	Olefin copolymer
PMA	Polymethacrylate
PPD	Pour point depressant
VO	Vegetable oil
IL	Ionic liquid
G	Graphene
GNP	Graphene nanoplatelet
CNT	Carbon nanotube
MEMS	Micro-electromechanical systems
NEMS	Nano-electromechanical systems

CHAPTER 1 : INTRODUCTION

In this chapter, the general overview of the research particularly the increasing world energy demand and also the need of a greener alternative was discussed. The problem statement for this project was also stated. To solve said problem, specific objective were focused. The scope of the study was also discussed.

1.1 Introduction

The rapid growth of population through modernization, industrial and economic development, socialization, political and technological innovation has resulted in the increased of world energy demand. According to Sun (1998), the absolute energy consumption in the world for the period of 1973 to 1990, has increased by 1378.57 Mtoe, starting approximately around 4139.39 Mtoe in 1973 to 5517.96 Mtoe in 1990. Continuously, the overall world energy consumption in 2030 has been predicted to increase by 33.5% from 2010 (Saidur, Abdelaziz, Demirbas, Hossain, & Mekhilef, 2011). An increased in energy consumption through rapid growth of population is caused by many factors such as the need of extra electricity, extra fossil fuels, extra natural gas and more. As far as these factors are being concerned, fossil fuel is the most highlighted factor since most of the daily energy usage is based on fossil fuel. Figure 1-1 shows that approximately 80% of total energy usage is from fossil fuel which is more than 400 EJ per year.

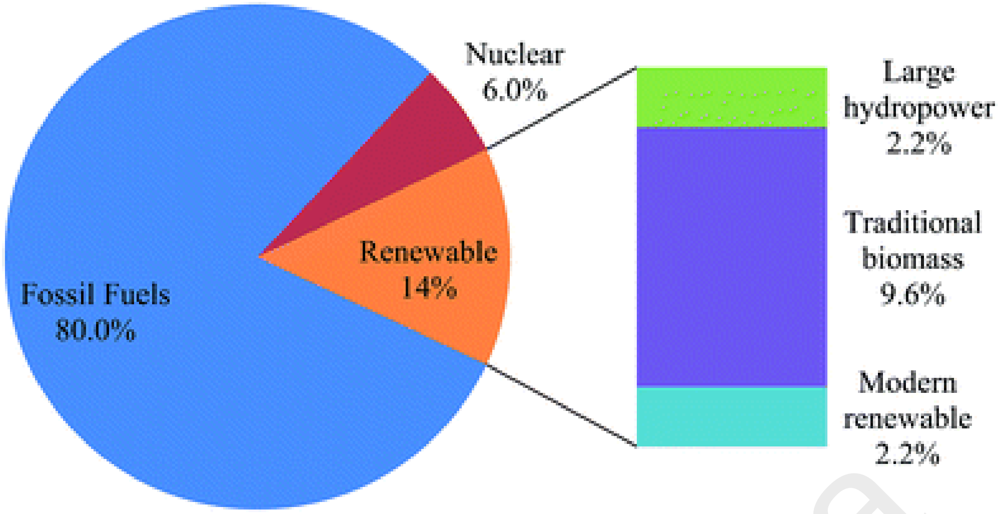


Figure 1-1: Fuel contribution to total world energy consumption. (M. N. A. M. Yusoff, N. W. M. Zulkifli, B. M. Masum, & H. H. Masjuki, 2015)

An increasing response for fossil fuels means more petroleum-based product such as fuel and lubricant are required to compensate with the higher energy demand. The fact that petroleum-based product has a lot of disadvantages towards the environment is already become a norm. It is estimated that around 30 to 40 million tons of petroleum-based lubricant is used per year, where about 55 percent of this quantity will end up into the environment (Dresel, 2007). A more frightening event is the fact that almost all of these petroleum-based lubricant products entering the environment are non-environmentally friendly and characterized as toxic. In addition, most of it also come from a non-renewable source. Studies has been conducted relating the environmental impacts of petroleum-based products to the global warming and fossil fuel depletion (Harding, Dennis, von Blottnitz, & Harrison, 2007). Disposal of petroleum-based lubricants gives negative impacts and harm the environment at all stages starting from production, usage to disposal phase as they contain toxic element (Schneider, 2006).

With petroleum resources are gradually diminishing and for the sake of environmental concerns, various counteractions have been proposed to address such ongoing threats (A.

Z. Syahir et al., 2017; M. Yusoff, N. Zulkifli, B. Masum, & H. Masjuki, 2015). Among the actions taken are the development of green energy systems and the use of renewable resources such as biodiesel, hydrogen, solar and wind as an alternative to petroleum-based products product (Bartz, 1998; Boroojeni et al., 2016). Despite all the alternatives such as solar, wind and nuclear energy being nourished, most of them still require lubricant for the efficiency of their operation. Thus, lubricants play an important role in this case. The term "bio based lubricant" or "bio-lubricant", is lubricant that is obtained from bio-based raw materials such as vegetable oil and animal fat (Salimon, Salih, & Yousif, 2010). The significant advantage of choosing bio-lubricant over conventional lubricant as the base oil component is that it is an environmentally acceptable and economically improved material with excellent low-temperature fluidity and cold starting, high-temperature oxidation resistance, renewable and technically feasible (Hamid, Yunus, Rashid, Choong, & Al-Muhtaseb, 2012). Besides, it also has higher lubricity, higher viscosity indices, good shear stability, good dispersancy, low volatility and biodegradable which bring down environmental hazards (Salimon, Salih, & Yousif, 2012). The conventional lubricants have obviously some drawbacks such as being harmful to environment, poor oxidative stability, sensitive to hydrolysis and low-temperature fluidity (Nagendramma & Kaul, 2012). Conventional lubricants contain these mixtures of paraffin, isoparaffines, naphthalene, aromates, and compounds of sulfur, phosphorous, nitrogen, and oxygen which some of them are harmful to the environment. (S. S. N. Azman, Zulkifli, Masjuki, Gulzar, & Zahid, 2016).

The absolute trait of a lubricant is not entirely based on the base oil. Several additives are added into the lubricant in order to improve the tribological performance of that base oil. Since most lubricants nowadays have reached their performance limits, a significant scientific task were appointed where a new lubrication formulations is to be develop that can attain energy efficiency across numerous fields (Akbulut, 2012). This endeavour for energy efficiency has led the research towards new materials, for use as lubricant additives. For bio-based lubricant, the friction and wear reducing performance can be further improve by the addition of friction modifier and anti-wear additive (S. S. N. Azman et al., 2016).

In this study, graphene has been selected as an additive because of its certain characteristics that can fulfil the desired of this study. Various study has proven that the addition of graphene will improve the tribological properties which is the wear and frictional performance of the lubricant (S. Azman, Zulkifli, & Masjuki, 2015; Choudhary, Mungse, & Khatri, 2012; Eswaraiah, Sankaranarayanan, & Ramaprabhu, 2011; Fan & Wang, 2015; Fan, Xia, Wang, & Li, 2014). Its excellent chemical and physical properties such as ultrathin structure, high thermal stability, ultra-smooth surface, ultimate mechanical strength and its two-dimensional shape may introduce an interesting wear reducing mechanism make it more favorable for lubrication purposes (Stephen Sie Kiong et al., 2017).

Through research and literatures, there are still few studies conducted concerning the dispersion of graphene as an additive specifically in a bio-based lubricant. Most of the studies agree in dispersing graphene in non-bio-based lubricant such as mineral-based lubricant, conventional lubricant such as in a fully-formulated motor oil (FFO) and more Thus, it can be said that there is still scarcity in knowledge regarding the dispersion of graphene in bio-based lubricant as well as how the dispersion affect the tribological properties of the lubricant completely. One of the features of graphene is the inertness of it. This in results give a bad dispersion stability when mix with lubricant.

The sedimentation of any nanoparticle can deteriorate the lubricant performance and the same can be said when using graphene as a lubricant additive. Hence, numerous techniques were introduced in order to conquer such difficulties such as physical graphene modification (Dou et al., 2016), chemical graphene modification (Lin, Wang, & Chen, 2011), and the usage of surfactant (Senatore, D'Agostino, Petrone, Ciambelli, & Sarno, 2013). As mentioned before, these techniques were used to disperse graphene in non-bio-based lubricant. Hence, this study is carried out to study the dispersion of graphene in bio-based lubricant and its effect on the tribological properties particularly in bio-based polyol esters namely Trimethylol propane, Neopentyl glycol and Pentaerythritol.

1.2 Problem Statement

Lubricants which are petroleum-based have been widely used in various industries nowadays. The use of this type of lubricant as mentioned earlier will contribute to the environmental pollution due to its non-biodegradable and high toxicity content. Thus, from this concern, the focus is now move towards another alternative which is the use of bio-based lubricant as the base oil in lubricant. The main purpose is to reduce the environmental problems, keeping the environment greener and free from any unwanted contaminants, apart from enhancing the wear and friction reduction properties. In the prior conducted studies, graphene which act as an additive has been added to improvise the bio-based lubricant. The selection of graphene as additive is due to its remarkable mechanical properties and its unique two-dimensional structure. Compared to other additives, the mechanical properties of graphene combined with its unique structure is unlike any other material which makes it a prime candidate as a lubricant additive.

On the other hand, the development and application of graphene nowadays has been growing rapidly in recent years. Countless studies have been carried out to investigate the tribological properties of graphene in lubricant. But, as mentioned earlier, little number of studies have been conducted related to the dispersion of graphene as a lubricant additive specifically in bio-based lubricant. By that, a study with the intention to investigate the dispersion of graphene in bio-based lubricant and to improve the dispersion through the addition of surfactant is executed.

1.3 Research Objective

The general aim in this study is to study the dispersion of graphene in bio-based lubricant. The study will focus on these following specific objectives;

1. To investigate the dispersion stability of graphene in different bio-based lubricant using UV-Vis spectrophotometer.
2. To investigate the tribological behaviour of graphene in bio-based lubricant using fourball tribotester.
3. To evaluate the suitable surfactant for graphene-contained bio-based lubricant in term of dispersion stability and tribological behaviour.

1.4 Scope of Research

Due to the increased of environmental concern day by day, a lot of research was done in order to reduce the environmental pollution specifically due to the petroleum-based product. Thus, a study of bio-based lubricant is done to compensate this problem. The base-stock oils used is TMP, NPG and PE esters which is derived from chemically-modified palm oils. Due to some drawbacks of these base-stock oils, graphene which act as an additive is added to improve the performance and the tribological properties. However, it is found that there is a deficiency on the dispersion of graphene dispersed in bio-based oils. Hence, several surfactants are used to readdress this weakness which is Triton X-100, Oleic acid and Ionic liquid.

In this study, experimental works were done using four-ball tribotester machine and high frequency reciprocating rig (HFRR) machine. Coefficient of friction and wear scars diameter was obtained from the four-ball tribotester machine while wear mechanism was obtained from the HFRR machine. This experimental study was done to investigate the dispersion stability and performance of graphene as an additive in bio-based lubricant and to study the effect of surfactant when added into bio-based lubricant containing graphene.

1.5 Organization of Dissertation

This dissertation consists of five chapters. The organization of each chapter is listed as follows:

Chapter 1 presents the general overview of the research particularly the increasing world energy demand and also the need of a greener alternative was discussed. This section also discusses the problem associated with mineral based lubricant. To solve said problem, specific objective were focused. The scope of the study was also discussed.

Chapter 2 touches on topics related to the title of the project. Discussion on the types of base oil which is mineral oil, synthetic oil and vegetable oil in which bio-based lubricant was studied in greater detail. This chapter will discuss on graphene as a lubricant additive. The dispersion stability of graphene in bio-based oils were also reviewed.

Chapter 3 describes the research methodologies and experimental techniques to achieve the outlined research objectives. These includes the selection of bio-based lubricant, dispersion stability observation, measurement of physical properties of lubricant and their tribological behaviour, as well as the post analysis of worn scar on the test sample.

Chapter 4 presents the results that have been obtained from the experimental work. This is followed by providing analysis and detailed discussion. These findings are then compared with the previous studies.

Chapter 5 concludes the research findings and puts forward some recommendations for the future study.

CHAPTER 2 : LITERATURE REVIEW

In this chapter, several topics related to the title of the project would be discussed. Sub chapter 2.1 would discuss several types of base oil which is mineral oil, synthetic oil and vegetable oil. Bio-based lubricant was studied more in-depth in sub chapter 2.2. Next, in sub chapter 2.3, a review on lubricant additive in general as well as graphene nano-platelet in specific were also discussed. Several works had been reviewed related to graphene nano-platelet mostly focusing on tribological aspect of it. The emerging usage of graphene nowadays in the industry and the ability of graphene to enhance the tribological properties specifically in reducing the friction and wear has made it the main intention of why it is chosen as an additive. Friction and wear characteristics are considered the vital aspects as it involves cost and maintenance of an equipment used in the industry. Sub chapter 2.4 will discuss on the graphene as a lubricant additive. In sub chapter 2.5, the study and research on the dispersion stability of graphene in bio-based oils were also investigated. To date, there is not much studies conducted addressing this topic. Yet, several information has been extracted in order to help and ease the tribological analysis of it. Comparative analysis, summary of certain works done by some researchers, working mechanism, classification and application on various type of lubricant were discussed.

2.1 Base Oil

Base oils are used to manufacture different kind of products including lubricating greases, motor oil and metal processing fluids. In addition, different kind of products require different number of compositions and properties in the oil. Lubricants are basically the combination of base stocks with standard lubricant additive packages (Carr & DeGeorge, 1989). The application is also different for every type of base oils. As mentioned, there are three main categories of base oil for lubricants which is mineral oil, synthetic oil and vegetable (biological) oil. In this study, the main concern is on the vegetable oil because of the advantages it possesses over the mineral and synthetic oils.

2.1.1 Mineral Oils

At present, the most common base oil used is the mineral oil, which produced from the middle range of petroleum-derived distillates and refinement of crude oil. Three types of mineral oil include naphthenic, aromatic and paraffinic oil. All these forms are reliant on the sources of mineral oil. Paraffinic oils are produced either by hydrocracking or solvent extraction process. They are known to be viscous, oxidation resistant as well as high flash and pour point. It is commonly used for manufacturing engine oils and industrial lubricants (Masson, Polomark, Bundalo-Perc, & Collins, 2006). Meanwhile, crude oil distillates can be used to produce naphthenic oils which have low viscosity, flash point, pour point, oxidative stability and mainly used in transformer oils and metal working fluids where there have moderate in working temperature. (Fukuhara & Tsubouchi, 2003). Last but not least, aromatic oils are products of refining process in manufacture of paraffinic oils. Aromatic oils are dark and have high flash point. Their main application are in the manufacturing of adhesive, seal compound and plasticizer.(Lorenzini et al., 2010).

2.1.2 Synthetic Oil

Synthetic oils are basically a lubricant which comprise of certain artificially-made chemical elements. It is normally manufactured using chemically-modified petroleum modules. The base oil is still dominated by the crude oil that is distilled, only then it is physically and chemically modified. One of the applications is in aircraft jet engines, since the working condition for this type of oils is in high extreme temperature. Fully synthetic, semi-synthetic, poly-alpha-olefin (PAO) are types of synthetic oil. Fandiño, Lugo, Comuñas, López, and Fernández (2010) stated that Polyalkylene glycol (PAG) is one of the best types of synthetic oils due to its great oxygen content and intrinsic polarity apart from having good lubricity, high viscosity index, low pour points, good thermal, mechanical, and oxidation stabilities, low volatility in high-temperature applications and resistance towards the formation of residue and deposits. It is also designed for automotive air conditioner compressors and used as chain oils, metalworking fluids, extreme-pressure gear lubricants and food-grade lubricants. Despite synthetic oil having most of the advantages, there are also some drawbacks as well, such as it solidified at low temperature, have some viscosity loss and sometimes, tend to undergo oxidation (Shahnazar, Bagheri, & Abd Hamid, 2016).

2.1.3 Vegetable Oils

As it is known, to dispose mineral oil-based lubricants is very hard to do because of its non-biodegradable in nature and high toxicity content. Thorough efforts have been done in order to properly dispose this type of lubricants. Not only that, It has been reported that yearly 12 million tons of lubricants waste are released to the environment and over 90% of this released are from mineral-based lubricants (O'Rourke & Connolly, 2003). This threat towards the environment can be avoided by either preventing undesirable losses, reclaiming and recycling mineral oil lubricants, or using environmentally friendly lubricants. Thus, vegetable oils would be the promising candidates to substitute for the mineral lubricants. Vegetable oils have several properties that are suitable for a lubrication, such as high lubricity, high viscosity index and low volatility while having a low toxicity level and is biodegradable (Jayadas & Nair, 2006). Vegetable oils comprise of triglycerides, which are glycerol molecules with three long-chain fatty acids attached at the hydroxyl group through ester linkages as presented in Figure 2-1.

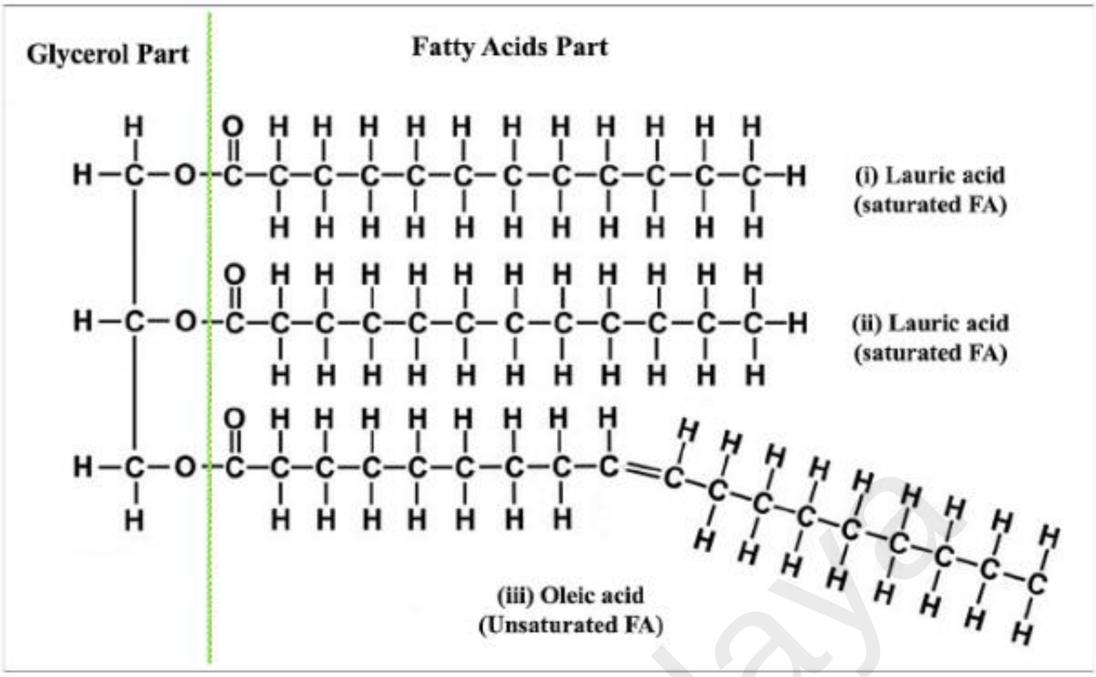


Figure 2-1: The triglyceride structure of common vegetable oils (Harrington, 1986)

Triglyceride structure is suitable for boundary lubrication due to its long and polar fatty acid chains which can provide high strength lubricant films that interact strongly with metallic surfaces (Zulkifli et al., 2016). The strong intermolecular interactions provide a long-lasting and heavy-duty lubricant film and also unaffected to change in temperature, providing a more stable viscosity. The chain length and number of double bonds of the fatty acids fluctuates. The composition is determined by the portion and location of the double bond. The long-chain carbon is normally held together with one, two, or three double bonds: oleic, linoleic, and linoleic fatty acid components, respectively and most plant-based oils contain at least four, and sometimes up to twelve different fatty acids (Gibson, Muhlhausler, & Makrides, 2011).

Vegetable oils possess an excellent lubricity properties, but very poor oxidation and low-temperature stability (B. K. Sharma, Adhvaryu, Liu, & Erhan, 2006). Thus, vegetable oil has to be chemically modified usually through transesterification (Demirbaş, 2002) and epoxidation of vegetable oil (Campanella, Rustoy, Baldessari, & Baltanás, 2010) in order to eliminate the exposed sites for oxidation occurrence and to disturb the formation of crystals at low temperatures. There are several different types of vegetable oil extracted from different type of sources. Such examples are shown in Table 2-1.

Table 2-1: Different types of vegetable-based oils, world production and type of fatty acids contained (Maleque, Masjuki, & Sapuan, 2003)

Source	World Production (Million ton per annum)	Type of Fatty acid	Carbon chain length & No. of double bonds
Soybean Oil	20	Linoleic Oleic	C18:2 C18:1
Groundnut oil	4	Linoleic Oleic	C18:2 C18:1
Palm oil	16	Palmitic oleic	C16:0 C18:1
Rapeseed oil	11.5	Oleic	C18:1
Sunflower oil	9	Linoleic Oleic	C18:2 C18:1
Beef tallow	7.5	Oleic Palmitic Stearic	C18:1 C16:0 C18:0
Lard	6	Oleic Palmitic	C18:1 C16:0
Coconut oil	3	Lauric	C12:0
Palm kernel oil	2	Lauric	C12:0
Olive oil	2	Oleic	C18:1
Fish oil	1.5	Long chain Fatty acids	C20:2 to 6 C22:2 to 6
Corn oil	1.8	Linoleic Oleic	C18:2 C18:1

In this study, TMP, NPG and PE esters derived from palm oil is used as the base oil with addition of graphene and surfactant. Figure 2-2 shows the synthesis of the esters and Figure 2-3 shows the palm fruit cross section.

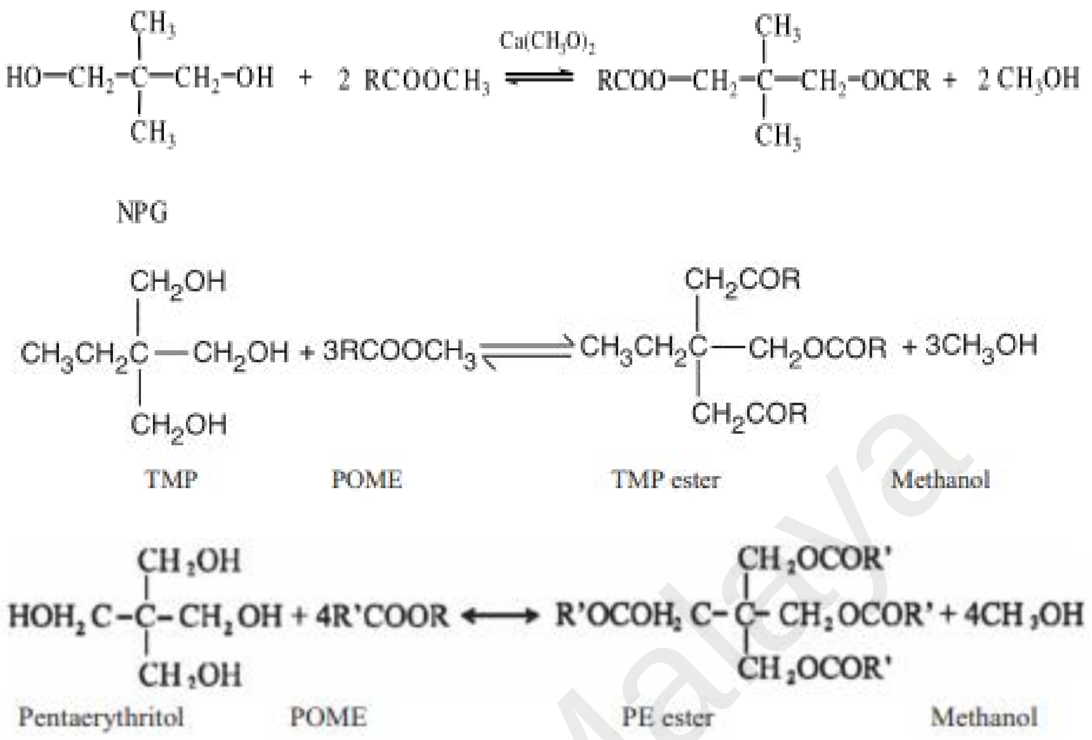


Figure 2-2: Synthesis of NPG, TMP and PE esters (Gryglewicz, Muszyński, & Nowicki, 2013)

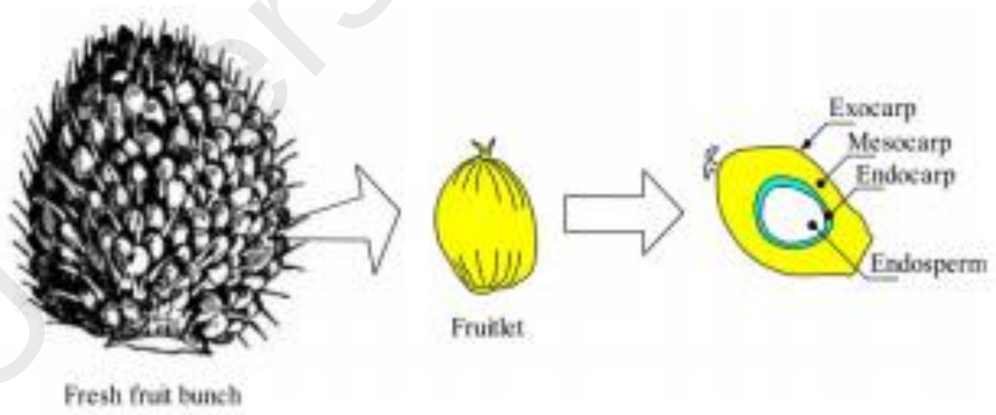


Figure 2-3: Palm fruit cross section diagram

Palm oil is an edible vegetable oil derived either from the mesocarp (flesh of the fruit) or from the endocarp (seed or kernel) of the oil palm. The immature fruits contain few oils as to compare with the mesocarp of the ripe fruits which the oil content is around 70-75% of its total weight. In its original form, the oil is orange-red in color due to high content of carotene. Palm oil also contain palmitic acid which is a type of fatty acid exist in our body, polyunsaturated linoleic acid, and stearic acid (Chilliard, Ferlay, & Doreau, 2001). With this features and composition, palm oil obtains great and strong interactions with the lubricated surfaced which make them as an anti-wear protector as well as friction modifier. Furthermore, palm oil also has a good film relationship because the present of long fatty acid chain and polar groups and this make them suitable and effective to become boundary and hydrodynamic lubricants (Noorawzi & Samion, 2016).

2.2 Bio-Based Lubricant

Bio-based lubricant is basically a mixture of base oil extracted from bio-based raw material and an additive. Such bio-based raw are from plant oils, animal fats or other environmentally kind of hydrocarbons, which are biodegradable and nontoxic to human and any other living organisms, especially in aquatic environments (Gnanasekaran & Chavidi, 2018). Table 2-2 shows several benefits and application of bio-based lubricant. The renewable and biodegradable nature of bio-based lubricants have made them suitable for various applications like for an engine lubrications (Agarwal, 2007), metal cutting operations (Lawal, Choudhury, & Nukman, 2012) and in biomedical and pharmaceutical sector (Mekonnen, Mussone, Khalil, & Bressler, 2013). Bio-based lubricants show great potential and ability to replace almost all petroleum-based lubricants due to high biodegradability and low toxicity content (Nagendramma & Kaul, 2012).

Table 2-2: Benefits and applications of bio-lubricants (Mobarak et al., 2014)

Benefits	Applications
Enrich the lubricity properties	- Minimum friction loss, - Energy saving from 5% to 15%
High Viscosity Index (VI)	High temperature application
Has low volatility	Exhaust emission reduction
Has high flash point	Industrial floor safety
Improved skin compatibility	Dermatological problems
Oil mist reduction	Inhalation of vapors
Rapid biodegradation	Toxicity reduction and Environmental hazards
Higher boiling temperatures	Reduced emissions
Higher detergency	No need the use of detergents as an additive

Various bio-lubricant-related research and development projects have been accomplished and it is found that bio-lubricant can be the efficient and inexpensive substitutes to petroleum-based oils. The summary of the research on vegetable oil-based bio-lubricant conducted by various researchers is shown in Table 2-3 and the results indicate that most of the bio-lubricants exhibited promising results.

Table 2-3: Summary of the work done by various researchers on vegetable oil lubricant

Bio-Lubricants	Reference Lubricant	Methodology	Result	Reference
Coconut Oil	SAE20W50	Four-ball tester	Lower friction and wear, improved lubricity	(Jayadas, Prabhakaran Nair, & G, 2007)
Palm Oil	SAE20W50	High frequency reciprocating rig (Ball-on-Flat). Steel–steel pair contacts.	Less corrosive in nature, Lower coefficient of friction, Good oxidation and anti-corrosion properties, Reactivity of unsaturated hydrocarbon chains, Strong stability of the lubricant film.	(Masjuki, Maleque, Kubo, & Nonaka, 1999), (A. K. Singh, 2011)
Waste Palm Oil	SAE40	Four-ball tribo-tester, with standard test method	Less corrosive in nature, Lower coefficient of friction, Good oxidation and anti-corrosion properties. Reactivity of unsaturated hydrocarbon chains. Strong stability of the lubricant film.	(Hisham et al., 2017)
Vegetable oil (Jatropha, Neem, Karanja, Soybean, Palm, Coconut, Castor, Olive, Mahua, Sunflower, etc.)	Petroleum based mineral oils	Different tribo-tester with standard test method	High flash point, High viscosity index, High lubricity, Low evaporative loss, Offer better performance, Less expensive, Cheaper and eco-friendly.	(Chauhan, 2013), (Black & Rawlins, 2009), (Fertier et al., 2013)
Castor Oil	Super refined mineral oil	Four-ball wear tester	High viscosity index, less deposit formation, lower volatility, high antioxidant concentration.	(Asadauskas, Perez, & Duda, 1997)

Soybean Oil	Petroleum based mineral oils	Four-ball tribo-tester	Lower friction, higher lubricity, cheaper non-toxic, ecofriendly and cheap.	(Ting & Chen, 2011)
Soybean Oil	Commercial synthetic lubricant	High frequency reciprocating tribometer test rig	Extremely high viscosity.	(Hwang & Erhan, 2006)
Palm oil based TMP ester	SAE40	High frequency reciprocating machine	Good wear prevention properties in terms of coefficient of friction and wear scar diameter.	(Zulkifli, Kalam, Masjuki, Shahabuddin, & Yunus, 2013)
Castor Oil and Palm Oil	SAE20W40	Pin on disc tribo wear tribometer	Reduced the coefficient of friction frictional force and wear, Excellent lubricity properties, Renewable and biodegradable, Eco-friendly, Possess lower volatility.	(Arumugam & Sriram, 2014)
Pongamia oil	SAE20W40	Four-stroke, single cylinder, water cooled, direct-injection diesel CI engine	Minimum BSEC and highest BTE at medium and high load conditions, Lesser frictional losses, Improve the efficiency, completely eliminate emission.	(A. Sharma & Murugan, 2017)
Jatropha Oil	SAE20W40	Pin on disc machine	Lower Wear Loss, Lower cumulative weight loss, Lower friction coefficient.	(Y. Singh, 2015)
Chemically modified rapeseed oil bio-lubricant	SAE20W40	High frequency reciprocating tribometer test rig	Good oxidative stability, Improved Cold Flow Property, Better performance in terms of frictional force and coefficient of friction.	(Sumeet & Pavankumar, 2016)

2.3 Lubricant Additive

Without a doubt, vegetable oil hold most of the desired lubricity properties, such as good contact lubrication, high viscosity index, high flash-point and low volatility. But then, they also have drawbacks that must be overcame which comprise poor low-temperature properties, susceptibility to oxidative degradation and tendency to undergo hydrolysis in acid medium (Masudi & Muraza, 2018). These drawbacks can be mitigated with relative ease through the use of additives. The lubricant additive or additive package has played a vital role in oil formulation process. Conventional additives are basically a chemical substance which are added into the base oils. This is done in order to improve the performance and the tribological properties of particular base oil and to enhance the lubricant properties based on the specific requirement.

For a boundary lubrication conditions, it is important for the additives to augment the ability to form a protective layer and when it is blended with the base oil, it also must have a well-balanced and optimized composition in order to improvise the overall performance of the lubricant. Commonly used additives nowadays are typically anti-wear additives, viscosity reformers, oxidation and corrosion inhibitors, surfactant, extreme pressure additives (which contain organic sulfur, phosphorus or chlorine compounds) and more (Randles et al., 2005). There are several types of lubricant additives used nowadays. The choice of lubricant additives is dependent on the intended application in the industry. Table 2-4 shows common types of lubricant additives, effects and the common chemical composition (Shahnazar et al., 2016)

Table 2-4 Common types of lubricant additives, effects and the common chemical composition.

Type of Additives	Lubricant Additives	Effects	Common Chemicals
Film-forming additives	Solid lubricants as friction modifiers	- Reduce friction between surfaces where liquid lubricants do not do pleasantly. - Key properties these additives have is yield strength, adhesion to substrate, cohesion, orientation and plastic flow	-Graphite and Molybdenum disulphide
	Organic friction modifiers	- Friction modifiers are the extras in boundary and mixed lubrication conditions. It is added in order to adjust friction characteristics and improve the lubricity and energy efficiency	- Carboxylic acids or their derivatives such as stearic acid and partial esters. - Organic polymers such as methacrylates
Deposit control additives	Anti-oxidants	- These additives prevent the formation of corrosive components by preventing oxidation occurring. It acts at two different behaviors: Peroxide inhibition and radical scavenging.	- Sulfur compounds -Sulfur-nitrogen compounds -Phosphorous compounds - Sulfur-phosphorous compounds - Aromatic amine compounds
	Zinc dithiophosphates (ZDDP)	Normally used as anti-oxidant and anti-wear additive. It will create a glassy phosphate layer on Fe-based surfaces when it is under high temperature and pressure. These in results will reduce the wear and friction.	ZDDP
	Detergents	It neutralizes acids that can attack metal surfaces due to its base-contained and to hang polar-oxygenated components in oil.	- arylsulfonic acids - carboxylic acids - petroleum oxidates

	Dispersants	Dispersants are deliberate to suspend the insoluble particles and contaminants in oil and keep the surfaces clean by mixing it with detergents. It also can keep nonpolar molecules suspended in lubricant by having polar groups.	
Anti-wear additives and extreme-pressure additives	Ash-less anti-wear and extreme-pressure additives Sulfur carriers	This term is applied to group of extreme pressure and anti-wear additives that contain Sulphur in their oxidation and they only contain one kind of heteroatom which is oxygen.	- Sulfurized Isobutene - Active-Type Sulfurized Olefins - Inactive Sulfurized a-Olefins
Viscosity control additives	Olefin copolymer viscosity modifiers (OCP)	OCP are commonly utilized viscosity modifier for engine oils which are having high thickening efficiency and low cost.	
	Polymethacrylate viscosity modifiers (PMA) and pour point depressants (PPD)	For PMA, it thickened the oil film and improvise the viscosity index (VI) whereas for PPD, it control wax crystallization and deposition in mineral lubricant.	Various methacrylate monomers are used for PMA construction.
	Pour point depressants (PPD)	PPDs vary the crystal size of wax and control their shape during growing. It doesn't fully stop wax crystal growth, but rather reduce the temperature at which a rigid structure is formed.	- Acrylates - Methacrylates - Olefin/maleic anhydrides - Styrene/acrylates - Vinyl acetate/fumarates.

To achieve high energy efficiency and systematic control of wear and friction, studies on nano-additives specifically nano-particles has significantly increased yearly. As shown in Figure 2-4, nanoparticle additives are a comparatively new class of lubricant additives.

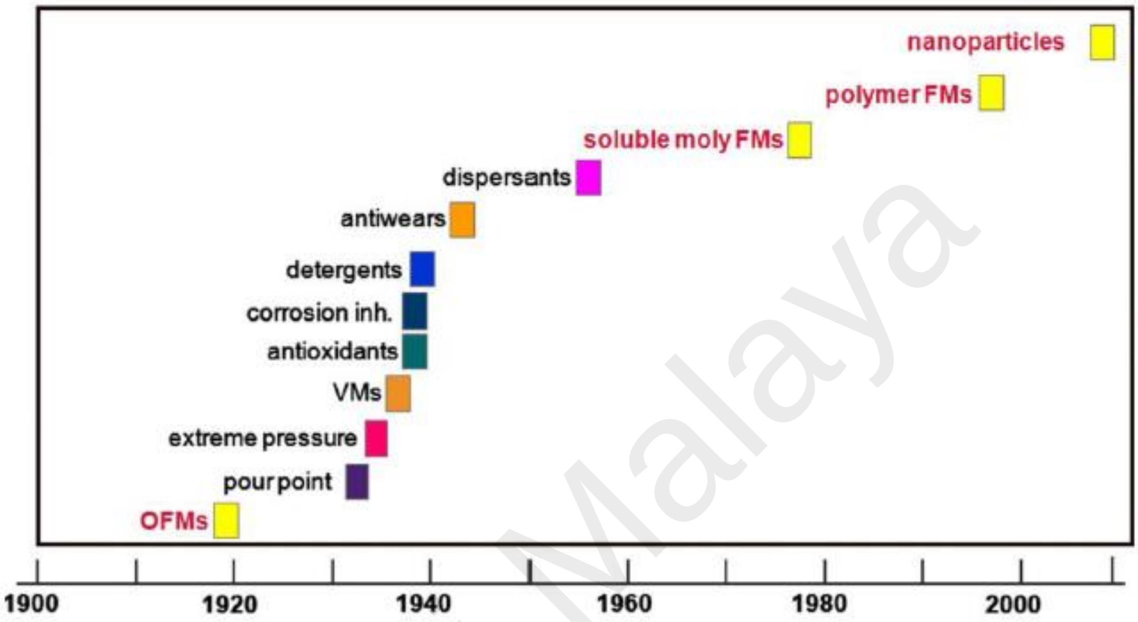


Figure 2-4: Historical development of lubricant additives

The trend for the studies related to nano additives in lubricants has been encouraging. Nanoparticles are claimed to be multipurpose, which can serve as anti-wear, extreme-pressure and friction modifier in the same time (Chou et al., 2010). Nanoparticle additives have superior tribological properties than traditional solid lubricant additives (Battez et al., 2008). Size and colloidal effect, protective film, and third body effects are several reasons why nano-additives can reduce friction and wear (Padgurskas, Rukuiza, Prosyčevas, & Kreivaitis, 2013).

Though numerous studies have displayed outstanding tribological performance by various type nanoparticle-contained lubricant, the selection of appropriate nanoparticle still remains a challenge. Various factors can affect the efficiency of nanoparticles such as their concentrations, their sizes and their compatibility with base oil (Peña-Parás et al., 2015). Studies by Stephen Sie Kiong et al. (2017) shows that 25 ppm and 50 ppm graphene can reduce friction coefficient and wear scar diameter as compared to pure vegetable oils. However, addition of up to 100 ppm of graphene nano-platelet resulted in aggregation and stacking, thus leading to higher friction and wear. Besides that, (Arwin & Rashmi, 2013) shows that the effect of high concentration of graphene nano-platelet which lead to a failure of forming a protective film layer over the solid surfaces. Not only that, higher concentration of graphene also effects the overall lubricating properties. These two studies conducted has proved that the amount of concentration of nano-additives is vital in improving the lubrication properties of base oils. In this study, graphene nano-platelet has been used as the lubricant additives.

2.4 Graphene Nano-platelets

Decreasing friction and wear-related mechanical failures in moving mechanical components have gained significant attentions year by year. This is due to the negative impact of friction on efficiency and durability of machineries. Subsequently, the effort widens involving the searching for novel materials, coatings and lubricants that would presumably scale back friction and wear. Graphene, a novel carbon-based nanomaterial has gained huge interests due to its potential applications in various fields (Y. Wang, Li, Tang, Lu, & Li, 2009). A number of graphene synthesis technique have been developed including chemical vapor deposition (CVD) onto conversion metal foil, mechanical exfoliation, chemical reduction of graphite oxide (GO) and epitaxial graphene (EG) on SiC as shown in Figure 2-5 (Mohan, Lau, Hui, & Bhattacharyya, 2018). Irrespective of the R&D efforts on graphene for an existing and future applications, the tribological potential as a lubricant additive specifically disperse in bio-based oils remains fairly undiscovered

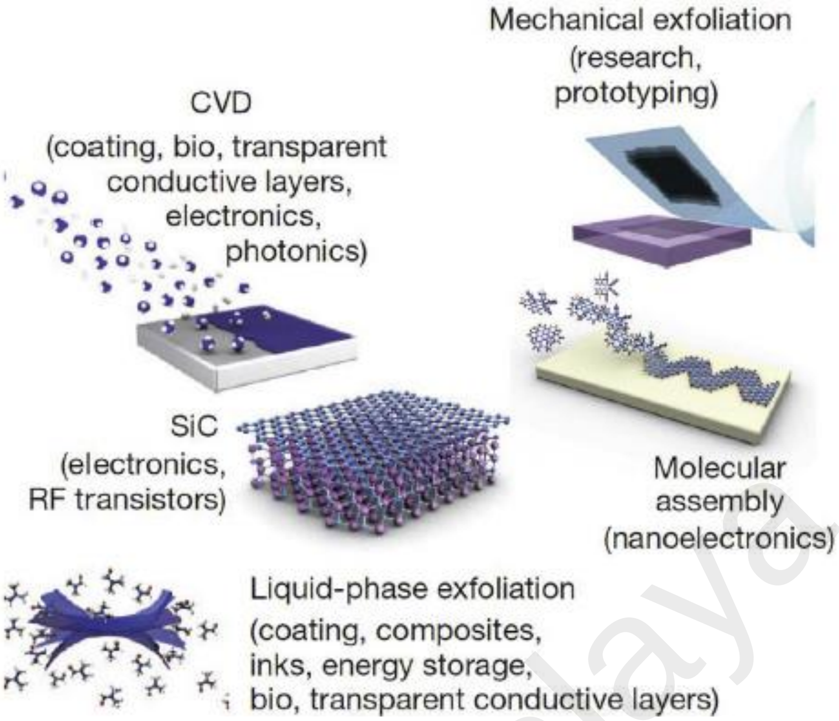


Figure 2-5: Different production approaches of graphene and its derivatives

Table 2-5 shows the overview of diverse methods to produce graphene. Based on the presented information, graphene production can be categorized into two types, transferred graphene and transfer-free graphene. Reduction of graphene oxide and the exfoliation technique is transferred graphene, since the transfer of graphene onto an appropriate substrate is happening. In contrast, CVD and EG method is transfer-free graphene as it is grown on metal foil and on a wide bandgap semiconductor substrate (SiC) without any transfer-occurring, respectively (Emtsev et al., 2009).

Table 2-5: Overview of diverse methods to produce graphene (Khan, Kermany, Ochsner, & Iacopi, 2017) .

Method	How to produce	Advantages	Disadvantages	Application
Micro-mechanical exfoliation	Peel off layers of graphite using scotch tape and repeat peeling results in graphene	- No need high-tech instrument - High quality graphene produced	-Not scalable	-Lab-based experiments
Liquid phase and thermal exfoliation	Graphene flakes are produced from graphite using chemical solvents or thermal shock	-Scalable to large-scale production	-The number of layers is firm to control -The process can introduce impurities	- Batteries of fuel cells - inks - conductive coatings
Chemical reduction of graphene oxide	Graphene oxide is ultrasonically exfoliated in an aqueous solution, processed by centrifugation, settled down as a thin film on substrate and reduced to graphene.			
CVD	Gases (contained carbon) decompose on a transition metal (ex: Ti, Cr) surface at high temperature (700–1000 °C) and transformed into graphene.	Scalable High quality Low cost Good control	Complex transfer process	Flexible, transparent electrode/ electronics, sensors, coating
EG (Thermal decomposition of SiC)	Evaporation of Si takes place at high temperature (>1200 °C) due to annealing and formation of graphene layer occur.	- Scalable - High quality - No transfer required - Good control over the process	- High cost of silicon carbide	- Sensors, current CMOS technology

2.4.1 Graphene as Lubricant Additive

In this study, graphene nano-platelet is being used as lubricant additive. The 2-dimensional structure of graphene provides tribological improvement via unique working mechanism which are not often seen by other conventional materials. Graphene has remarkable properties such as excellent electrical, mechanical, thermal and optical properties which enables it to be used as either solid or liquid-based lubricant. Specifically, its extraordinary strength, high chemical inertness, easiness to shear and atomically smooth surface are advantageous in exhibiting exceptional tribological performance (Berman, Erdemir, & Sumant, 2014). Being ultra-thin, graphene can be applied at nano or micro-scale systems such as in MEMS (micro-electromechanical systems) and NEMS (nano-electromechanical systems) (Khan et al., 2017).

Apart from that, there were also several studies being conducted related to the dispersion of graphene. Firstly, a study performed by Stephen Sie Kiong et al. (2017). The method they used in this study is that graphene nano-sheets were added to vegetable oils (VO) at 25 ppm, 50 ppm and 100 ppm respectively and homogenized (distribute uniformly) using acoustic cavitation and hydrodynamic cavitation. One pure VO and three graphene nano-fluid samples at different concentrations were prepared in this study. The VO and three prepared nano-fluids were tested under Four-Ball Tribotester. It shows that 25 ppm and 50 ppm graphene can reduce friction coefficient and wear scar diameter as compared to pure VO. However, addition of up to 100 ppm resulted in aggregation and stacking, thus leading to higher friction and wear.

Next, a study conducted by M.D. Avilés (2017). In their study, a fully-formulated motor oil (FFO), an additive-free base oil (B) and ionic liquids (IL) have been chosen as the base lubricants and graphene (G) as the lubricant additive. Three experiment were conducted, firstly, FFO + G. Secondly, B + G. Lastly, B+IL+G. The observation and analyzation are done by using Raman microscopy through the present of bands around the wear path. The results show that the addition of graphene to the fully-formulated oil reduces the friction coefficient by approximately 70%, and the wear rate of the steel disc by 60%, with respect to the base oil. The tribological performance of the additive-free oil (B) is not improved by the addition of graphene because the poor dispersion of graphene in the mineral oil. To compensate this, it is necessary to previously disperse graphene together with ionic liquid as surfactant.

Another study is done by Arwin and Rashmi (2013). In their study, Trimethylolpropane (TMP) ester and a mixture of 20% palm based TMP ester with 80% palm-based cooking oil was prepared. Nano-graphene platelet (NGPs) were dispersed in each bio-lubricant proportionately from 0.01% to 0.1% by weight. The frictional coefficient was then evaluated using a four-ball test machine. From the results, it shows that the addition of NGPs as an additive result in the reduction of coefficient of friction, achieving a reduction maximum reduction of 10% in palm oil TMP esters, and an impressive 17.9% reduction in the mix blend. Besides, a failure of the graphene to form a protective film over solid surfaces at higher temperatures and the tendency to agglomerate at higher concentrations of NGPs also had been observed. Thus, a solution is proposed to tackle this problem by the addition of dispersant or surfactant.

Thus, from the three studies conducted, it can be said that an addition of graphene in bio-based oils improved the tribological performance specifically on the friction coefficient and wear scars diameter. Besides, an addition of surfactant or dispersant is desired in order to compensate and help to improvise several weaknesses of the graphene.

2.4.2 Dispersion Stability of Graphene in Lubricant

Due to the structural uniqueness and astounding properties of graphene, the prospect of utilizing graphene in various application continues to gain attention in the scientific community. However, the preparation for a stable dispersion for graphene continues to be a hard task especially without the assistance of dispersant/surfactant and modification done to graphene. The destabilization of graphene dispersion is the result of particle aggregation by the graphene in the dispersion itself. Particle aggregation or particle agglomeration is the formation of particle clusters in a dispersion medium. In this process, particles (in this case, graphene) dispersed in the liquid medium starts to stick to each other which will then form an irregular cluster of particles. Other names for this phenomenon are flocculation and coagulation. The occurrence of this phenomenon will result in unstable colloidal suspension particles provides a graphical overview for the agglomeration of particles.

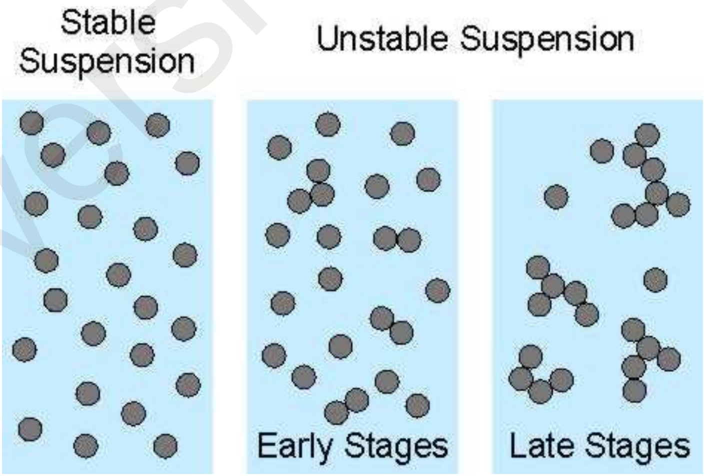


Figure 2-6: Agglomeration of nanoparticles

To maintain a stable dispersion, an energy barrier must be introduced to counteract the aggregation of particles. This can be achieved by either steric or electrostatic repulsion. A sufficient energy barrier will allow Brownian motion to maintain the stability of the dispersion (Johnson, Dobson, & Coleman, 2015). This can be achieved by the selection of solvent, modification to the graphene itself or the introduction of a suitable surfactant.

2.4.2.1 Solvent Selection

By definition, a solvent is a material which is able to dissolve a solute resulting to the formation of a solution. This means that by carefully selecting a suitable solvent, a stable graphene dispersion can be achieved. There are several solvent that has been reported to be able to disperse graphene with relatively good dispersion stability particularly N-Methyl-2-Pyrrolidone (NMP), Dimethyl sulfoxide (DMSO) and Dimethylformamide (DMF) (Hernandez, Lotya, Rickard, Bergin, & Coleman, 2009).

Hernandez et al. (2009) has done a comprehensive study on the solubility of graphene in a huge variety of solvent. They had dispersed graphene into 40 different solvent at 0.1 mg/mL concentration in order to study graphene solubility. Graphene dispersibility was measured using the graphene concentration after centrifugation. By associating it with Hansen solubility parameter, it was found that solvents which are good at dispersing graphene should have Hansen solubility similar to graphene. Hansen solubility parameter are expressed by dispersive (δ_D), Polar (δ_P), and hydrogen-bonding (δ_H) which for graphene are δ_D= 18.0 MPa$^{1/2}$, δ_P= 9.3 MPa$^{1/2}$ and δ_H= 7.7 MPa$^{1/2}$. However, out of all solvent tested in this study, only water have been study in lubricant application and it is only limited to water-based lubrication.

Ionic liquid has also been reported to be capable in forming a stable graphene dispersion. The usage of ionic liquid for the exfoliation of graphite into graphene has been gaining interest in the scientific community. Researches regarding graphene dispersion are usually interconnected with study for the exfoliation of graphite. Although dispersion and exfoliation are two different processes, they are highly associated with each other. This is because one of the main methods of graphene production is liquid exfoliation where a liquid medium or a solvent is needed to carry the newly exfoliated graphene.

As mentioned previously, the interaction between graphene and solvent can be investigated by studying both surface energy of graphene and Hansen solubility parameters. Shih, Lin, Strano, and Blankschtein (2010) have created a theoretical framework to evaluate the mechanism of graphene-solvent interaction using molecular dynamics simulation and kinetic theory of colloid aggregation. Using this method, they ranked the solvent according to their ability to dissolve pure graphene which rank are as follows, NMP ≈ DMSO > DMF > GBL > Water. This means that the ability of dispersing graphene depends on the selection of solvent or in the case for lubricant, the selection of base oil.

By selecting a base oil with suitable properties to graphene, it is possible to form a stable graphene nanolubricant on its own. However, many base oils used as lubricant does not fulfil these properties. As an example, S. S. N. Azman et al. (2016) have measured the dispersion stability of graphene nanoplatelet in PAO and TMP ester in addition to other lubricant properties. They found that the graphene was unable maintain a stable suspension after three days as sedimentation was seen in all concentration (0.01 wt.% - 3 wt.%). It was found that higher graphene concentration is detrimental to the stability of graphene-contained lubricant as they are more prone to sedimentation. This can be explained by the higher agglomeration tendency seen in higher graphene concentration. The increased amount of graphene in the base oil causes more tendency for graphene to interact with each other causing the increased agglomeration tendency

In a study, N. Azman, Syahrullail, and Rahim (2018) used refined, bleached and deodorized (RBD) palm kernel oil as lubricant base oil and graphene as additive with various dispersion methods. The three methods used i.e., via magnetic stirrer, overhead stirrer and high shear homogenizer are two-step method which means that the graphene was produced in a separate process before the dispersion in base oil. It was found that the selection of dispersion method does effect dispersion stability of graphene nanolubricant. Using high shear homogenizer, it was found the graphene nanolubricant is able to form a more uniform dispersion. The uniform dispersion was then seen to lead into improved tribological performance.

2.4.2.2 Surface Modification for Dispersion

In order to further explain the inner mechanism of surface modification for graphene, it is imperative to discuss on the structure and types of graphene derivative available. The two important graphene derivatives are graphene oxide and reduced graphene oxide. Graphene is a two-dimensional carbon allotrope where the chemical structure is made up of solely carbon bonded together to form a sheet-like structure. On the other hand, graphene oxide is the chemically modified graphene which have functional groups such as carboxyl group (-COOH), hydroxy group (O-H) and carbonyl group (C=O). Graphene oxide are formed by the oxidation of graphene and most commonly obtained from the exfoliation graphite oxide. It is also reported that carbon to oxygen ratio of graphene oxide is three to one.

If graphene oxide undergoes reduction process, reduced graphene oxide is formed. Although reduced graphene oxide contains the same functional group as graphene oxide, the number of those functional group is drastically lower. The structural and physical properties of reduced graphene oxide is similar to that of graphene. The reduction process from graphene oxide will not effectively remove all the functional group and also will have some defect on the graphene structure. The difference between graphene derivatives is shown in Figure 2-7.

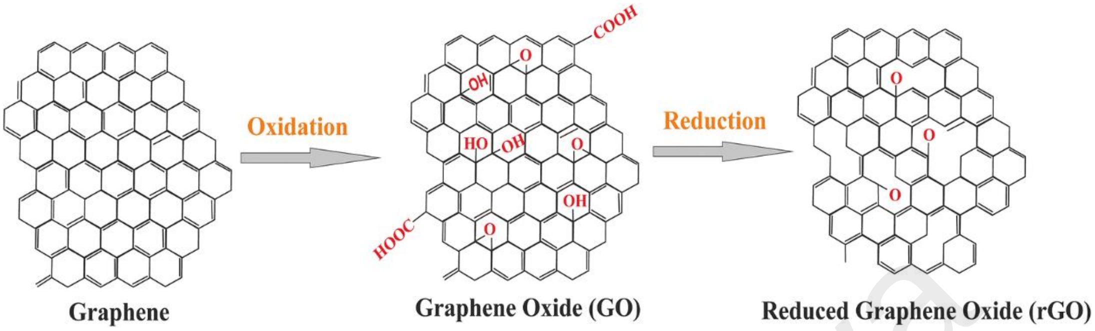


Figure 2-7: Chemical structure and process to obtain graphene derivative

Functionalization of graphene sheets is important in order to improve the dispersion stability of graphene suspension without the introduction of solvent and also foreign material. Graphene is functionalized by the bonding of graphene surface sheet with functional groups hence changing its surface energy to ease its dispersibility. For pure or pristine graphene sheet, researchers have only abled to functionalize it with organic functional group such free radical and dienophiles (Georgakilas et al., 2012). The functionalization of pure graphene is due to the formation of covalent group of organic functional group with C=C bond located on the graphene sheet.

As mentioned before, graphene oxide is technically graphene that contains functional group. The presence of these functional groups is very advantageous in the functionalization of graphene. Functional groups from the graphene sheet makes it vulnerable to chemical attack hence the different in physical and chemical properties. Though usually seen as disadvantageous, it also makes it easier to successfully do chemical modification. This makes graphene oxide to be a prime candidate as a starting material to be use for graphene functionalization. In this case, the selected functional group will attach itself to the oxygen atom located in the functional group in the graphene oxide sheet. By using graphene oxide, more functional groups can be added to the graphene sheets. For reduced graphene oxide, the functionalization is similar to graphene oxide however due to significantly lower number of functional groups, foreign functional group attached to the graphene is lesser.

A study conducted by Mungse, Kumar, and Khatri (2015) was able to successfully produced functionalized alkylated graphene from graphene oxide. This was done by grafting octadecylamine (ODA) to the sheet of graphene oxide. It was found that by successfully functionalized the graphene a stable dispersion can be achieved even after 1 month. At low concentration, the ODA-graphene was seen to exhibit significant improvement to the tribological performance in term of friction and wear in a pin-on-disk setup. Fan and Wang (2015) have done an extensive study on modifying graphene using ionic liquid as modifying agent on both graphene and graphene. It was found that the modification allows for a stable and homogenous suspension for graphene oxide. However, it was seen that the modified graphene sustains a loss in dispersion stability as sedimentation was observed after 120 hours. However, even with the loss in dispersion stability, the coefficient of friction and wear loss have seen a significant improvement for all modified samples.

Another way to improve the dispersibility of graphene without chemically modifying it is to do a physical modification. As of now, there is only one way to successfully modify the structure of graphene to prevent aggregation. Such way is by creating a crumpled graphene ball (Dou et al., 2016). In the case of graphene, the aggregation usually means the graphene sheet sticks to each other. By making it into a crumpled ball shape, it will become harder for graphene to form a cluster hence increasing its dispersibility. It was found that the crumpled graphene has successfully form a stable dispersion at high concentration. Not only that, the friction and wear reducing performance of lubricating oil significantly reduced.

2.4.2.3 Addition of Surfactant

The selection of base oil and graphene modification can be done to improve the dispersion stability of graphene suspension. However, there are some problems with these two methods for lubrication purposes. As mention earlier, base oil that usually used in a lubricant is not an effective solvent for dispersing graphene. Solvents that are good at dispersing graphene does not have a noticeable tribological properties with the exception of water (but only limited to water-based lubrication). This makes it very hard to select a good base oil for the lubricant. The lack of dispersion stability is crucial as a long shelf life is needed in order to use graphene as a commercial lubricant additive.

The functionalization of graphene also posed a problem for another reason. In subchapter 2.4.2.2, it was stated most of graphene functionalization primarily uses graphene oxide as a base material and rarely uses graphene. The problem lies with the selection of graphene oxide as a base material as the structure of graphene oxide contains many defects in the graphene structure. Even after the reduction process that usually done after the functionalization, the defect on the graphene structure still remains. The defect on the graphene structure is very important as it may alter the properties of the graphene. The changes in physical and chemical properties have also been reported after the addition of foreign functional group.

Another way to improve the dispersion stability of nanoparticle suspension is through the addition of a stabilizing agent. Stabilizing agent or stabilizer is an additive added into the solvent or base oil to obstruct the agglomeration and sedimentation of nanoparticle. The addition of this agent may lead to properties changes to the overall mixture. However, addition of foreign material is normal for lubricant as lubricant is commercially made up of 70% base oil and 30% additives. These stabilizing agents are usually categorized under surfactant or dispersant for lubricant additive. For lubrication, the utilization of surfactant or dispersant is a more cost-effective solution for improving dispersion stability of nanolubricant at least until graphene functionalization is up-scaled enough to be cheap in bulk and a base oil which has a good lubricant properties and good solubility to graphene is found.

In a study by S. Liang et al. (2016), graphite was exfoliated in deionized water to produce graphene. This is called a one-step process as it only takes one process to form graphene and produce a graphene suspension for usage. It was reported that this in-situ exfoliated graphene is only able to form a stable suspension with the help of Triton X-100 which is a non-ionic surfactant. It was seen that the addition of the surfactant not only improved the dispersion stability, it also helps in graphene exfoliation and contributes to protective layer formation during the tribological testing.

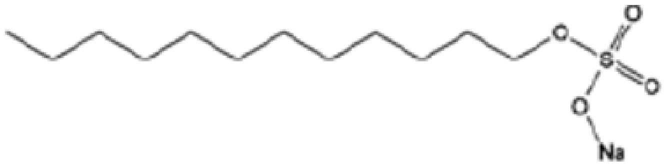
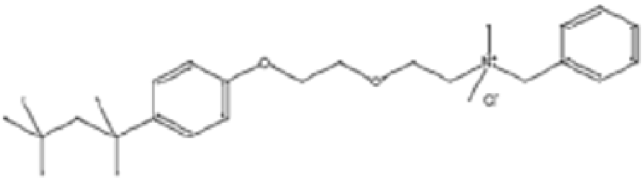
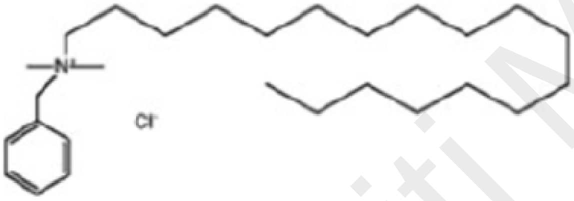
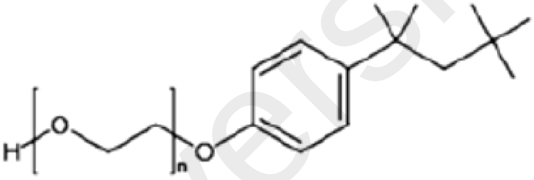
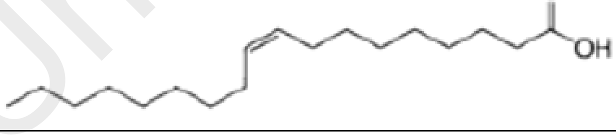
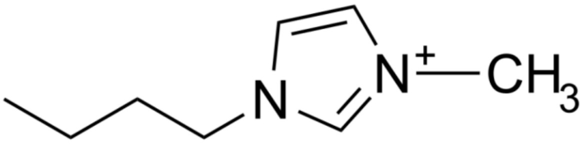
Ota, Hait, Sastry, and Ramakumar (2015) validated the prospect of using graphene in a hydrocarbon medium. Various hydrocarbon oil was selected to dispersed graphene in such as alkyl benzene and API grade base oil with diverse viscosities. To prevent re-agglomeration of graphene particle, polyisobutylene succinic imide have been used as a dispersant. The interaction between dispersant and pristine graphite is deemed important as this will result in better exfoliation process by effectively reduce the graphene size. As a result, the formulated lubricant was shown to have a significant improvement in thermal conductivity and tribological performance.

2.5 Surfactant / Dispersant

Graphene platelets are actually derived from graphite. It generally contains hydroxyl and carboxyl functional groups which make graphene platelets strongly hydrophilic and easy to coagulate in oil. To prevent any coagulation or agglomeration occurring, it is important to have a uniform dispersion of the graphene platelet in the base oil and to achieve this, surfactant is needed. Thus, surfactant or dispersant is added to actually enhance the dispersion stability of an additive in base oils. It is an easy and economic method. Some of the commonly used surfactants by the researchers nowadays include Triton X-100 (non-ionic type of surfactant) by S. Liang et al. (2016), oleic Acid (ionic type of surfactant) by W. Zhang et al. (2011) and ionic liquid (ionic type of surfactant) by M.D. Avilés (2017).

Most studies related to the addition of dispersants has testified that the use of surfactant was not only favourable in suspending the additives, but also reduced the friction and wear. Table 2-6 shows some typical surfactants used, their chemical structure and functionality (Gulzar, 2017). It has been proved that the surfactant can enfold one nanoparticle to repel to each other and by this means, a uniform suspension is formed (Huang, Tu, Gan, & Li, 2006). And by right, surfactant would improve the overall dispersion stability of the graphene platelet. But the main concern is that, there were zero to few studies being done regarding the study of the dispersion stability of graphene in bio-based oils. Some of the studies are dispersing graphene in mineral-based oils (Huang et al., 2006), water-based lubricants (Kinoshita, Nishina, Alias, & Fujii, 2014; S. Liang et al., 2016), disperse in organic solvent (Choudhary et al., 2012) and any other various fields. Thus, the main focus of this study is towards the dispersion stability of graphene in bio-based lubricants by the addition of surfactant.

Table 2-6: Common type of surfactant, their chemical structure and functionality

Surfactant	**Functionality**
Sodium dodecyl sulfate 	Anionic
Benzethonium chloride 	Cationic
Benzalkonium chloride 	Cationic
Triton X-102 	Non-ionic
Oleic Acid 	Anionic
Ionic Liquid 	Anionic

When nanoparticles are poured into a fluid, the size of the particle is small enough to remain uniformly dispersed by Brownian motion due to random motion of particles. The suspended particle may hold together and form bigger agglomerates which will eventually settled down due to gravitational pull. The agglomeration of nanoparticle would not only cause sedimentation and clogging, but also cause the loss of wear protection and friction reducing ability in a lubricant, and this is unfavorable. Thus, dispersion stability is highly demanded for consistent lubrication performance (Heidlebaugh, Domenech, Iasella, & Velankar, 2014). For an effective lubrication formula, stable suspension is required where the particles do not mount up at major rate. Numerous nanoparticles dispersion methods have been employed including magnetic stirring, chemical agitation, agitation using ultrasonic shaker, mechanical ball milling agitation, ultrasonic probe and ultrasonic. There were also numbers of method in analyzing the dispersion stability of lubricant methods including sedimentation test, spectral absorbency, zeta potential, and metallographic micrographs stability test (Gulzar, 2017).

There are several methods proposed by some researchers in order to enhance and address issues related to the dispersion stability of an additives in the base oils. Basically, the methods are through surface functionalization and it can be divided into two. The first one is electrostatic stabilization which integrated normally via the adsorption of ionic surfactant such as oleic acid and ionic liquid on the additives surface. The second method is steric stabilization where the additive's surface is functionalize with a polymer (Warshel & Levitt, 1976). One of the generally practiced surface functionalization methods is through the effect of surfactant (Chen, Wang, Zeng, & Zhang, 2006). Besides that, nanoparticle surface modification (Li, Cao, Zhang, & Dang, 2006).

2.6 EDX and Raman Analysis of Lubricant Samples

Energy dispersive X-ray spectroscopy or EDX is an X-ray technique that is used to determine and identify the composition of element of a material. It can also be used to detect the element present on the worn scar surface after a lubricant testing. By detecting element present on the worn surface, it is possible to theorize the possible lubricating mechanism during the lubricant operating condition.

The utilization of this technique in tribological study is not uncommon. Zulkifli et al. (2016) used EDX in order to determine the working mechanism of chemically modified TMP ester. Samples from fourball tribotest detected a higher trace of Oxygen element on the smoother worn surface. This can be attributed to the formation of oxide layer during the testing period. The oxide layer protects the bare metal surface of the fourball samples. Hence, the increase in Oxygen element from EDX spectroscopy is beneficial to the lubricant performance as a better oxide layer formation will protect the bare metal surface of the contacting surface. For graphene, it is quite direct as the graphene is a carbon allotrope hence it can be detected by the increase Carbon element on the EDX spectroscopy.

Raman spectroscopy is used to detect the molecular vibration on the worn surface area hence allowing mechanism analysis of the lubricant samples. Using this method, Raman peaks can be detected at certain wavenumber. These peaks are important to determine the involvement of graphene during lubrication process as EDX spectroscopy alone can only detect the presence of carbon element which can come from many sources. Hence, both EDX spectroscopy and Raman spectroscopy can be used together to fully determine the lubricating mechanism of graphene-contained lubricant. In Raman spectroscopy, graphene can be determine by its D band (~1350 cm^{-1})and G band (~1580 cm^{-1})

(Schuepfer et al., 2020). D band is caused by disordered graphene structure whereas G band is detected from stretching of C-C bond from graphitic structure.

2.7 Summary and Research Gap

Table 2-7 shows several studies conducted in relation to the dispersion of graphene. As far as the research conducted by the author, it can be said that there is zero to few studies done regarding the dispersion of graphene specifically in bio-based lubricant. Most of the studies dispersed graphene as an additive in water, followed by in mineral oil and the least one, in bio-based oil (vegetable oil). The results for all the studies uniformly said that the addition of graphene has improve the tribological performance in term of the friction coefficient and wear scars diameter. Several studies also proposed the addition of surfactant in order to improve the dispersion stability of graphene floated in the base oils. But not all surfactant was tested.

Table 2-7: Studies conducted related to the dispersion of graphene

Journal/Article Title	Methodology and Main Finding	Reference
Tribological Investigation of Graphene as Lubricant Additive in Vegetable Oil	This paper used graphene in different concentration to pure vegetable oils. The results shows that addition of graphene at certain concentration has reduced the coefficient of friction as well as the wear scars diameter. Excess addition of graphene will cause aggregation and stacking.	(Stephen Sie Kiong et al., 2017)

Table 2-7 Continued

Graphene as a lubricant additive. Effect of the base oil, contact materials and sliding conditions	This paper used graphene in fully formulated commercial oil, additive-free oil (mineral oil) and ionic liquid. The addition of graphene to the fully-formulated oil reduces the friction coefficient and the wear rate of the steel disc. On the other hand, tribological performance of the additive-free oil is not improved by the addition of graphene because of poor dispersion. Ionic liquid has been add with additive-free oil and thus enhanced the dispersion stability of graphene.	(M.D. Avilés, 2017)
Tribological Evaluation of Nano Graphene Platelets as an Additive to Bio-lubricant Base Fluid	This paper used graphene nano-platelet (NGPs) into (i) 100% TMP ester (ii) 20% TMP ester + 80% cooking oil. The addition of NGPs results in the reduction of coefficient of friction in both cases. Graphene failed to form protective layer in high temperature. High concentration of NGPs caused aggregation. Surfactant need to be added to improve the dispersion.	(Arwin & Rashmi, 2013)
Frictional behavior of oxide graphene nano-sheets as water-base lubricant additive	Water is added with (i) Graphene oxide (ii) oxide multiwall carbon nanotubes (CNTs-COOH). The addition of GO in pure water improve the anti-wear ability and decrease the friction coefficient. The water with GO showed better tribological properties than the water with oxide multiwall carbon nanotubes (CNTs-COOH).	(Song & Li, 2011)
In-situ exfoliated graphene for high-performance water-based lubricants	Water is added with graphene and non-ionic surfactant, Triton X-100. The graphene dispersions show high stability due to the assistance of non-ionic surfactant, Triton X-100. The in-situ exfoliated graphene possesses brilliant frictional and anti-wear properties as compared with pure deionized water. Triton X-100 ease the deposition procedure of the graphene layer by adjusting the dispersion wettability of the sliding surfaces.	(S. Liang et al., 2016)

Table 2-7 Continued

Tribological properties of monolayer graphene oxide sheets as water-based lubricant additives	Graphene oxide is added into purified water and in poly-alpha-olefin (PAO) for comparison. It was found that adding GO particles into water improved lubrication and provided a very low friction coefficient and no obvious surface wear. For PAO, the friction coefficient fluctuated.	(Kinoshita et al., 2014)
Investigation of the tribology behavior of the graphene nano-sheets as oil additives on textured alloy cast iron surface	Graphene nano-sheets (GNS) is added on alloy cast iron plate (original surface, dimple density of 22.1%, 19.6% and 44.2%). GNS was added into PAO4 oil as lubricant and Span-80 was used as a dispersing agent. A combined effect between GNS additives and laser surface texturing (LST) was also done. High friction and wear were achieved under laser surface texturing alone. The GNS additives modified by Span-80 were well dispersed in PAO4 oil, wear rate reduced, especially on the textured surface.	(Zheng, Cai, Shen, Li, & Zhu, 2016)

Thus, due to these voids which is the shortage of studies related to the dispersion of graphene in bio-based oil as well as lack of studies on the dispersion stability when added with different type of surfactant has risen the intention of the study to fill in the gap as seen in Table 2-8.

Table 2-8: Research gap of the study

Graphene	With dispersion study	Surfactant	(M.D. Avilés, 2017)	(Zheng, Cai, Shen, Li, & Zhu, 2016)	(Liang et al., 2016)				**This project**
		Chemically modified	(Mungse, Kumar, & Khatri, 2015), (Wei et al., 2011)	(Chen, Xia, Jia, Liu, & Zhang, 2014)					
	Only tribological study		(Eswaraiah, Sankaranarayanan, & Ramaprabhu, 2011)	(Kinoshita, Nishina, Alias, & Fujii, 2014)	(Song & Li, 2011), (Kinoshita et al., 2014)			(Zen & W, 2013)	
Nanoparticle additive			(Peng, Kang, Hwang, Shyr, & Chang, 2009)	(Yue et al., 2011)		(Rapoport et al., 2003)			
No-Additive							(Stephen Sie Kiong et al., 2017)		
			Parafin/mineral oil	PAO			Vegetable oil	Modified vegetable oil	Ester based
			Mineral-based		Water-based	Mix oil	Bio-based Lubricant		

CHAPTER 3 : METHODOLOGY

In order to successfully understand the effect of graphene stability in bio-based oil to its tribological behavior, a set of sequential and attentive methodologies have been created and implemented. The first step is to carefully select the base oil to be used throughout the project. Then, tribological test was conducted to measure the lubricant performance of the base oils without any addition of additives. This follows with the examination of suitable graphene concentration and compatibility of base oil with graphene to produce a stable and enhanced graphene nanolubricant. The dispersion stability was measured using sedimentation test and UV-Vis spectroscopy. To study the prospect of graphene additive in bio-based lubricant, dispersion stability was measured in the course of one month. After one month, samples were taken to do tribological testing to correlate between dispersion stability and tribological behavior.

The next stage of the project involves the introduction of surfactant to improve the dispersion stability of graphene suspension. During this stage, three type of surfactant is selected to see their compatibility with the graphene suspensions. Same as previous stage, the dispersion stability is measured for one month. Samples would undergo tribological testing to ensure the addition of surfactant will not deteriorate the tribological performance. Figure 3-1 was created to provide an overview for this project. Important research activities are shown in the flowchart.

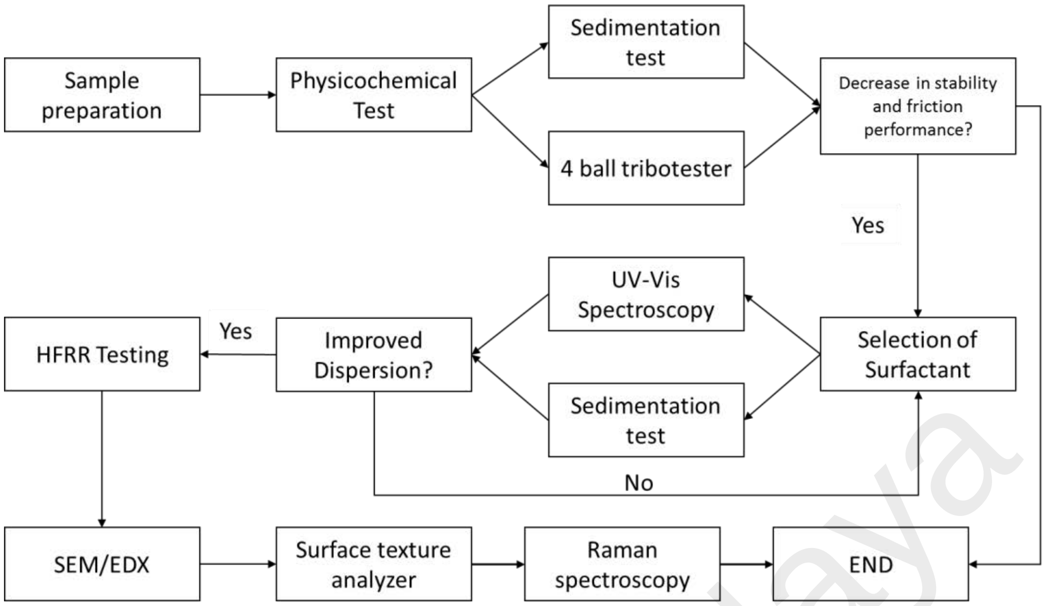


Figure 3-1: Flowchart for the entirety of the project

3.1 Sample Preparation

This subsection will provide information on the sample preparation used in this study. This subsection will only focus on the acquirement and preparation of each individual sample component.

3.1.1 Selection of Base Oil

In this study, three bio-based polyol esters were selected as the base oil for the development of bio-based lubricant. The three mentioned polyol esters are neopentyl glycol dioleate (NPG), trimethylol propane trioleate (TMP) and pentaerythritol tetraoleate (PE) esters. All base oils were purchase from Shandong Ruijie Chemical Industry Co., Limited. Polyol esters were chosen due to their good properties to be used as lubricating oil. The fatty acid chain for the polyol ester is the same to control the effect of varying fatty acid chain number on graphene dispersion stability, friction, wear and its physical properties. This means the ‘tail’ part of the polyol esters are made up of oleic acid chains ($C_{18}H_{34}O_2$). The chemical structure of the polyol ester is shown in Figure 3-2.

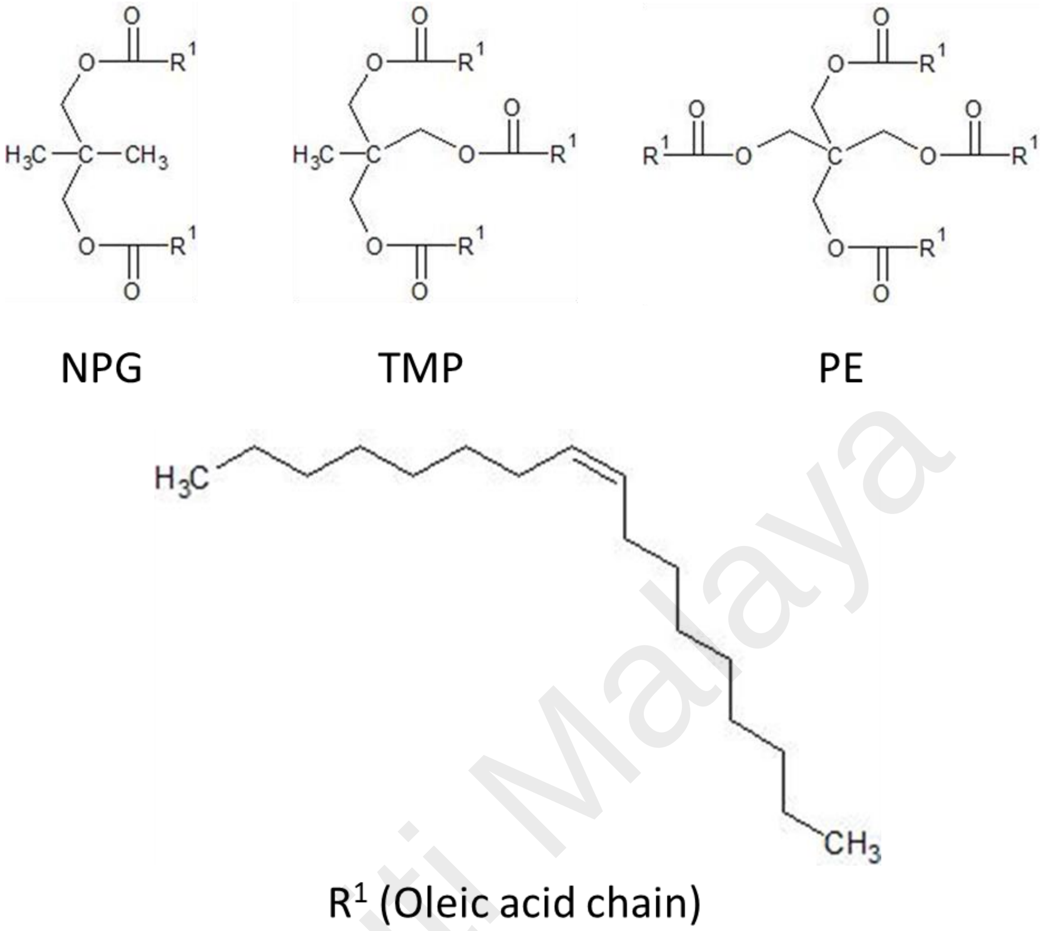
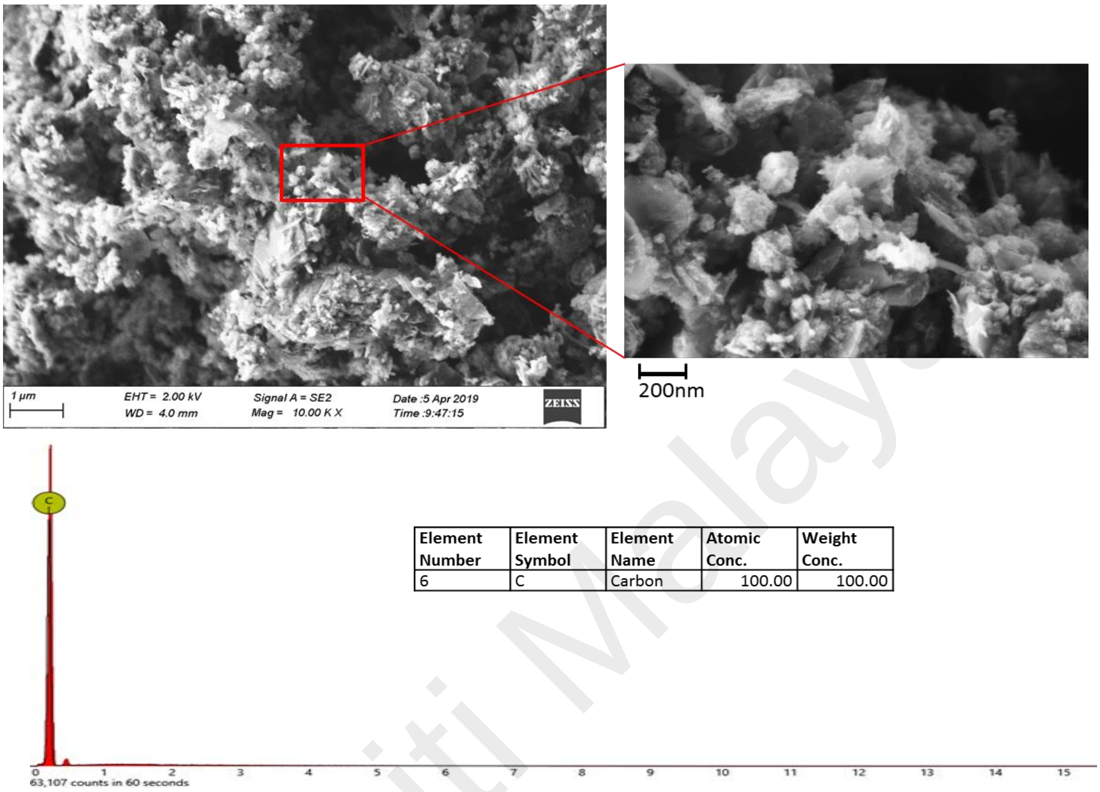


Figure 3-2: Chemical structure of selected polyol esters

3.1.2 Graphene Nanoplatelet

For this study, graphene nanoplatelet is selected as the only nanoparticle to be dispersed in the base oil. Other graphene derivative such as graphene oxide and reduced graphene oxide was considered but only graphene was selected in the end. This was done to focus solely on the dispersibility of graphene in various bio-base lubricant and the inclusion of other graphene derivative may overcomplicate the study. Graphene nanoplatelet possess excellent mechanical and barrier properties which can help in tribological behaviour and its two-dimensional structure can provide unique frictional behaviour. Graphene nanoplatelet was purchase from Low Dimensional Material Research Centre in University of Malaya. Information regarding graphene properties was given by the supplier. The morphology of graphene nanoparticle is shown in Figure 3-3 and Table 3-1 displays the given graphene properties.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	100.00	100.00

Figure 3-3: FESEM micrograph focusing on graphene morphology and EDX spectrum on graphene particle

Table 3-1: Properties of graphene nanoplatelet

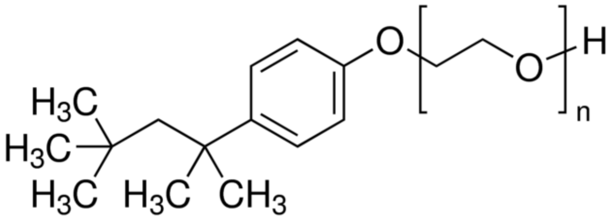
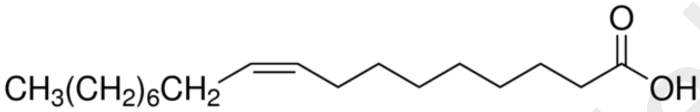
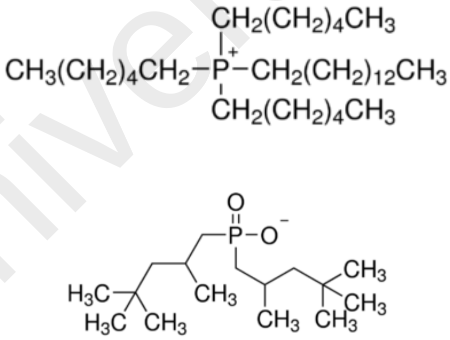
Name	Graphene nanoplatelet
Appearance (Form)	Powder
Appearance (Color)	Black
Purity (%)	99
Morphology	Non-spherical
Thickness	~5nm
Surface area	120m^2/g

*Data provided by the manufacturer

3.1.3 Surfactant

After studying the effect of dispersion stability of graphene in bio-based lubricant, it is empirical to provide a proper solution to the dispersion stability problem encountered in the study. For this study, it was decided that surfactant will be used as a mean to improve the dispersion stability of graphene. By using surfactant, the structural properties of graphene were retained. The usage of surfactant is also common in lubricant usually use to suspend contaminant and carbon deposit. To study the compatibility between surfactant and graphene dispersion, three material have been selected to be use as surfactants. The materials selected are Triton X-100, oleic acid and ionic liquid. Oleic acid and Triton X-100 is procured from Sigma-Aldrich Corporation. The ionic liquid selected is Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate. Ionic liquid was purchased from IoLiTec-Ionic Liquids Technologies GmbH. The selected surfactant's chemical structure and properties is shown in Table 3-2.

Table 3-2: Chemical structure and properties of surfactant used in the study

Triton™ X-100		
 Chemical Structure	Grade	Laboratory Grade
	Type of Surfactant	Non-ionic surfactant
	Color	Faintly yellow
	Form	Liquid
Oleic acid		
 Chemical Structure	Purity	>90%
	Type of Surfactant	Anionic
	Color	Colorless
	Form	Liquid
Ionic Liquid - Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate		
 Chemical Structure	Purity	>90%
	Type of Surfactant	Anionic
	Color	Colorless
	Form	Liquid

*Data given by the manufacturer

3.1.4 Lubricant Formulation

For the formulation of the lubricant, magnetic stirrer (Brand: Fisher Scientific) was used to mix the base oil and the additive together. The three base oils do not mix with each other and blend separately to form a graphene dispersion. Firstly, 100ml of the base oil was poured into a beaker with the magnetic stirrer inside. Then, a measured quantity of graphene was then added into the base oil. The stirrer is then set to 700rpm at room temperature for 1 hour.

For the first part of the experiment, graphene was blended with bio-based oil at the concentration of 0.01 wt.%, 0.03 wt.%, 0.05 wt.%, 0.07 wt.% and 0.10 wt.%. As a result, 18 samples were produced for the first part of the experiment. After testing, the samples with the best tribological performance and dispersion stability for each sample were selected. The selected samples were blended together with three surfactants at 1.0wt.%.

Table 3-3: Sample details for the first part of the experiment.

No.	Sample Name	Concentration (wt. %)	No.	Sample Name	Concentration (wt. %.)
1	NPG	100 NPG	10	0.05 TMP	99.95 TMP 0.05 G
2	0.01 NPG	99.99 NPG 0.01 G	11	0.07 TMP	99.93 TMP 0.07 G
3	0.03 NPG	99.97 NPG 0.03 G	12	0.10 TMP	99.90 TMP 0.10 G
4	0.05 NPG	99.95 NPG 0.05 G	13	PE	100 PE
5	0.07 NPG	99.93 NPG 0.07 G	14	0.01 PE	99.99 PE 0.01 G
6	0.10 NPG	99.90 NPG 0.10 G	15	0.03 PE	99.97 PE 0.03 G
7	TMP	100 TMP	16	0.05 PE	99.95 PE 0.05 G
8	0.01 TMP	99.99 TMP 0.01 G	17	0.07 PE	99.93 PE 0.07 G
9	0.03 TMP	99.97 TMP 0.03	18	0.10 PE	99.90 PE 0.10 G

3.1.5 Summary of Material Used

This subchapter listed the material used in the study along with their manufacturer. Table 3-4 shows all the material that was utilized and used throughout the study

Table 3-4: Material used in the study along with their manufacturer

Material	Manufacturer
Neopentyl glycol dioleate (NPG)	Shandong Ruijie Chemical Industry Co., Limited
Trimethylol propane trioleate (TMP)	Shandong Ruijie Chemical Industry Co., Limited
Pentaerythritol tetraoleate (PE)	Shandong Ruijie Chemical Industry Co., Limited
Graphene nanoplatelet	Low Dimensional Material Research Centre in University of Malaya
Triton™ X-100	Sigma-Aldrich Corporation
Oleic acid	Sigma-Aldrich Corporation
Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate	IoLiTec-Ionic Liquids Technologies GmbH

3.2 Experimental Procedure

This subsection will provide information on the experimental procedure of the study. Each test that has been conducted was discussed.

3.2.1 Dispersion Stability

There are several procedures that can be used to test the dispersion stability of graphene nanoplatelet in bio-based lubricant. However, only two methods were used to collect the data on the dispersion stability of graphene for this study. Both methods were chosen due to the method is measured in real-time aging and not accelerated aging. Other alternative techniques to measure dispersion stability are dynamic light scattering which allows measurement of particle size in the solvent, SEM technique can be used on the after dried up particle, and zeta potential in which a higher zeta potential will indicate a more stable dispersion.

3.2.1.1 Sedimentation Method

Sedimentation method is also known as observation stability test. This method is one of the simplest ways to evaluate the dispersion stability of nanoparticle-contained lubricant. However, its downside is the time taken to obtain the result. The prepared samples were put in small vial after its dispersion. The condition of the lubricant was then measured optically and recorded by photograph for over one month. This method was selected because it can be used to directly measure the actual shelf life of graphene suspension for when it will be used commercially. The condition of which the vials are stored is closely maintained to ensure repeatability of the test. Disturbance and movement of the vials is also limited.

3.2.1.2 Ultraviolet–Visible Spectroscopy/Spectrophotometry (UV-Vis)

Another disadvantage of solely using sedimentation stability method is that the result obtained can only be interpret subjectively. Hence, UV-Vis was done to validate the result obtained from sedimentation test by quantifying the data obtained. UV-Vis absorbance measurements are able to measure and characterize the dispersion stability of the nanolubricant. Basically, this method allows the measurement of opacity of the nanolubricant. As the nanolubricant continues to sediment, the opacity of the lubricant decreases as the nanoparticle is no longer suspended and sediments. UV-Vis is able to detect this change and give quantifiable result. Figure 3-4 shows the SPEKOL 1500 UV-Vis machine used throughout the study.

Figure 3-4: SPEKOL 1500 Ultraviolet–visible spectroscopy

3.2.2 Lubricant Analysis

One of the physical properties measured for lubricant analysis is kinematic viscosities at 40°C and 100°C according to ASTM D2270. From this, viscosity index was calculated. Density was then measured at 15°C according ASTM D4052. All the test were conducted using Anton Paar Stabinger SVM^{TM} 3000. It is important to analyze the density as it is associated to the viscosity of the lubricant. If there is any calculation needs to be done based on the viscosity of the fluid, the density must be known first. In fact, if the density of a lubricant increases, the fluid becomes thicker and the viscosity value becomes higher. Viscosity, on the other hand, simply means the intermolecular friction between liquid molecules. It can be a measure of thickness created between the contact surface and fluids. Thus, a wide discrepancy of viscosity may lead to the change of lubricant regime under the same condition. Viscosity index is a measure of viscosity change with respect to temperature. High viscosity index means the viscosity can withstand much higher temperature range and this is favorable.

3.2.3 Tribological Testing

There are various ways to measure the tribological performance of the lubricant samples. Post testing analysis of the lubricant sample will also be discussed.

3.2.3.1 Wear Preventive Test

For the first part of the study, tribological performance of lubricant sample was tested using fourball tribotester machine. The machine used is DUCOM TR-30H fourball tester. The main function of this machine was to measure the tribological performance of the sample specifically to determine the relative wear preventive and load bearing capacity of lubricating fluids which are in rotational contact. Apart from that, this machine was also used to determine the wear scars diameter as well as the coefficient of friction. Figure 3-5 shows the schematic diagram for the fourball tribotester machine and the elemental composition of the steel ball is shown in

Table 3-5.

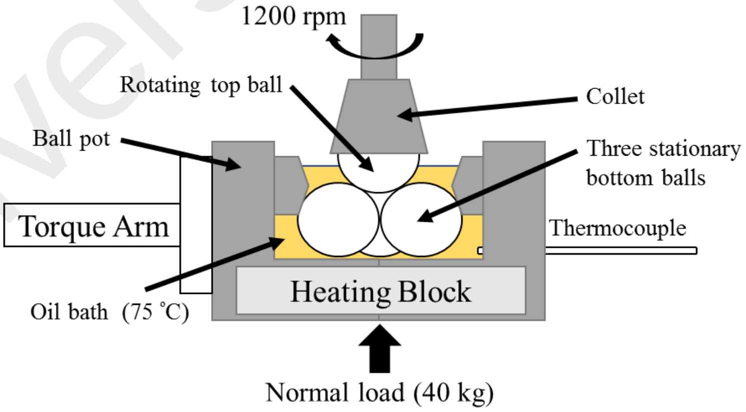


Figure 3-5: Schematic diagram of the fourball tribotester

Table 3-5: Elemental composition of AISI 52100 Steel balls

Element	Fe	C	Zn	Si	P	S	Cr	Mn	Ni
Composition (%)	85.06	10.2	2.15	0.45	0.12	0.07	1.46	0.42	0.06

The balls used were AISI52100 alloy steel balls. The procedures of using this machine are as follows. Firstly, there would be three ball bearing clamped together using a torque wrench and is shown in Figure 3-6. The balls were first wiped with toluene or heptane as well as the ball pot in order to be cleaned and remove any contaminant present on the surface of the balls. Then, the sample lubricant was poured into the ball pot assembly. The fourth ball was then locked on the spindle and placed on the top of the three ball.

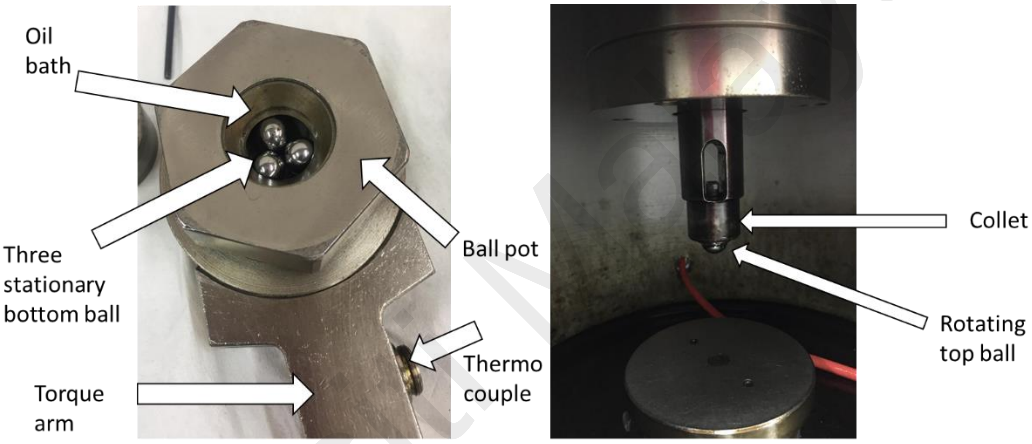


Figure 3-6: (Left) Three balls locked on the holder and (Right) The fourth ball locked on the spindle

The next step was to set up the working parameter for the test using WinduCom software on the computer connected to the machine. The test parameter was set according to the ASTM D4172-B as shown in Table 3-6. Finally, the 'RUN' button is clicked to operate the machine. After running the test, the wear scar diameter from the tribotest located on surface of the three balls were measured using optical microscope.

Table 3-6: ASTM D4172-B test parameter

Load (kg)	Duration (s)	Temperature, °C	RPM
40	3600	75 ± 2	1200 ± 60

3.2.3.2 High Frequency Reciprocating Rig (HFRR)

High frequency reciprocating rig (HFRR) (model number: TR-281-M8) was used to simulate reciprocating contact between two surfaces. An example of this interaction is the cylinder wall-piston interaction in internal combustion engine. Unlike fourball tribotest, HFRR uses two different contacting components that can be configured according to one's needs. The materials can be the same or different depending on the study. For this experiment, grey cast iron plate and stainless steel cylindrical roller bearing were used as the two contacting surfaces. This was done to ensure line contact between the two surfaces. Line contact enable a more in-depth analysis of the wear mechanism of graphene-contained lubricant. The cast iron plate was stationary and the steel roller will have reciprocating motion. The test parameter is shown in Table 3-7.

Table 3-7: HFRR test parameters

Load	100 N
Stroke length	5 mm
Frequency	10 Hz
Oil bath temperature	75°C
Time	3600s
Materials	Top: AISI 52100 roller bearing Bottom: Grey cast iron plate

3.2.3.3 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a type of scanning electron where focused electron beam is used to scan surface of material at nanoscale and generate grayscale images of sample at high magnification. Interaction of electron and particles in the sample give surface information such as surface topography and composition. SEM machine used was the Carl Zeiss UltraPlus model AG ULTRA55. In this project, wear scar on the surface of grey cast iron was analyzed. The samples were rinsed with acetone before the observation using SEM. Type of wear scar present on the surface was detected and further understanding of the wear mechanism can be achieved.

3.2.3.4 Energy Dispersive X-ray Spectroscopy (EDX)

Energy dispersive X-ray (EDX) Spectroscopy is a chemical microanalysis technique used in conjunction with SEM. X-ray emitted from sample is detect during bombardment of electron beam to characterize the elemental composition of analyzed volume. The sample were rinsed with acetone before undergoing EDX analysis. EDX was used to obtain the chemical composition of element on the wear scar analyze by SEM. Then, the data were analyzed and compared with chemical composition of material before the test. Therefore, nanoparticles deposited on the surface can be identified.

3.2.3.5 Field Emission Scanning Electron Microscopy (FESEM)

The mechanism of field emission scanning electron microscopy (FESEM) is similar to that of SEM. The difference is FESEM is able to give higher quality imaging and higher magnification compare to that of SEM. Although it is not use much in this study, it is crucial nonetheless especially in conforming the structure of graphene nanoparticle. SEM is unable to provide an acceptable imaging when studying graphene structure. The electromagnetic beam gun in FESEM provide a more powerful electron beam which results in high magnification, high resolution and better image quality.

3.2.3.6 3D Optical Surface Texture Analyser

Optical surface texture analyser is used to detect the surface roughness of the worn surface from the HFRR testing. The equipment used in this study was Infinite Focus Real 3D Alicona located in the Faculty of Dentistry, University Malaya. The surface roughness obtained by using this equipment is important to determine the wear severity of the lubricant samples.

3.2.3.7 Raman Spectroscopy

Raman spectroscopy was used to detect the molecular vibration on the worn surface area hence allowing mechanism analysis of the lubricant samples. Using this method, Raman peaks can be detected at certain wavenumber. In order to completely analyse the lubricating mechanism of the lubricant samples, the Raman spectrum analysis was backed up with the elemental analysis obtained from EDX analysis.

CHAPTER 4 : RESULTS AND DISCUSSION

In this chapter, the dispersion stability of graphene in bio-based lubricant is reported and discussed. The relationship between the dispersion stability and tribological properties will also be made along with the solution to improve the dispersion stability was provided. At the first part of the study, only graphene and base oil were tested using fourball tribotester. The dispersion stability was observed and studied for over one month. After one month, the tribological performance was tested. This was done to study the direct effect of unstable dispersion towards tribological behavior of bio-based lubricant.

In the next phase, a suitable surfactant was proposed to improve the dispersion stability of bio-based lubricant. To do this, three surfactants were selected as stabilizing agent for the graphene suspension. The dispersion stability was observed measured for the duration of one month. The best performing surfactant was taken for further tribological testing. This was done to see whether or not the tribological behavior decreased due addition of surfactant. The tribological performance and wear mechanism was studied using HFRR.

4.1 Viscosity and Density of Graphene-contained Lubricant

It is imperative to study the viscosity and the density because it will affect the lubricant performance. Significant increase in viscosity will cause a shift in the Stribeck curve hence changing the lubrication regime of the lubricant at the same operating condition. If there is change in the lubricant regime, then it will be hard to study the actual effect of graphene in lubricant performance as the difference in tribological performance may be the cause of different lubricant regime.

As shown in Table 4-1, there were no significant differences in the viscosity, viscosity index and density after the dispersion of graphene in the bio-based lubricant. The reason for the lack of change may be attributed to the low graphene concentration. This coincide with the result obtained by Zin et al. (2016) where viscosity did not change the properties at low nanoparticle concentration. Similarly, S. S. N. Azman et al. (2016) also found that adding graphene to polyalphaolefin-TMP blend will only cause a significant viscosity change, but only at higher concentration (>0.5 wt.%). The lack of changes in physical properties is good as there is no change in lubrication regime during tribological testing.

Table 4-1: Viscosity and Density of graphene-contained lubricant

Sample	Viscosity at 40°C (mm^2/s)	Viscosity at 100°C (mm^2/s)	Viscosity Index	Density (g/cm^3)
NPG BASE	26.086	6.3539	210.8	0.9084
0.01 NPG	26.460	6.3539	209.6	0.9083
0.03 NPG	25.956	6.3532	212.3	0.9085
0.05 NPG	25.694	6.3539	212.8	0.9084
0.07 NPG	25.982	6.3485	211.7	0.9076
0.10 NPG	26.217	6.3612	209.7	0.9080
TMP BASE	48.447	9.648	188.9	0.9196
0.01 TMP	48.397	9.641	189.0	0.9197
0.03 TMP	48.445	9.652	189.0	0.9197
0.05 TMP	48.493	9.6681	189.3	0.9197
0.07 TMP	49.512	9.7984	188.4	0.9198
0.10 TMP	49.312	9.7751	188.6	0.9198
PE BASE	63.407	11.855	186.1	0.9295
0.01 PE	64.014	11.855	184.0	0.9298
0.03 PE	63.956	11.862	184.4	0.9297
0.05 PE	62.843	11.855	186.7	0.9294
0.07 PE	63.488	11.805	184.7	0.9292
0.10 PE	63.216	11.815	185.8	0.9295

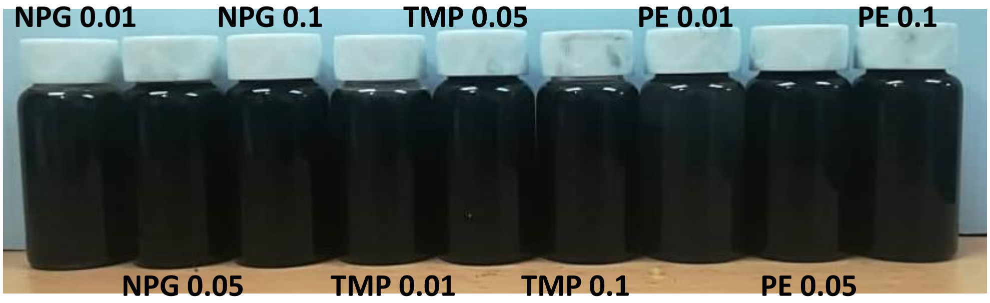
Although there were no significant changes after the addition of graphene, there was a visible difference when compared between base oils. There was an increment in viscosity and density from NPG ester to PE ester. This is because of the molecular size of the bio-based polyol ester. A smaller size molecule, in this case NPG ester, will have a lower viscosity compared to a larger size molecule (Knothe & Steidley, 2005). This means that although it is easy to compare the effect of graphene on the tribological behaviour, it is difficult to make direct comparison between base oil unless the lubrication regime is proven the same for all base oil.

4.2 Dispersion Stability of Graphene Nanolubricant

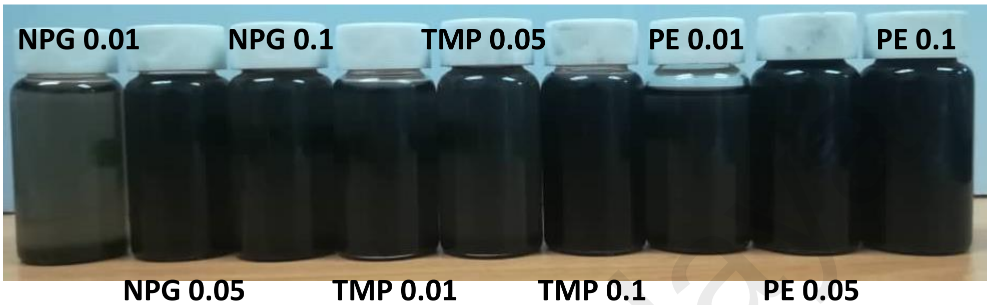
Dispersion stability was measured by using sedimentation method and UV-Vis spectroscopy. Both methods use real time aging meaning the samples are left undisturbed for one month (the duration of the observation). When dispersed in the base oil, graphene nanoparticle was suspended in lubricant (base oil). The ability to sustain this dispersion/suspension can be measured by its dispersion stability.

4.2.1 Sedimentation Method

After the dispersion, the samples containing graphene were then observed for a duration of 1 month. Among the parameter that was observed includes the sedimentation and also intensity of the colour black. As can be seen, the graphene dispersion was stable 1 week after the dispersion. It is also noted that the dispersion does not involve any ultrasonication process nor the usage of dispersant. Hence, the dispersion of graphene is solely based on the interaction between the bio-based lubricant and the graphene itself. Figure 4-1 shows the sedimentation observation for a period of one month.



After 1 week



After 2 weeks

After 4 weeks

Figure 4-1: Sedimentation observation of graphene dispersions

For all samples, graphene dispersion remained stable for 1 week. This means that the dispersion technique used in this study has successfully formed a stable dispersion. There was no sedimentation observed during this time. The black colour of the graphene dispersion also did not lose any intensity for all sample.

Sedimentation started to occur 2 weeks after dispersion for NPG 0.01 while others still maintain a stable dispersion. However, NPG 0.01, TMP 0.01 and TMP 0.05 showed a decreased level in the black colour intensity which indicates a low but stable dispersion.

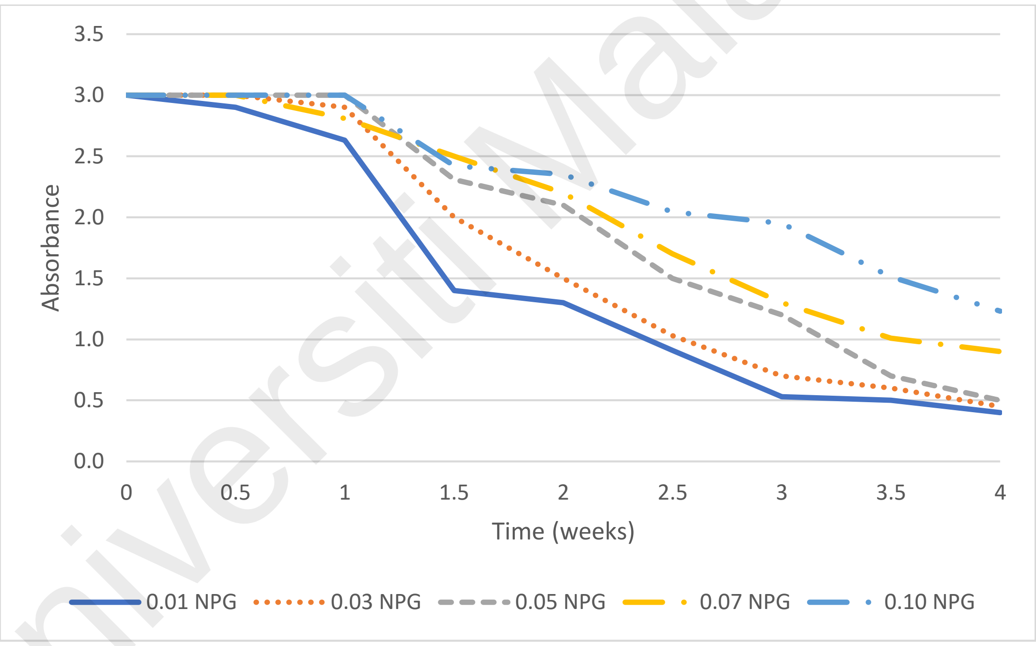
For comparison, a study by Guo and Zhang (2016) found that graphene have sedimented after 2 weeks in pure polyalphaolefin-2 oil at almost the same rate as NPG at the same graphene concentration. Other sample exhibited a more stable dispersion.

After 1 month, sedimentation layer was formed in NPG ester at all concentration. It can also be seen that the intensity of black colour has gradually faded for all NPG samples. This was more visible in NPG 0.01 and NPG 0.05 where the colour of sample has gradually turn back to the colour of its base oil. The NPG 0.1 sample maintained some dark colour of the solution. Meanwhile, TMP ester started to lose its black colour intensity at 0.01 and 0.05 wt.% concentration of graphene. Stable dispersion has been observed in TMP 0.1, PE 0.05 and PE 0.1. The findings suggested that the dispersibility of graphene in the polyol esters follows the pattern of PE>TMP>NPG ester. Interestingly, the pattern also follows the number of fatty acid chain present or the molecular branch present in the esters as shown in Figure 3-2. As mention before, the fatty acid chain length for all three sample is the same which is the oleate chain containing 18 carbon chain with one double bond.

Though it can clearly be observed the dispersion stability by using this method. The sedimentation method is a qualitative method which means that the result obtained by this method can only interpreted subjectively. Hence, in order to strengthen the result, it is important to do UV-Vis method which is a quantitative method.

4.2.2 UV-Vis Spectroscopy

Figure 4-2 presents the UV-Vis absorbency for test samples. For clarity, the maximum absorbance value that can be detected by the machine in UV-Vis spectroscopy is 3.00. However, it is important to note that the UV-Vis spectroscopy can detect the change of opacity as observed during sedimentation test. This means that above 3.00 absorbance value can be considered as stable. With the exception of some NPG samples, all samples have shown a stable dispersion. NPG 0.01 started to lose its dispersion stability in the middle of the 1st week. Though, the decrease in absorbance was not that significant. After three weeks, all of the samples gradually exhibited a decrease in absorbance value.



(a)

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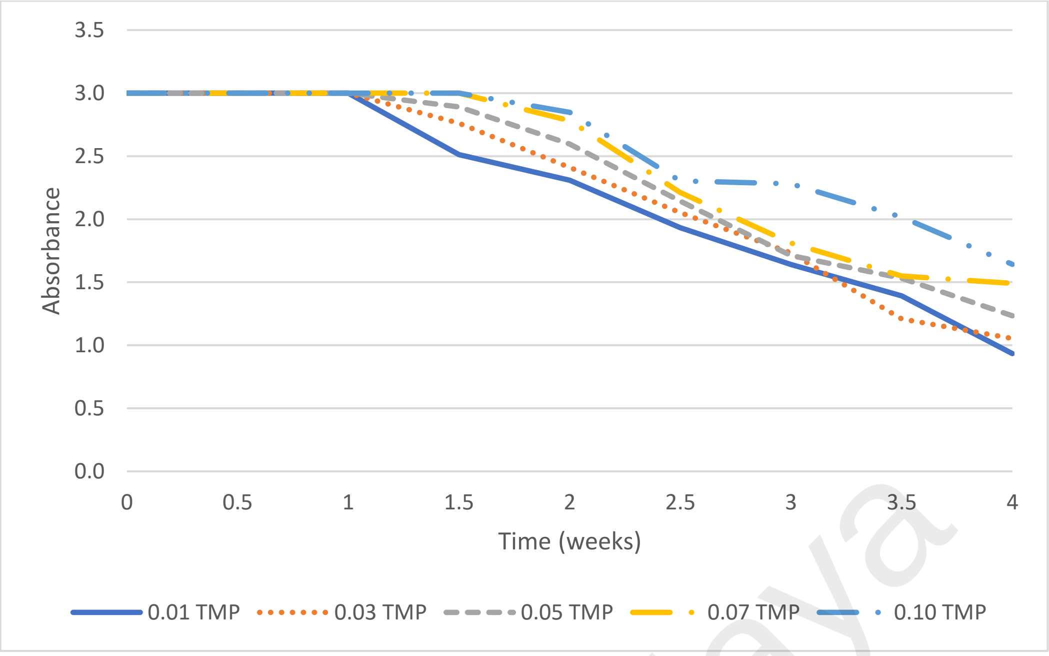

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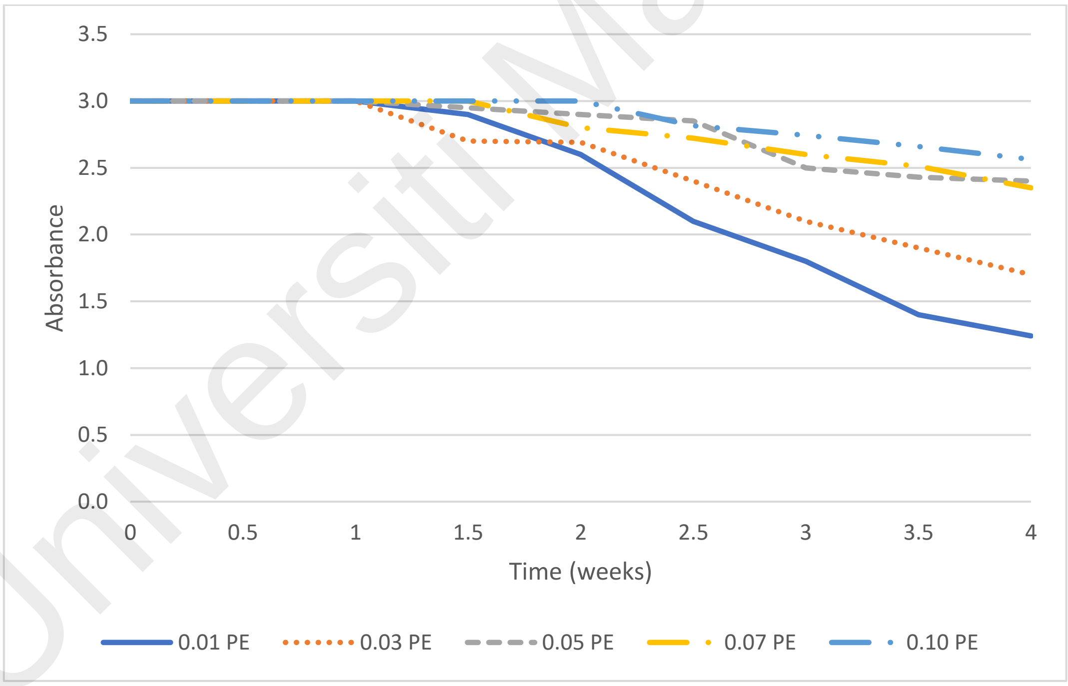


(c)

Figure 4-2: UV-Vis absorbency of (a) NPG, (b) TMP and (c) PE samples for 4 weeks

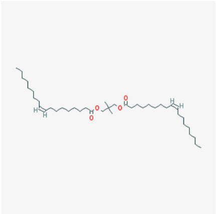
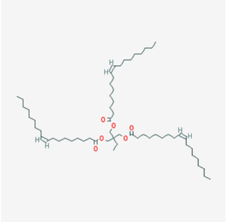
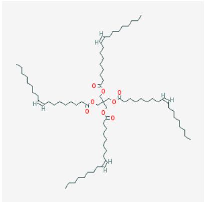
Results from UV-Vis spectroscopy indicate that higher graphene concentration will results in larger absorbance value (better dispersion stability). However, it must be noted that the UV-Vis spectroscopy provides an actual value on the opacity of the lubricant. Since the opacity of the lubricants comes from the graphene dispersed in the lubricant, a higher concentration value can result in higher absorbance value (Tantra, Schulze, & Quincey, 2010). This means that the higher absorbance value exhibited by higher graphene concentration may not be an indication of dispersion stability.

It is noteworthy to discuss on the dispersion stability on various bio-based oil. The polarity of the base oil plays an important part in creating a stable graphene dispersion. Hence it is important to measure the polarity of base oil used in the study. This is important as graphene was reported to exhibit a more stable dispersion in non-polar solvent (H. Wang et al., 2015). In this study, the polarity was calculated using the non-polarity index as proposed by Van der Waal (1985). This tool is able to determine the non-polarity of the polyol ester. The equation used to calculate the non-polarity index is as follows;

$$Non\text{-}polarity\ index = \frac{total\ number\ of\ carbon\ atom \times molecular\ weight}{number\ of\ carboxylic\ group \times 100} \quad (4\text{-}1)$$

From Equation 4-1, it can be seen that the number of oleic acid chain have a more prominent effect to the polarity compared to the number of carboxylic groups. This may be due to the length of oleic acid chain being long ($C_{18}H_{34}O_2$). The increased number of carbon atom will then increase the molecular weight hence the difference in non-polarity index for NPG ester, TMP ester and PE ester. The properties and calculated non-polarity index of the base oils is shown in Table 4-2. The properties were obtained from the chemical structure of the base oils.

Table 4-2: Properties and non-polarity index for all base oil

Properties	**Neopentylglycol Dioleate**	**Trimethyolpropane Trioleate**	**Pentaerythrityl Tetraoleate**
Chemical structure			
Number of carbon atom	41	60	77
Molecular weight	633.055	927.334	1193.959
Number of carboxylic groups	2	3	4
Non-polarity index	**129.77**	**185.51**	**229.00**

The difference in dispersion stability may also be because of the difference in surface energy between the base oil and graphene itself. This means that the surface energy of graphene is more similar to PE ester compared to TMP ester and NPG ester as the more branch structure will exhibit more surface tension (Doll, Moser, & Erhan, 2007). This is important as graphene is known to have higher surface energy (K.-Y. Liang & Yang, 2018).The similar surface energy allows graphene to dispersed more freely while a huge surface energy difference encourage graphene agglomeration hence sedimentation seen in Figure 4-1.

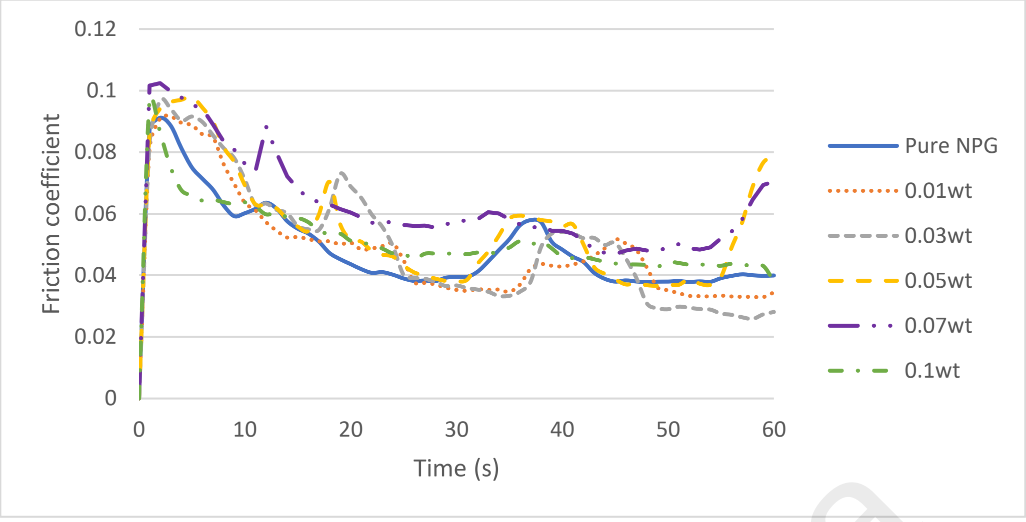
4.3 Wear Preventive Test of Graphene-contained Bio-based Lubricant

Tribological behaviour of the lubricant samples can be analysed by measuring its coefficient of friction and wear scar diameter from fourball tribotester. By using this parameter, the frictional performance and degree of wear can be known.

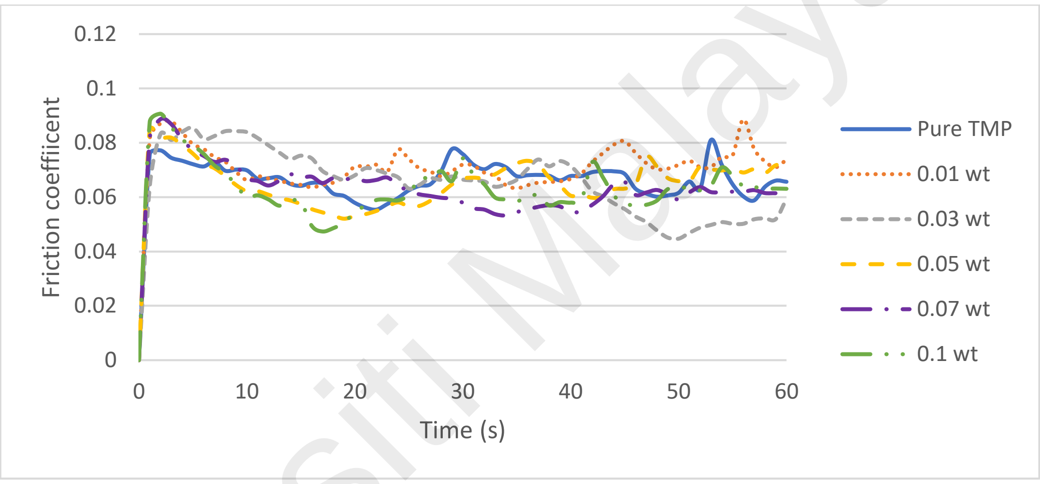
4.3.1 Coefficient of Friction (COF) Analysis

The frictional trend of all sample did not change even after the addition of graphene. All sample started with a high COF running-in period of which it was then decreased until their steady state condition where the frictional trend will not see significant changes. When comparing the base oils with each other, it can be seen that NPG ester exhibited a higher COF during its running-in period and a significantly lower COF during its steady state period. The lower COF during its steady state period resulted in a lower average COF for NPG ester. However, the high friction in its running-in period may not be preferable in short-term application. TMP ester exhibited a more stable trend where the COF during the running-in period was lower and more similar to the COF during its steady state period. For PE ester, the COF during steady state period is similar to TMP ester however, all PE ester sample exhibited a higher COF in running-in period hence resulting in higher average COF.

The difference between the frictional performance between all the base oil may be also be related to their viscosity. A. Z. Syahir et al. (2017) suggested that the lower viscosity oils result in lower internal friction between the liquid hence influences the film forming ability of the oil. Since the presences of additional fatty acid chain of the base oil increases the viscosity, the frictional performance also follows a different pattern of NPG>TMP>PE as seen in Figure 4-3 and Figure 4-4.



(a)



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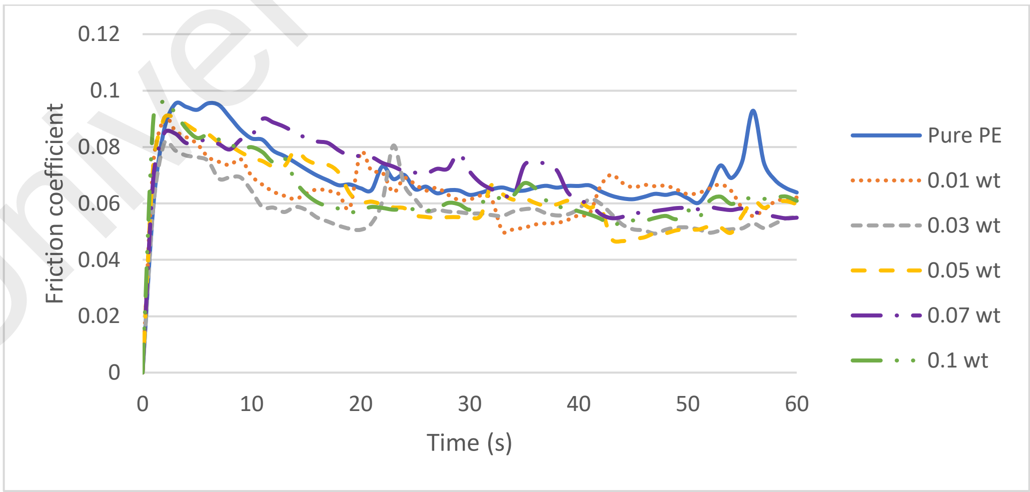


(c)

Figure 4-3: Tribological behaviour of (a) NPG, (b) TMP and (c) PE

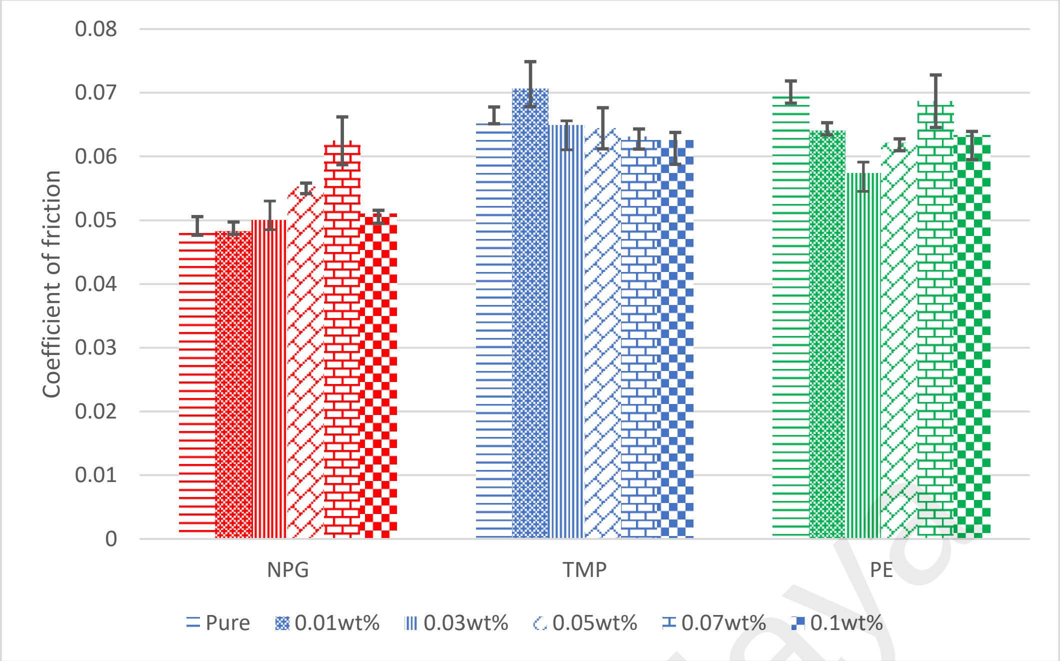


Figure 4-4: Average coefficient of friction of lubricant samples

Based on Figure 4-4, it can be seen that graphene has an effect to the average COF of the bio-ester lubricant. However, the effect that graphene may not be a positive one. NPG ester which has the lowest average COF between the base oil experiences a deterioration in frictional performance after the addition of graphene. Significant changes (increased by 22.7%) in the COF of NPG ester can be seen at 0.07wt.% graphene concentration. The increased in frictional force is similar to the study by Policandriotes and Filip (2011), where the addition of carbon-based nanoadditives increased the COF at low concentration which was attributed to additive instability. Graphene did not give notable changes to the COF of TMP ester with the highest being a 7% increase at 0.01wt.% graphene concentration.

The bio-ester lubricant that exhibited a good frictional performance improvement after the addition of graphene is the PE ester. Out of all the samples, PE ester benefits the most from the using graphene as an additive. The highest improvement can be seen at 0.03wt.% where the COF improves by 15%. Graphene in PE ester produced lower friction whereas graphene increases friction in all NPG samples. This can be inferred that graphene is more compatible with PE ester especially when compared to NPG ester. The improvement in frictional performance is similar to various study. Kinoshita et al. (2014) found that graphene can significantly improve the frictional performance of purified water.

4.3.2 Wear Scar Diameter Analysis

In term of wear, the main wear mode observed for all samples was abrasive wear. The wear scar was observed on the steel ball from the fourball tribotest which explains the round shape of the scar. From Figure 4-5, it is presented that the wear reducing performance of graphene was more prominent when compared to its friction reducing performance. Of all the sample, only 0.03wt.% NPG have shown an increase in wear scar diameter even then the increase is not significant (an increase of 6%). Other sample have seen a positive effect from the addition of graphene. When comparing the performance of each base oil, the wear reducing performance of all bio-based polyol ester were almost similar with the largest difference is between NPG and TMP ester and even then, the difference is less than 10%. This means that the wear reducing performance of all base oil is similar regardless of the chemical structure.

For NPG and TMP ester, the significant wear decrease was seen at 0.07wt.% graphene concentration where graphene was able to reduce the wear scar diameter by ~24% and ~25% respectively. Graphene is able to decrease the friction and wear by forming a layer on top of the contacting surface (Diana Berman, Ali Erdemir, & Anirudha V. Sumant, 2013b). However, the formation of this layer can only be reliable as its dispersion in the base oil. This is due to the fact that the continuous supply of graphene is needed to maintain the film which avoids direct contact between the two contacting surfaces (Mungse & Khatri, 2014).

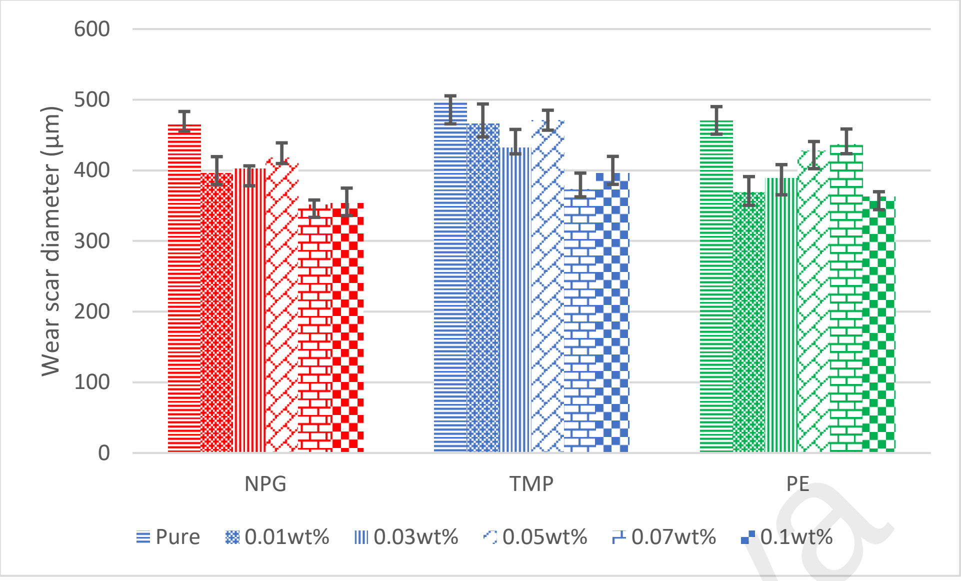


Figure 4-5: Wear scar diameter for lubricant samples

4.4 Effect of Dispersion Stability on the Tribological Behaviour of Bio-based Lubricant

This section focuses on the effect of graphene suspension stability in NPG, TMP and PE esters on their tribological behaviour. This can be achieved by testing the samples again after one month. Since it was seen that different stability can be measured by using different base oil, it is possible to correlate between dispersion stability and tribological behaviour.

4.4.1 Coefficient of Friction (COF) Analysis

After 1 month, the samples containing 0.01wt%, 0.05wt% and 0.1wt% graphene were taken for additional tribological testing. This was done to study the effect of dispersion to the tribological performance of graphene-contained bio-based lubricant. The best and worst graphene dispersion was 0.1wt% PE ester and 0.05wt% NPG ester respectively as shown in Figure 4-1 and Figure 4-2 as stated before, NPG ester exhibited the lowest dispersion stability followed by TMP ester and then PE ester. As can be seen in Figure

4-6, all of the sample with the exception of 0.1wt% PE ester which shows a similar frictional performance (a decrease of 3%). The decrement varies in magnitude with all sample however it can be seen that sample with a lower dispersion stability suffers more when compared to the more stable dispersion. NPG ester deteriorates more at 17%-31% when compared to their frictional performance one month prior. In comparison, TMP only decrease its frictional performance at 10%-15% and PE ester at 5%-10%.

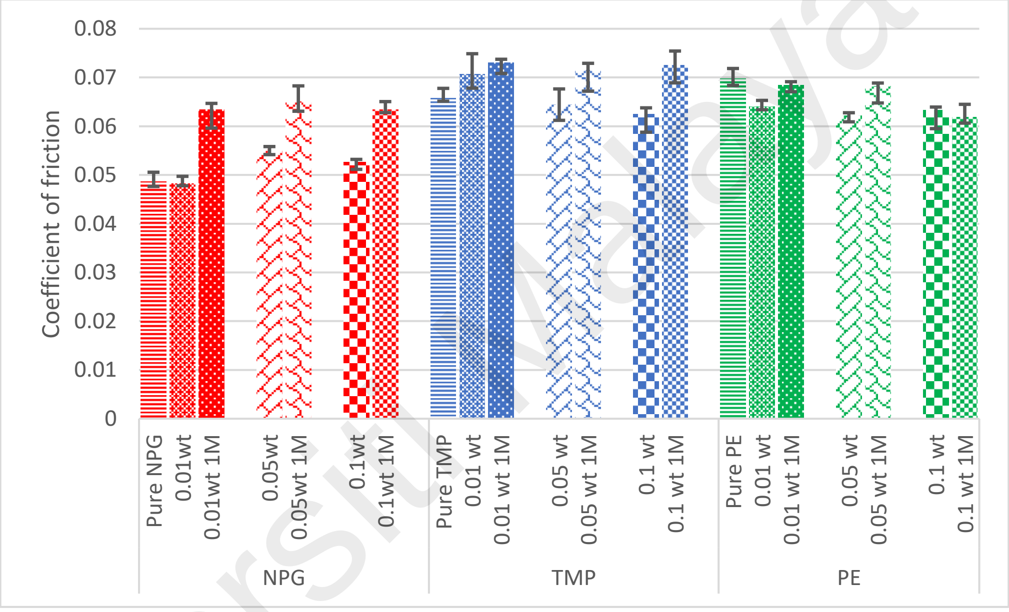


Figure 4-6: Coefficient of friction for Bio-ester lubricant after 1 month

The only sample that fully maintained its tribological properties is 0.1wt% PE ester. In Figure 4-1 and Figure 4-2, it can be seen that this sample was able to retain its dispersion stability in the course of 1 month. This means that the dispersion stability of graphene does affect the tribological properties degradation of the tested samples. In comparison, 0.05wt% PE ester which have one of the better dispersion stabilities, has been able to retain some of its friction reducing properties even after 1 month. The sample was able to reduce the frictional force of PE ester by 2% which is a decrease from its frictional performance 1 month prior by 11%. This means that although the dispersion of graphene is visibly stable, there is still some degradation that occurs during the one-month period. Atif and Inam (2016) suggested that the graphene tends to agglomerate due to their van der Waals force and this agglomeration may decrease the tribological properties of the lubricant (Guo & Zhang, 2016). These researches may explain why the 1-month-old 0.05wt% PE ester exhibited a lower friction reducing performance compare to its fresh counterpart.

Although the addition of graphene has increased the frictional force of NPG ester, the frictional force further increases after leaving it for 1 month. Previously, graphene increases the friction by 15% however after 1 month the friction of NPG ester increases by 35%. The further increase in frictional performance may be a result from agglomeration of graphene inside the NPG ester.

4.4.2 Wear Scar Diameter Analysis

In term of wear, the main wear mode of the contacting surface did not change after 1 month and remains mostly as abrasive wear. However, the wear scar diameter does increase in magnitude in almost all the sample. It can be observed in Figure 4-7 that the increase in wear scar diameter is in conjunction to the frictional trend of the sample after 1 month. It can be seen that all the sample did not increase past the base oil performance. This means that although the protective layer of graphene may not be reliable the protective layer of the base oil still retains its protection.

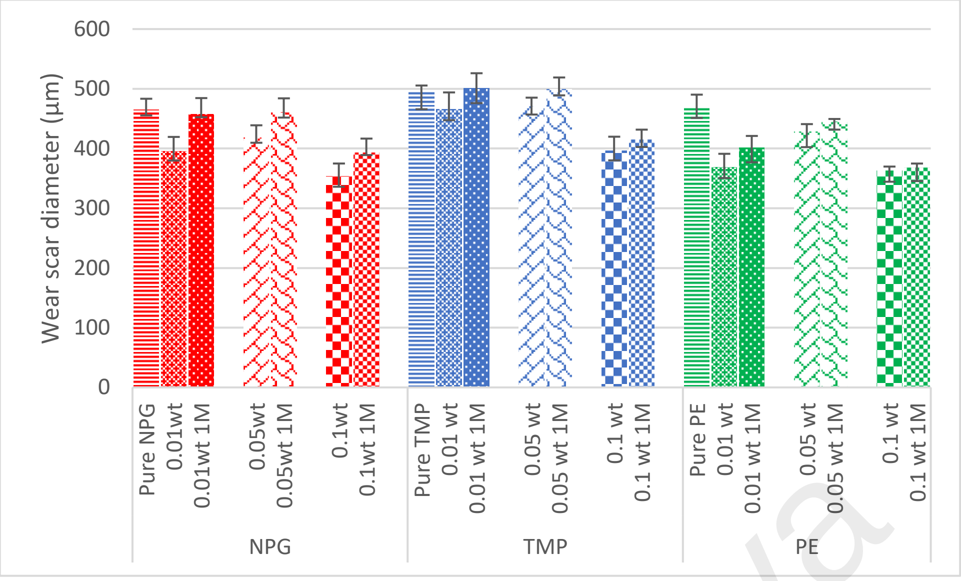
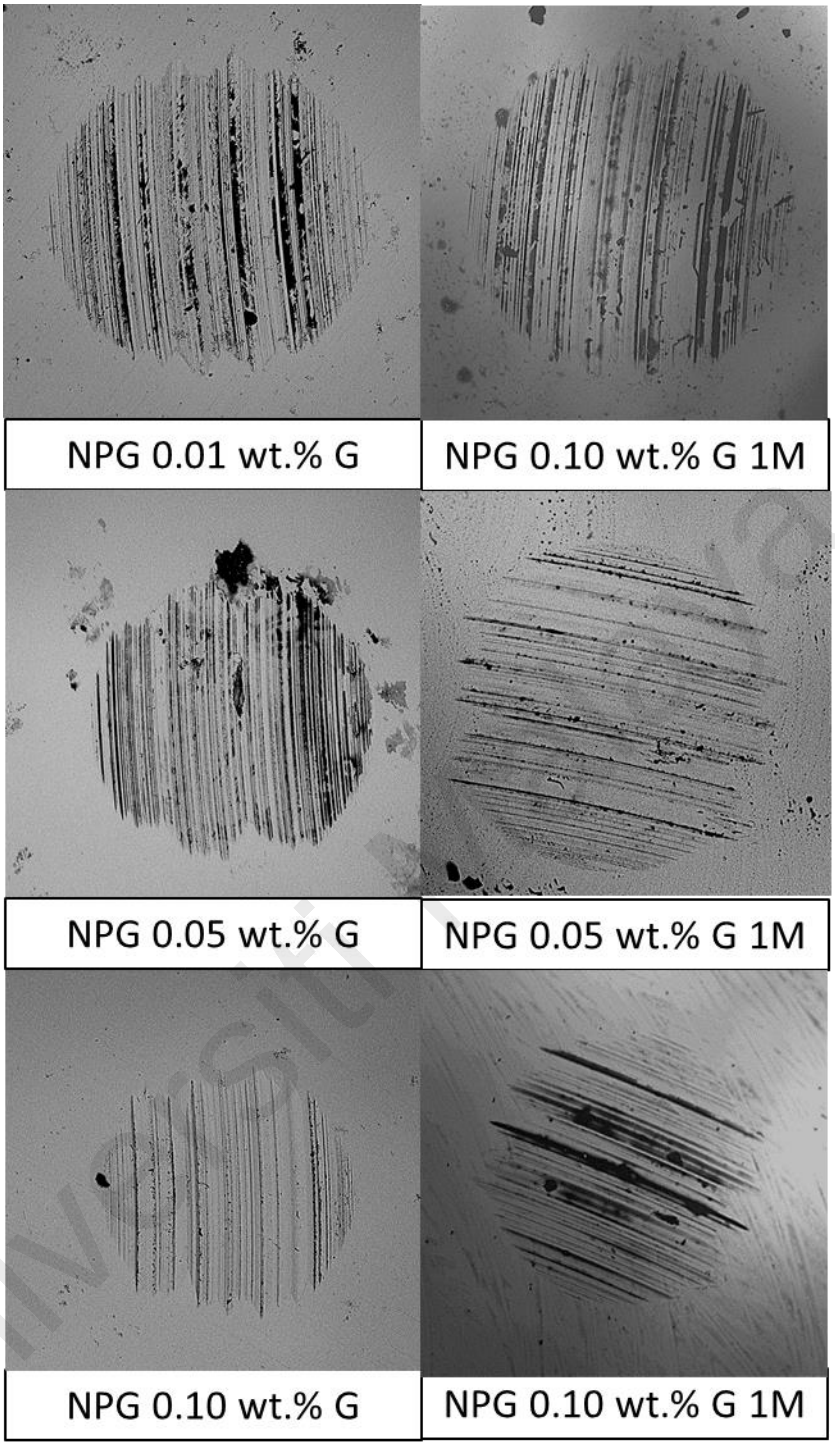


Figure 4-7: the wear scar diameter of NPG and PE ester after 1 month

For NPG ester, the wear reducing performance have a more apparent reduction (10% - 15%) compared to other base oil. The lack of dispersion stability may be the cause of this reduction as the insufficient supply of graphene may hinder the graphene to form a reliable protective layer (Mungse & Khatri, 2014). The insufficient supply might be due to most of the graphene being agglomerated and formed a sedimentation layer as seen in Figure 4-1. This also means that the NPG ester is starved from its additive due to sedimentation. TMP ester samples which have moderate dispersion stability is able to maintain some of its wear reducing properties (5% - 8%). Just like their frictional performance, the PE ester samples retains most of their wear reducing performance. The better dispersion allows a more continuous supply of graphene to the contacting surfaces. Hence allowing a better formation of graphene layer that reduces the contact between bare steel surfaces. Figure 4-8 shows the worn surface of the fourball samples before and after one month.



NPG 0.01 wt.% G

NPG 0.10 wt.% G 1M

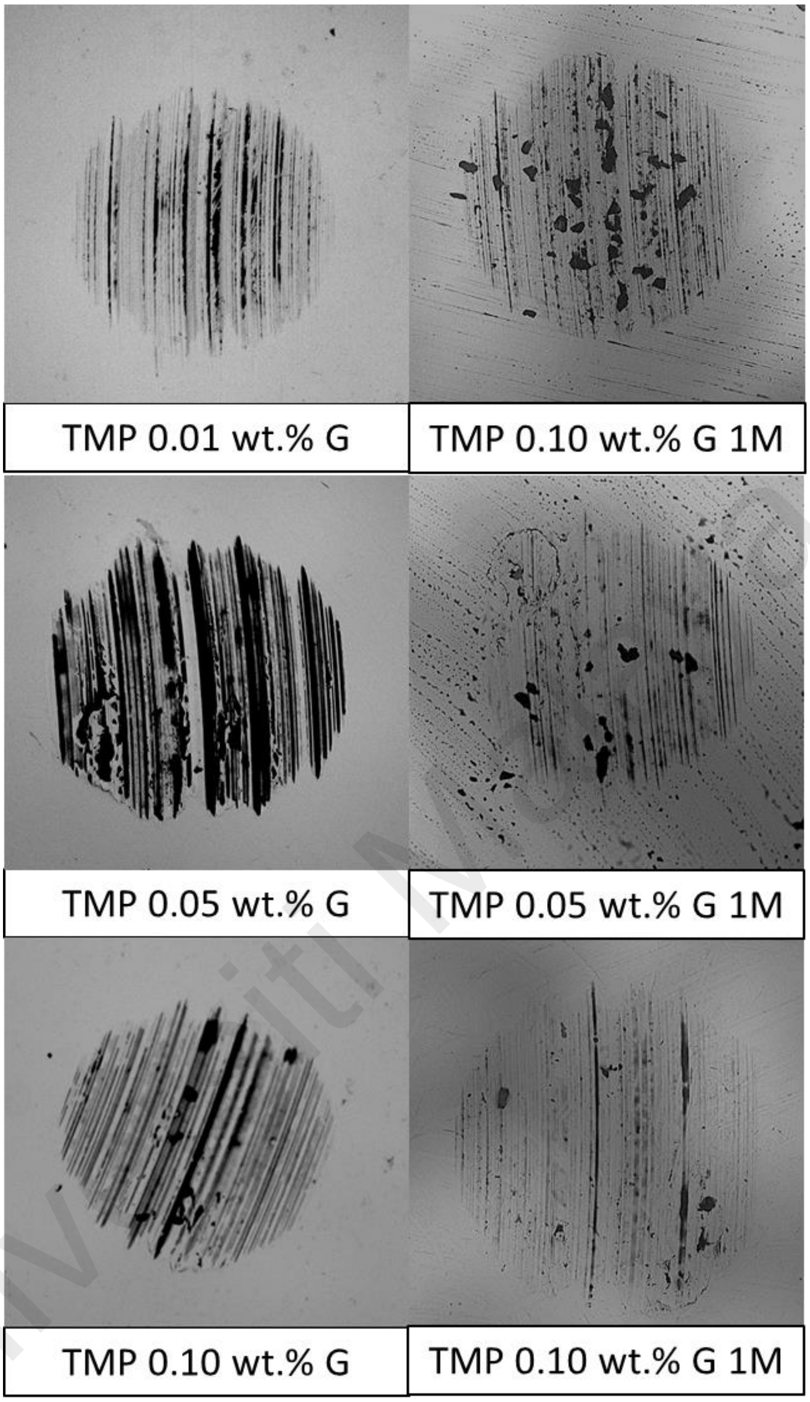
NPG 0.05 wt.% G

NPG 0.05 wt.% G 1M

NPG 0.10 wt.% G

NPG 0.10 wt.% G 1M

(a)



TMP 0.01 wt.% G

TMP 0.10 wt.% G 1M

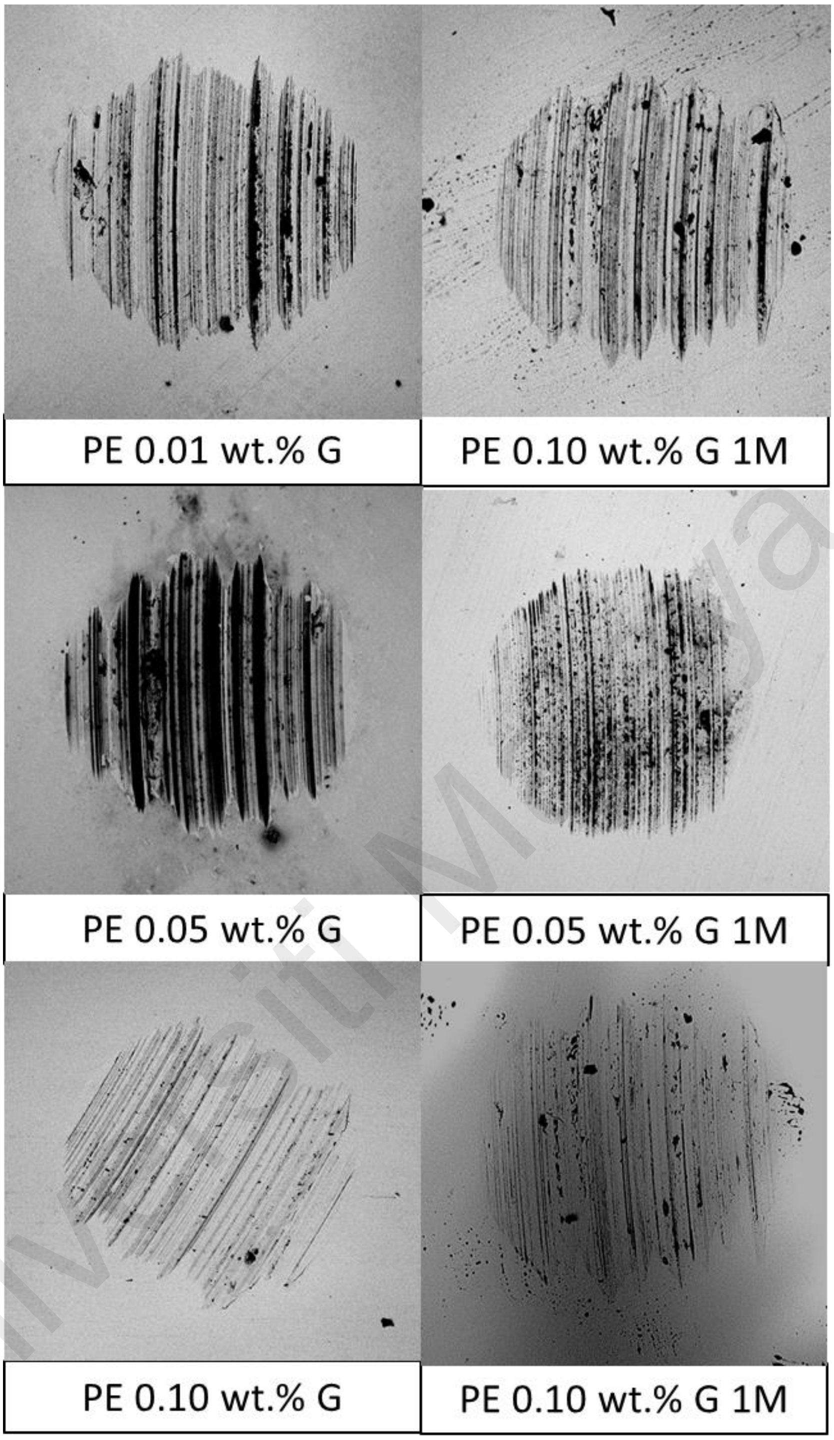
TMP 0.05 wt.% G

TMP 0.05 wt.% G 1M

TMP 0.10 wt.% G

TMP 0.10 wt.% G 1M

(b)



(c)

Figure 4-8: SEM images of worn surface before and after one month

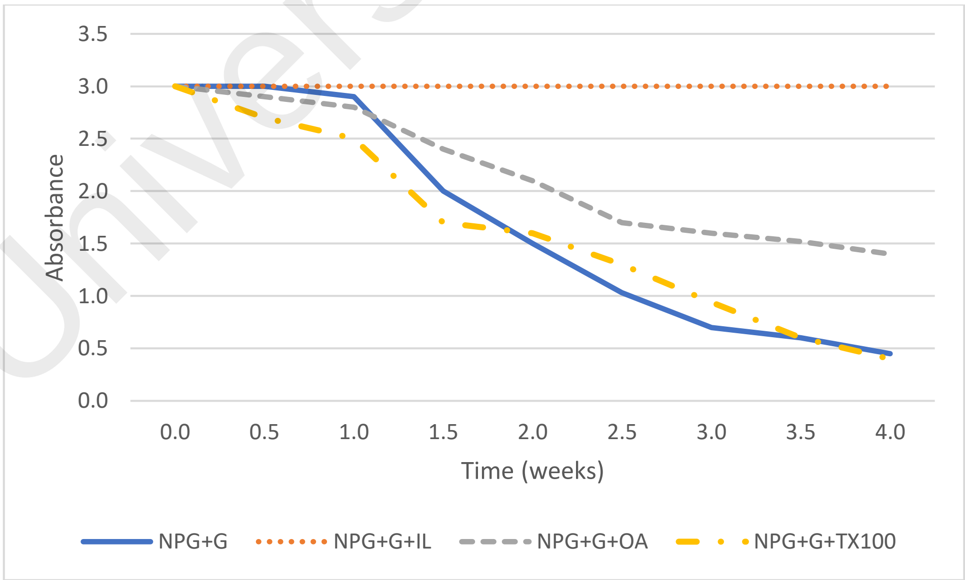
4.5 Effect of Surfactant on the Dispersion Stability and Other Properties of Nanographene Samples

From the tribological testing done in first part of the study, the optimum concentration of graphene for all base oils can be said at both 0.03 wt.% and 0.1 wt.%. However, sedimentation and agglomeration are more prominent in 0.03 wt.% making it easier to study the effect of surfactant on the dispersion stability of graphene. Hence, NPG 0.03, TMP 0.03 and PE 0.03 were selected for further study. The samples were blended with three different surfactants i.e. Triton X-100, oleic acid and ionic liquid.

4.5.1 Dispersion Stability

To study the dispersion stability of surfactant aided graphene, UV-Vis spectroscopy was used to measure the stability of graphene in bio-based lubricant. This was done to accurately measure and compare the performance of utilized surfactants. Figure 4-9

Figure 4-9 shows the dispersion stability of surfactant-aided graphene.



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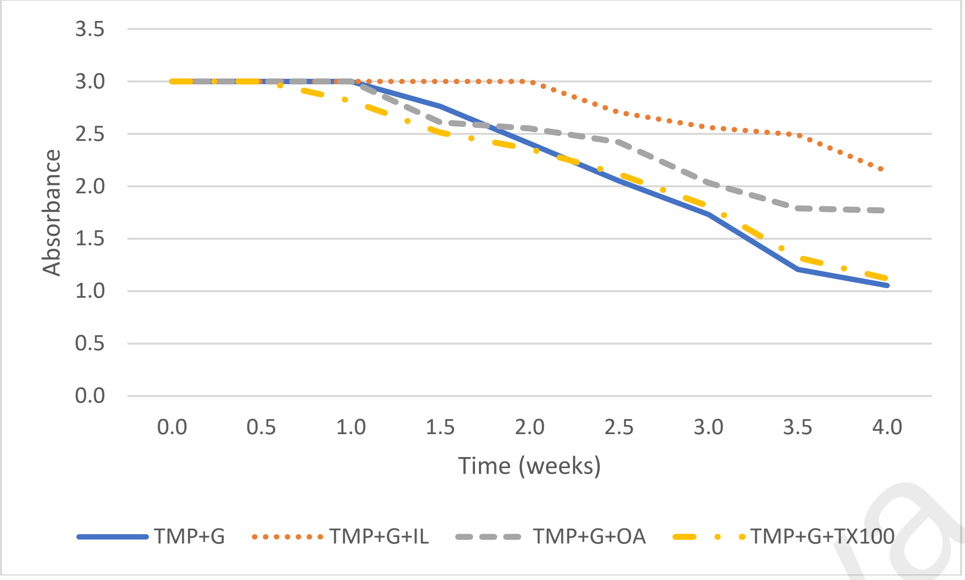

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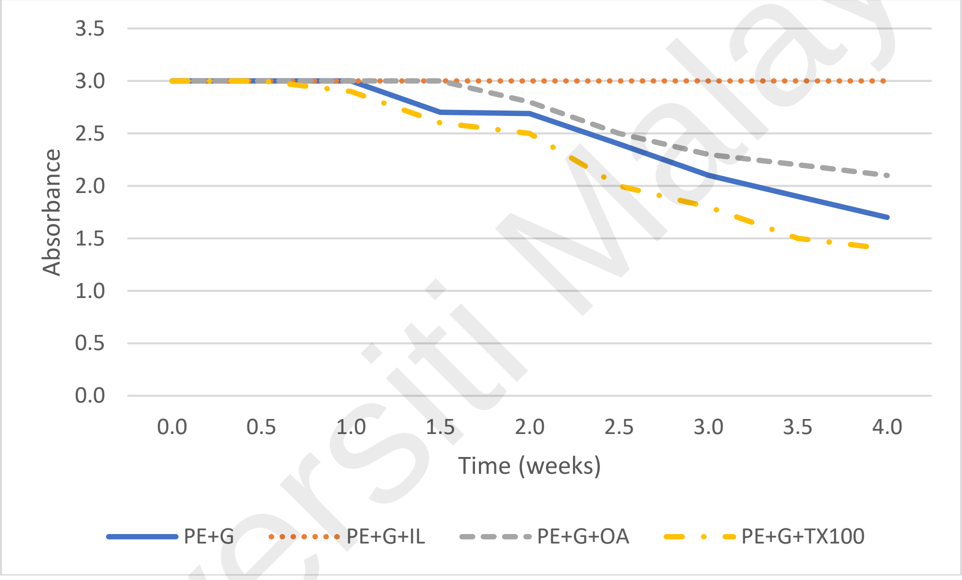

(c)

Figure 4-9: UV-Vis Absorbency of graphene dispersed in (a) NPG, (b) TMP and (c) PE aided by surfactants

From the UV-Vis spectroscopy results, it can be seen that the dispersion stability of graphene was improved by using surfactant as a stabilizing agent. However, it is important to consider the compatibility of the surfactant with both graphene and the base oil. Considering this, the three surfactant is not selected randomly but is selected based on the literature review done. Triton X100 which categorized as non-ionic surfactant is usually used as laboratory detergent. In a study by S. Liang et al. (2016), Triton X100 was used as surfactant for the liquid exfoliation of graphene in deionized water. This results in increased exfoliation rate of graphene due to stabilized graphene dispersion. Further tribological test resulted in more reduction in frictional and wear when using Triton X100 and graphene together. However, the test only considered deionized water as the base oil and not bio-based lubricant.

Gulzar (2017) have achieved significant result by using oleic acid to improve the dispersion stability of CuO and MoS_2 nanoparticle in bio-based oil. He also found that the improved dispersion stability also allows for a better lubrication performance. Ionic liquid was chosen because of the growing interest as using IL as a solvent for graphene exfoliation in liquid. There are also several reports that the utilization of ionic liquid may in fact further improve the tribological performance of lubricants (González et al., 2016; Lhermerout, Diederichs, & Perkin, 2018; Sanes et al., 2017).

As can be seen in Figure 4-9, there is a matter of compatibility when choosing a suitable surfactant for graphene in bio-based oil. It was seen that graphene suspension stability did not significantly changed when using Triton X100 which is a non-ionic surfactant. This can be seen in all Triton X100 samples when compared to samples without surfactant. It was also seen that the samples destabilize earlier (absorbance below 3.00) for all Triton X100 samples. More importantly, PE+G+Triton exhibited lower absorbance value after 1 month which indicates less stable suspension after using Triton X100 as surfactant. Yu and Xie (2012) have discussed that one of the key components in using a surfactant is its selection. Based on the result for Triton X100, it can be concluded that the surfactant is not compatible in using graphene and bio-based polyol ester lubricant.

Moving on, it was found that the usage of anionic surfactant was more suitable to improve the dispersion stability of graphene in bio-based polyol ester. Both anionic surfactants, oleic acid and ionic liquid, exhibited a more stable dispersion compared to the base samples. Samples containing oleic acid have seen a comparable increment while ionic liquid has significantly increased the dispersion stability of graphene particularly in PE+IL and NPG+IL where the dispersion were stable even after 1 month.

It can be seen that the presence of IL increased the stability of graphene dispersion. Ionic liquid can easily disperse graphene and is able to provide a more stable dispersion to the samples. This can be supported by a study by B. Zhang et al. (2010)where graphene oxide is able to form a stable colloidal suspension without the aid of surfactant/dispersant. In this case, ionic liquid improves the graphene dispersion by being the mediator between graphene and the bio-based oil to form a more uniform dispersion. Contrary to the assumed "cation-π" interaction, J. Wang, Chu, and Li (2008) found that the high dielectric constant from the IL can shield the strong "π-π" stacking interaction by the carbon allotrope hence effectively dispersing the nanoparticles. The reduced dispersion stability with respect to time occurred due to the agglomeration of graphene where the nanoparticle lumps together and form a sedimentation layer.

4.5.2 Physical Properties

After the addition of surfactants, the lubricant samples containing graphene did not exhibit major changes in terms of viscosity, viscosity index and density as can be seen in Table 4-3.

Table 4-3: Viscosity and density of lubricant samples with surfactants

Samples	Kinematic viscosity @40ºC	Kinematic viscosity @100ºC	Viscosity Index	Density
NPG	26.086	6.3539	210.8	0.9084
NPG+G	26.217	6.3612	209.7	0.9080
NPG+G+IL	27.568	6.6109	209.9	0.9100
NPG+G+OA	27.036	6.4318	204.6	0.9093
NPG+G+TX100	27.104	6.5221	209.6	0.9123
TMP	48.447	9.648	188.9	0.9196
TMP+G	49.312	9.7751	188.6	0.9198
TMP+G+IL	51.814	9.9973	183.8	0.9200
TMP+G+OA	50.787	9.8337	183.6	0.9205
TMP+G+TX100	50.826	9.9255	186.1	0.9211
PE	63.407	11.855	186.1	0.9295
PE+G	63.216	11.815	185.8	0.9295
PE+G+IL	65.366	11.886	178.9	0.9298
PE+G+OA	64.215	11.855	183.4	0.9299
PE+G+TX100	64.129	11.821	182.9	0.9311

4.5.3 Tribological Behaviour

To ensure the performance of the lubricant samples is maintained after the addition of surfactants, lubricant samples with surfactants were tribologically tested using high frequency reciprocating rig (HFRR). This rig was used to simulate actual working principle of engine oil in piston ring-cylinder wall interaction. The performance of lubricant samples must be measured to identify whether there is incompatibility between the surfactant and the lubricant sample. There also might be a notable synergy between the additives.

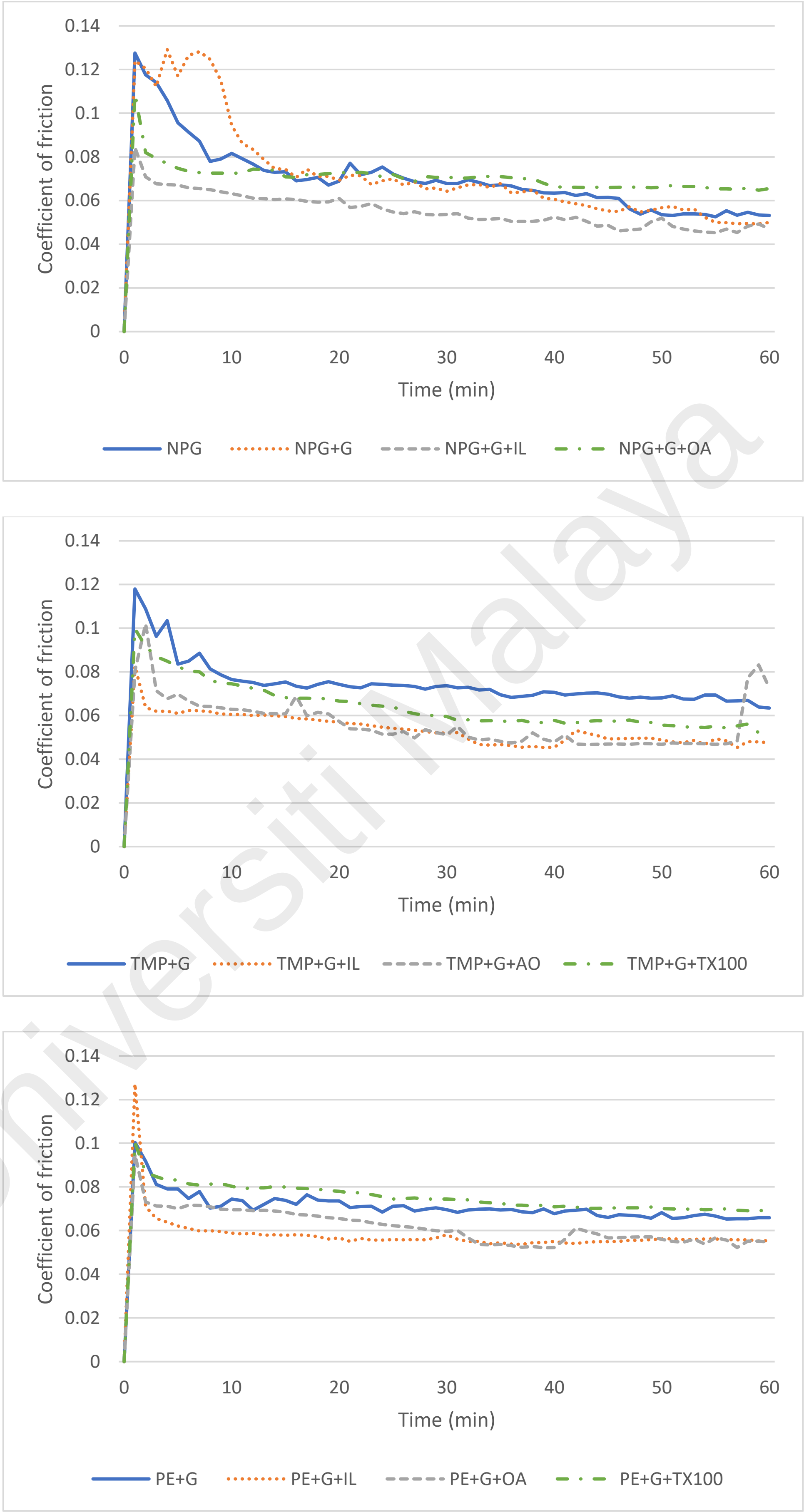

Figure 4-10: Frictional trend of lubricant samples with surfactants

Frictional trend can be explained by analysing the running-in period which is the initial period and the steady-state period where the frictional trend settles down. From Figure 4-10, it can be seen that the surfactant addition affected the frictional performance of lubricants with nanographene.

For NPG base oil, the addition of various surfactant reduced the COF compared to that of NPG+G. Further inspection on the frictional trend during testing showed that NPG+G sample exhibit an extended running-in period compared to other samples. However, this is even out with its relatively low friction during its steady-state period. The addition of the surfactants stabilized and shortened the running-in period of the lubricant samples. However, for NPG+G+OA, the trade-off was the higher friction during steady-state period which resulted in a higher average COF. The higher friction during steady-state period will result in higher frictional energy loss if the sample is used in a machine. Both NPG+G+IL and NPG+G+TX100 exhibited better frictional performance compared to NPG+G sample.

Initially, TMP+G experienced higher COF during the first 8 minutes without the addition of surfactants. After surfactant addition, it can be seen the frictional performance was improved for all samples (TMP+G+TX100> TMP+G+OA > TMP+G+IL). Although both oleic acid and ionic liquid have a similar effect on overall frictional performance, TMP+G+OA exhibited a more erratic frictional trend compared to TMP+G+IL which indicates slip-stick phenomenon occurs during testing. The lower friction was attributed towards the graphene being distribution in a more uniform manner compared to samples without surfactant, where agglomeration will increase the friction during contact (Kim et al., 2012).

For PE ester, PE+G+IL exhibited a higher running-in period COF compared to other samples however it also has the lowest steady state COF compared to other samples. Unlike NPG samples, the effect of Triton X-100 and oleic acid to the frictional performance were reversed in PE sample, meaning that Triton X-100 increases the friction while the oleic acid reduce the friction in the case for PE+G sample. This indicates that there is a matter of compatibility when adding surfactant into lubricant sample as some surfactant maybe incompatible with different base oil (Gao et al., 2019).

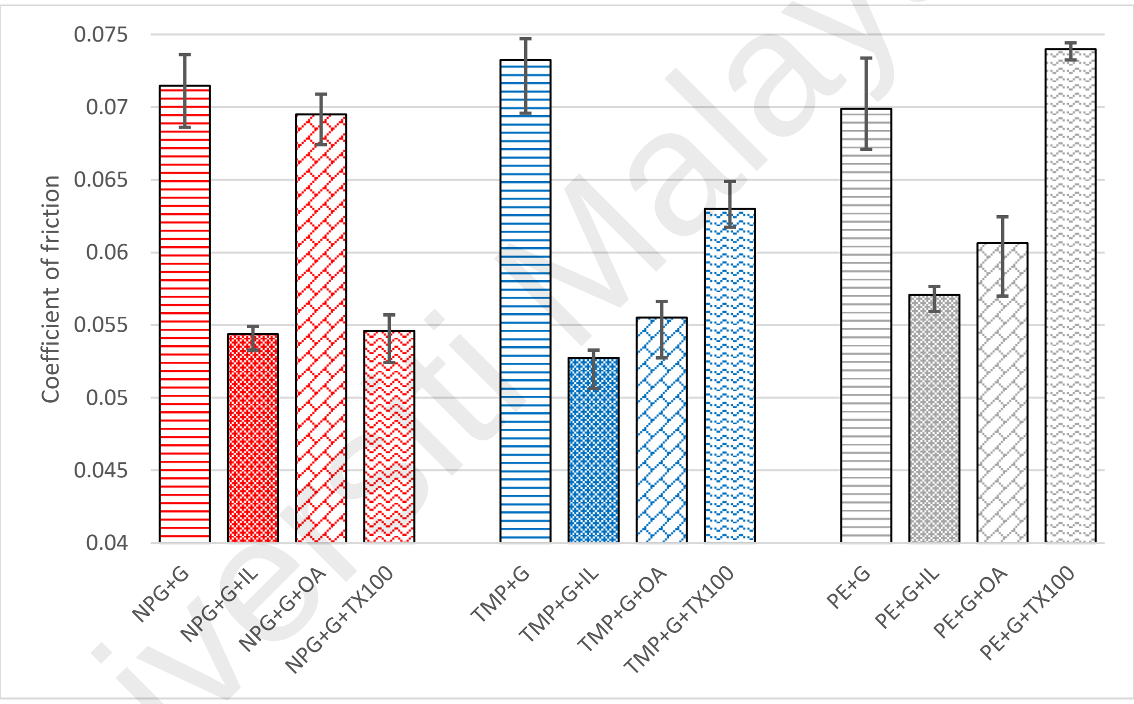

Figure 4-11: Overall friction of lubricant sample with surfactant

In overall, the addition of surfactant was able to reduce the overall frictional performance for all lubricant sample with the exception of PE+G+TX100 as can be seen in Figure 4-11. The exception can be attributed the instability of graphene suspension after Triton X-100 was added as in Figure 4-9, where it can be clearly be seen that the only the combination of PE+G+TX100 was the only sample that was unable to form a stable suspension. This high friction exhibited by PE+G+TX100 can be attributed to the non-uniform graphene distribution within the PE base oil (Kim et al., 2012).

The effect of surfactant on the overall friction of graphene-contained lubricant sample is significant as the COF during steady-state is much lower. In Figure 4-3 and Figure 4-10, it can be seen that graphene does not have a prominent effect during the earlier stages of experiment. This is because under pressure and shear action, graphene enters the contacting area hence forming a deposited layer to protect metal surfaces (Paul, Hirani, Kuila, & Murmu, 2019). Higher suspension stability will lead to the better tribological behaviour due to better supply of graphene into the contacting area (Diana Berman, Ali Erdemir, & Anirudha V Sumant, 2013a). Not only that, the addition of surfactant strengthens the sample's resistance towards agglomeration and sedimentation which in turn provides a more uniform and stronger tribofilm formation (Kim et al., 2012).

From Figure 4-11, it can also be seen that graphene-contained biolubricant achieved a significantly lower overall friction when paired with ionic liquid compared to other samples. This indicates that there is a synergy when graphene is coupled with ionic liquid as additives. It can also be seen that the best dispersion was achieved by using ionic liquid as in Figure 4-9

4.6 Synergy between Graphene and Ionic Liquid as Bio-based Lubricant Additive

From the previous subchapter, it was seen that the combination of graphene and ionic liquid showed the most promising improvements compared to those of other surfactants in terms of both graphene dispersion and tribological behaviour for the all involved bio-based oils. However, a question must be asked on whether such significant improvements come from the incredible performance of ionic liquid alone or if there is a synergy between graphene and ionic liquid that allows further improvement of the tribological performance of biolubricant. To obtain an insight, further experiment using TMP ester as the base oil was conducted to solely focus on the interaction between graphene and ionic liquid. This selection was based on the tribological performance of TMP+G+IL whereby such combination achieved the most friction reduction (by ~27%) when compared to TMP+G. TMP, TMP+G, TMP+IL and TMP+G+IL in term of frictional performance using HFRR.

Figure 4-12 shows the frictional performance of all TMP ester samples. It can be seen that the addition of 1 wt% ionic liquid did have an effect on the tribological performance of TMP ester. However, the improvement was not as significant as TMP+G+IL. This indicates that the combination of graphene and ionic liquid improves more than the cumulative improvement of using graphene and ionic liquid alone. The significant improvement by TMP+G+IL justify the presence of synergistic behaviour between graphene and ionic liquid. To look it more objectively, TMP+G, TMP+IL and TMP+G+IL achieved an overall friction reduction by 7%, 13% and 33% when comparing to TMP ester.

Another important factor to take note of in Figure 4-12 is that the addition of ionic liquid on its own was capable of reducing the tribological performance of TMP base oil. Unlike oleic acid and Triton X-100, ionic liquid is a molten salt which are known to have an outstanding tribological performance. Particularly, the ionic liquid used, trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (or [$P_{14,6,6,6}$] [TMPP]) have a good tribological properties due to the fact that it is halogen-free (A.

Syahir et al., 2020) and it being a phosphonium-phosphate ionic liquid (Zhou, Leonard, Guo, & Qu, 2017).

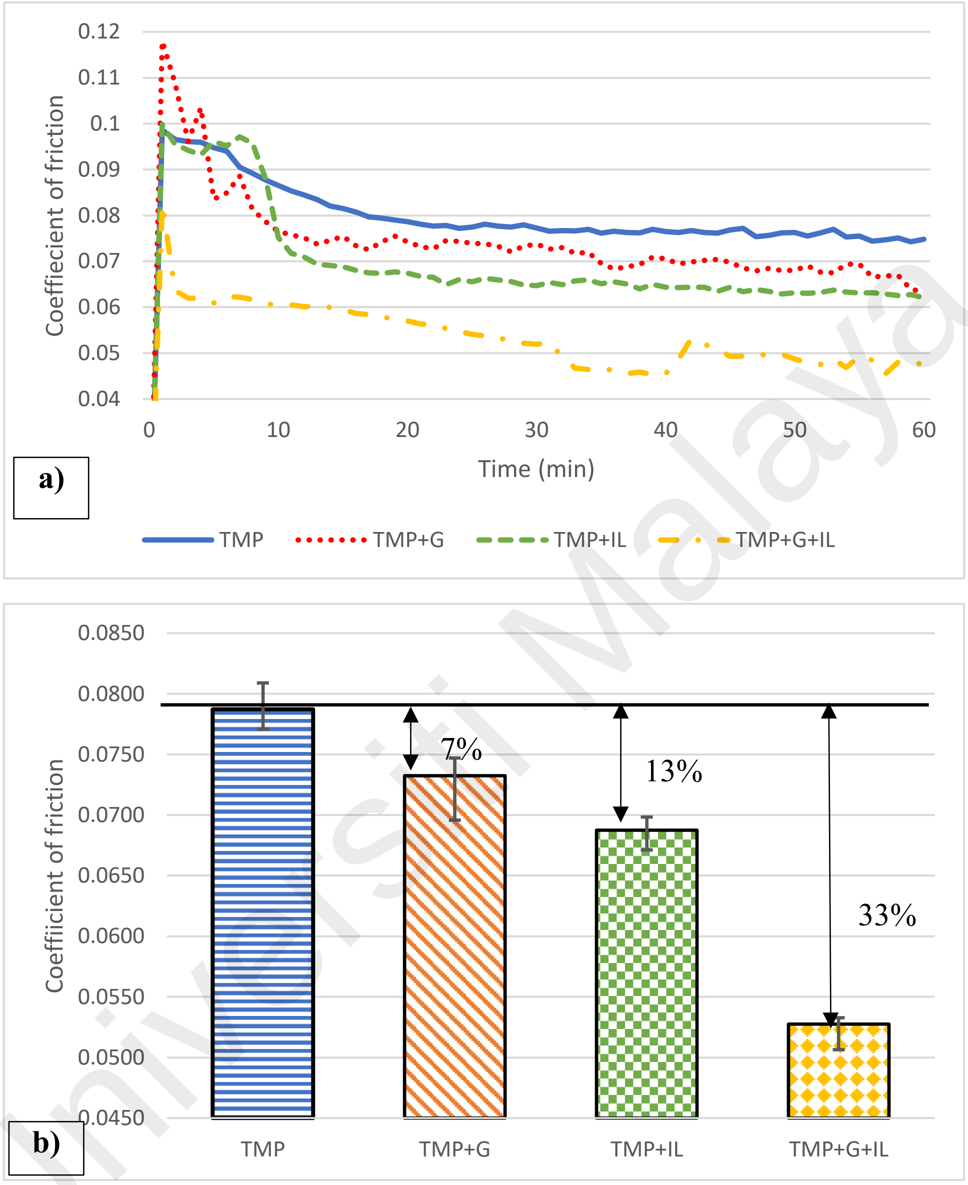

Figure 4-12: Comparison of a) frictional behaviour and b) average COF between TMP samples using HFRR

Ionic liquid is able to reduce the tribological performance of the base oil by helping in the formation of tribofilm during contact. Different from graphene, it has been theorized that the ionic liquid forms its tribolayer in a multi-step tribolayer formation (Zhou et al., 2017). The first step is initiation by direct surface reaction where oxygen from the atmosphere reacts with the ferrous element of the contacting surface will an oxide layer that will help to protect the contacting surface. Next, the process carries on with wear debris generation and breakdown whereby some of the debris from the initial contact were trapped within the contacting area. This wear debris will reduce in size due to the grinding process between contacting surface. Finally, the debris particle will chemically react with reactive element such as oxygen and ionic liquid to form iron oxide and iron phosphate that will improve the tribofilm growth by nucleation.

The synergistic behaviour between ionic liquid and graphene can be clearly seen in its frictional performance from HFRR testing. With such significant improvement compared to other samples, this synergy must be studied further. There are reported synergies between graphene and ionic liquid however it used a halogenic ionic liquid mixed in isoparaffinic oil and fully formulated oil (Sanes et al., 2017). The oil in which the ionic liquid and graphene dispersed in is important as the using different base oil will disturb the synergy between the two lubricant additives. In a study, Qu et al. (2012) have reported the good synergistic behaviour between ionic liquid and ZDDP. This is due to the two-layer tribofilm formation by ZDDP and ionic liquid which consist of a tribo-boundary film with a plastic deformation zone below it. The tribo-boundary film is said to act as an antiwear and anti-scuffing protective layer.

Although the frictional improvement synergy between ionic liquid and graphene was proven, their antiwear performance is still untested. To achieve this, the cast iron samples used in the HFRR testing was observed using Alicona surface profilometer for measuring surface roughness and scanning electron microscope to visualize the scar from the tribotest. This is important as the antiwear performance is crucial to ensure the synergy between the two additives does offer a significant trade-off to another critical lubricant properties.

Cast iron samples lubricated by TMP samples were observed under SEM and the result is shown in Figure 4-13. By just changing the additive composition, four different wear scars with different wear modes were observed. Plain TMP ester was seen to a lot more abrasive scratches compared to other samples. In Figure 4-13, there were four main wear modes detected. The unique characteristic detected for abrasive scratches was the multiple linear thin scar which indicates minor material removal. Delamination was determined by the surface that was seen to be peeled off during the test. The nonlinear scar which can propagate was referred as abrasive cracks. The dark spots particularly in TMP+IL indicates the presence of corrosive attack spots.

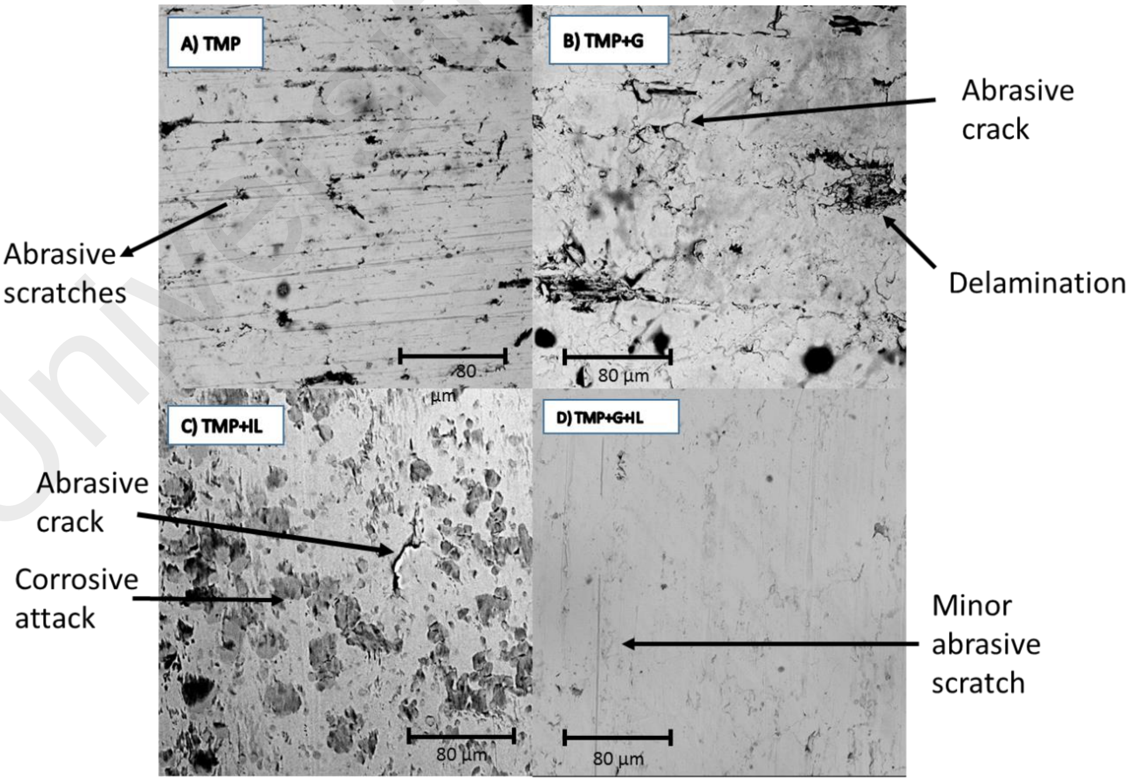

Figure 4-13: SEM images for cast iron sample lubricated by a) TMP, b) TMP+G, c) TMP+IL and d) TMP+G+IL

The addition of graphene in TMP ester reduced the abrasive scratches that were prominent in pure TMP sample. However, the wear mode shifts towards cracking and material removal (delamination). Severe material removal with moderate cracking was observed by graphene additives. This is in coherence with report by Eswaraiah et al. (2011), where they also reported wear mode change to material removal by the addition of graphene in an engine oil. However, the study reported graphene has reduced the wear scar area on the contacting area, indicating graphene can improve wear reducing performance even though the wear mode has changed.

Different from graphene, ionic liquid changed the wear mode to corrosion with minor cracking though both have reduced abrasive scratches present in pure TMP sample. The cracks on ionic liquid sample were not as bad as those of graphene sample, which is an improvement. However, the degree of corrosive wear of TMP+IL was severe. The presence of corrosive attack can be due to ionic liquid being a more reactive substance compared to the inert graphene. The presence of corrosive attack has been noted when using ionic liquid as a lubricant additive particularly in TMP ester (A. Syahir et al., 2020). C. Zhang et al. (2021) attributed the corrosion attack when using ionic liquid due to the tribochemical reactions during operation. This means that the testing condition activates the reaction between ionic liquid and the bare metal surface hence accelerating the corrosion attack on the metal surface. However, the utilization of an optimum ionic liquid concentration can defer the corrosive attack.

The most important thing to take note of is the combination of graphene and ionic liquid resulted in a much smoother surface finishes compared to those of other three samples. The abrasive scratches from the TMP ester are reduced significantly. This indicates that the tribofilm formed by TMP+G+IL was able to withstand the load during the experiment, hence providing better protection for the contacting surfaces. On another note, there was no sign of corrosive attack and delamination in the sample as well. This means that the synergy between the two additives is present. This is due to both additives having different anti-wear mechanisms from one another. Ionic liquid adsorb on to the contacting surface to prevent contact between asperities whereas graphene forms a protective layer on the contacting area (Sanes et al., 2017). Using this logic, the stronger tribofilm due to better film adsorption can reduce the delamination wear whereas the corrosive attack on the material can be prevented by graphene which is an inert material.

Three-dimensional (3D) surface topography for worn cast iron surfaces from HFRR tests are represented in Figure 4-14. During testing, the hydrophilic head (ester) of TMP ester is adsorbed into the metal surfaces creating a tribolayer with its hydrophobic tail (oleate chain) (Ji, Wang, Zhang, & Tan, 2015). This layer provides protection for the contacting surface. Under high loading, the lamellar or two dimensional structure of graphene allows it to form a protective layer which ease the sliding motion between the contacting surfaces (Paul et al., 2019). Meanwhile, ionic liquid is adsorbed onto the metallic surface due to its ionic nature (A. Syahir et al., 2020). All of this mechanism allows ease the operating condition hence lowering the wear of the contacting surface which can be measured by its surface roughness.

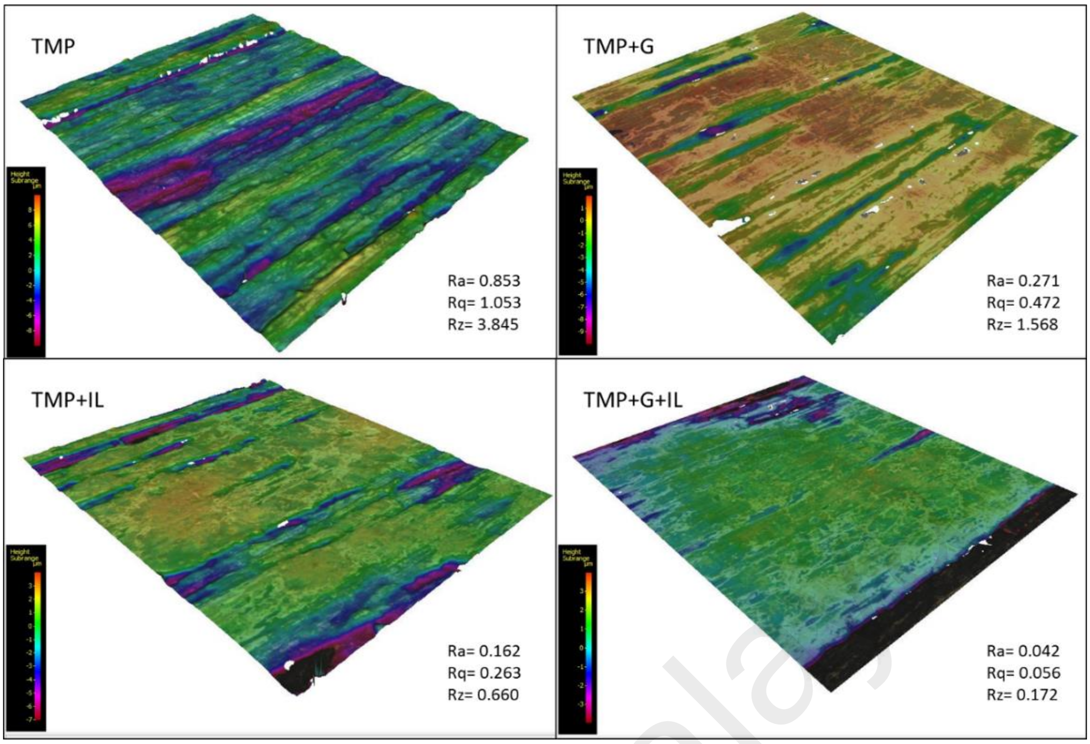

Figure 4-14: 3D topography of worn cast iron surface lubricated with (top left) TMP, (top right) TMP +G, (bottom left) TMP+IL and (bottom right) TMP+G+IL

Comparing to that of TMP ester, the surface roughness of the worn cast iron was significantly reduced by the addition of graphene (Ra = 0.271 µm, Rq = 0.472 µm and Rz = 1.568 µm against Ra = 0.853 µm, Rq = 1.053 µm and Rz = 3.845 µm). This correlates with the frictional performance during the HFRR testing which indicates the successful formation of enhanced tribolayer. Ionic liquid also reduced the surface roughness with a value of Ra = 0.162 µm, Rq = 0.263 µm and Rz = 0.660 µm. It can be noted that the surface roughness of TMP ester with ionic liquid sample has lower surface roughness compared to graphene samples. However, this can be attributed to the different wear modes between the samples. Since the delamination wear was more present in TMP+G sample, the surface roughness was higher due to the material removal creating a larger scar. Meanwhile, the lower surface roughness of TMP+IL sample was more prone to corrosive attacks.

The synergy between ionic liquid and graphene was clearly shown through the resulting surface roughness. When compared to base TMP ester, an almost 95% improvement on the surface roughness can be easily seen by using these two additives (Ra = 0.853 µm, Rq = 1.053 µm and Rz = 3.845 µm against Ra = 0.042 µm, Rq = 0.056 µm and Rz = 0.172 µm). This tremendous improvement can be expected from the frictional performance in Figure 4-12 and the SEM images in Figure 4-13. The significant improvement on the frictional trend indicates a smoother operating condition hence less metal-to-metal contact can be assumed which reduces the wear between the surfaces. At the same time, the smoother wear mark seen in the SEM images indicates a more uniform surface in the wear area hence the significantly lower surface roughness.

With such excellent result in its frictional performance, wear and surface roughness, the synergy between graphene and ionic liquid can be studied further particularly in its tribofilm formation mechanism. By knowing its functionalities during operating condition, a more in-depth knowledge can be obtained. To achieve this, energy dispersive X-ray spectroscopy (EDX) was used to know the element found inside the wear scar and Raman spectroscopy will obtained the binding energy on the worn surface. These two methods will provide an insight on how graphene and ionic liquid synergizes with each other. Only TMP, TMP+G and TMP+G+IL were analysed as this study only focuses on graphene as an additive and how ionic liquid improve the performance of graphene additive.

Table 4-4: EDX spectroscopy on worn cast iron surface lubricated by TMP, TMP+G and TMP+G+IL

Elements	Fe	C	O	P
TMP	89.36	6.32	2.51	-
TMP+G	75.71	15.45	8.83	-
TMP+G+IL	59.99	30.83	9.04	0.15

From the EDX spectroscopy in Table 4-4, it was analysed that there are three prominent elements detected on the worn surface. The most common one was iron (Fe) which is due to the material of cast iron plate. This element can be an indicator of the bare metal surface of the cast iron plate after the tribological test. The detected carbon element can also be attributed to the cast iron composition (usually contains more than 2% of carbon). However, the abundance of carbon element can be due to the lubricated layer by TMP ester which is mostly made up of carbon due to its alkyl chain (C-C chain) and also graphene which is completely made up of carbon. The oxygen represents the oxide layer formation by the lubricant due to its tribochemistry reaction during the testing period.

When comparing between the samples, there were some notable changes in the element composition going from TMP to TMP+G to TMP+G+IL. The first change was in the number of iron element detected by EDX spectroscopy decreases from TMP to TMP+G+IL. This indicates that there was lesser exposed iron surface due to the presence of more additive which also means a more effective protective film is form by TMP+G and TMP+G+IL.

The next change was the presence of carbon element is higher in TMP+G+IL followed by TMP+G. The increase in carbon element was due to the utilization of graphene as an additive. Being completely made up of carbon atom, graphene tribolayer residue from the tribological testing increases the carbon element count. In another perspective, it can be seen that carbon element from the TMP+G+IL sample is much higher than TMP+G sample. This indicates that TMP+G+IL forms a more efficient graphene tribofilm compared to TMP+G due to better dispersibility of graphene in the sample (as can be seen in Figure 4-9) which translates to better graphene circulation to form a more effective tribofilm (Berman et al., 2013a; Mungse et al., 2015). However, the increase of carbon count might be attributed to the ionic liquid adsorbed in the metallic surface (ionic liquid is mostly consist of carbon element).

In term of oxygen element detected on the worn surface, significant improvement can be seen with the addition of additives. However, there was minimal changes between TMP+G and TMP+G+IL which indicate the synergy between graphene and ionic liquid does not have a significant effect on the oxygen element count on the worn surfaces. In a study by Zulkifli et al. (2016), it was proposed that TMP ester forms an oxidation layer on the worn surface which acts as protection from metal-to-metal contact. If the oxygen count comes from the protective mechanism of TMP ester, it can be said that the low count of oxygen on TMP sample was due to the tribolayer is solely dependent on the oxidation layer. This caused the oxidation layer to breakdown faster unlike with the addition of additive whereby graphene and ionic liquid helped the tribolayer allowing more oxygen residue on the worn surface.

The final notable change was the presence of phosphorus element on the worn surface of TMP+G+IL alone. The ionic liquid selected in this experiment consist from a phosphonium cation and phosphate anion in which both contains phosphorus element. It can be noted the phosphorus count was quite low compared to other elements, however it is important nonetheless. This is because of there are only two phosphorus elements in a single structure of the ionic liquid. The presence of phosphorus is important as it signify ionic liquid not only helps in increasing dispersion stability of graphene but it also plays a part in reducing the frictional and wear performance of the lubricant.

Figure 4-15 shows the Raman spectroscopy of the worn cast iron surface. By utilizing the reading of Raman spectrograph, it is possible to understand the lubricating mechanism of the lubricant samples particularly the synergy between graphene and ionic liquid. This technique uses the interaction between the laser light and the molecular vibrations which results in an energy shift. This shift can be used to determine the vibration modes of the substances that resides on the worn surface. Significant peaks from the Raman shift were discussed on how it can be interpreted with the support of EDX analysis done earlier.

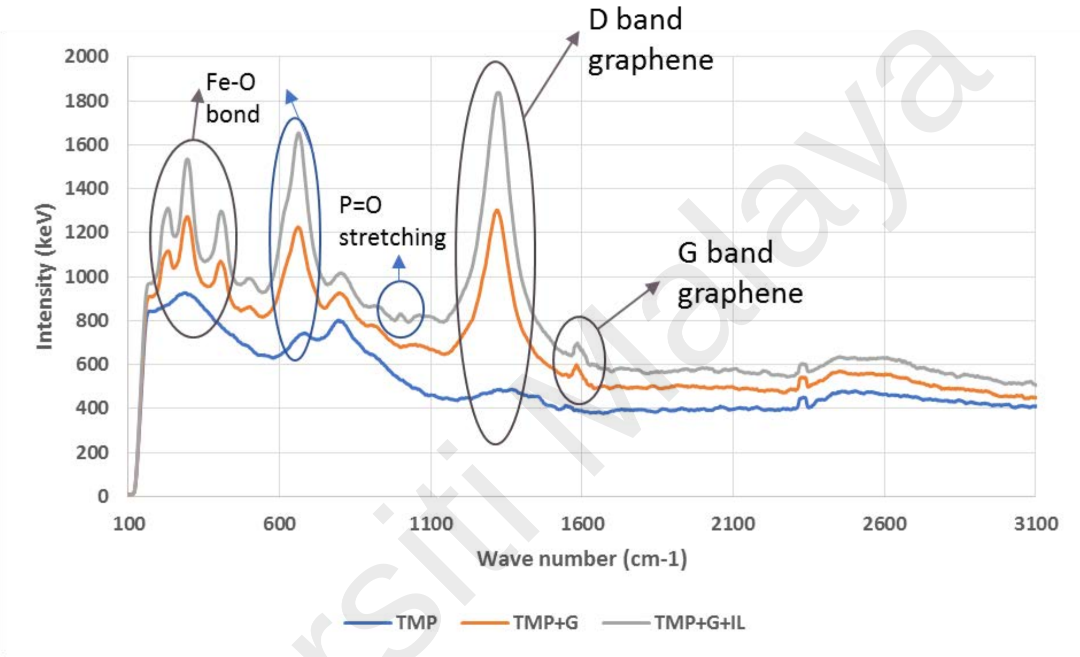

Figure 4-15: Raman spectroscopy on worn cast iron surface lubricated by TMP, TMP+G and TMP+G+IL

When compared with the literature studies, inspection of the Raman spectrograph indicates the presence of Fe_2O_3 (iron (II) oxide) and Fe_3O_4 (iron (III) oxide). This is important as the formation of oxide layer is important for the tribological performance of lubricant and since the base metal is cast iron, iron oxide will represent that oxide layer. There are acceptable consistency for the highest Raman peak at ~667, ~413, ~299 and ~225 cm^{-1} (Shebanova & Lazor, 2003). The Raman reading obtained from the sample particularly in lower wavenumber (100-800 cm^{-1}) emits a similar reading of hematite, a common iron oxide mineral. From this, some vibrational mode of iron oxide can be determined. A_{1g} is indicates the symmetric stretch of oxygen in Fe-O bonds which can be represented by the 667 peak cm^{-1}. E_g and T_{2g} shows both asymmetric and symmetric of oxygen bond respect to iron which are indicated by 413 (E_g), 299 (E_g) and 225 (T_{2g}) cm^{-1} peaks.

When compared between samples, it can be seen the four peaks that represents iron oxide can only be clearly seen in TMP+G and TMP+G+IL whereas only two peaks were present in TMP sample. Since the Raman spectrum indicates the presences of molecular bonds, it can be said the Fe-O is lesser in TMP ester which indicates a lower amount oxide layer residue. As discussed previously, TMP samples solely relies on the formation of oxide layer as the main lubricating mechanism, hence the lower iron oxide layer. This is supported with the lower oxygen element count from the EDX analysis. With additives, other lubricating mechanism were introduced hence the presence of higher amount of iron oxide.

Raman spectroscopy also confirms that the improvement in tribological performance of TMP ester was attributed to graphene entering the contacting surfaces and forming a deposition layer on the cast iron plate. In Figure 4-15, it can be seen that there is a Raman peak on ~1320 cm^{-1} and ~1585 cm^{-1} which represents the D band and G band. Both of these are the characteristic peaks that can be used to identify the presence of graphene. The G band is exhibited by the in-plane vibration of carbon atom which are sp^2 bonded. The D band comes from the out of plane vibration which can be attributed to graphene structural defect. When compared between these two peaks, it can clearly be seen that I_D/I_G ratio is more than one which indicates high structural damage in graphene deposited on the worn cast iron plate. This damage in graphene structure can indicate that the deposited graphene layer acts as sacrificial layer during the testing period to protect the contacting surfaces. It can also be seen that the intensity of D band and G band was higher in TMP+G+IL sample indicating higher amount of graphene deposited on the worn surface. This can be attributed to the higher supply of graphene due to better graphene dispersion. This in result caused an increase in I_D/I_G ratio for TMP+G+IL (~3 compared to ~2 in TMP+G spectra) as more graphene defect meant a better sacrificial layer formation.

There is one peak that is only exhibited in the Raman spectrum of TMP+G+IL at the ~1000 cm^{-1} shift. When compared to literature, a possible explanation is that the peak indicates P=O stretching due to the utilization of phosphonium ionic liquid (Frost, Martens, Williams, & Kloprogge, 2002). Another peak that may arises due to the P=O stretching is at ~946 cm^{-1}. However, both of these peaks were quite low in intensity which indicates low traces of phosphorus-oxygen bond. This is in line with the finding of EDX analysis where low phosphorus count is detected on the worn surface.

From the results obtained, some lubricating mechanism can be deduced particularly when using TMP+G+IL as it contains all of the lubricant sample component. The first important mechanism was the formation of oxide layer due to the tribochemical reaction during the testing period. The higher temperature around the contacting area during the sliding motion promotes the in situ metal oxidation hence forming the oxide layers (Quinn, 1962). This oxidation was further promoted due to TMP ester having hydroxyl group which contains oxygen (A. Syahir et al., 2020)

. The lubricating mechanism can also be deduced. Graphene enters the contact area and forms a deposition layer which protects the sliding surfaces. This deposition layer will sacrifice itself in order to protect the contacting surface. The utilization of ionic liquid as surfactant allows higher dispersion of graphene in the base oil hence allowing a more uniform deposition layer which results in a more effective sacrificial layer. Ionic liquid also plays an important role in easing the friction and wear other than provides uniformity to graphene dispersion. Ionic liquid also formed a protective layer on the worn surface. However, the P=O stretching band in the Raman spectrum indicates that the ionic liquid does not adsorbed on the bare metal surface but it rather bond with the oxygen from the oxidation layer. This will strengthen the oxide layer hence providing a secure protection of the contacting surface from wear.

CHAPTER 5 : CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this study, graphene nanoplatelet was dispersed into three different bio-based polyol esters at various concentration. Samples were observed in order to study dispersion stability in bio-based lubricant for over one month. The lubricant properties of the samples were measured and its tribological behaviour was observed. Based on the results, several conclusions can be made:

1. It was found that the viscosity and density of the bio-based lubricant do not exhibit a significant change after the addition of graphene. Graphene dispersion is stable for the first week after dispersion and sedimentation is seen after one month. The UV-Vis absorbance value increases with increased concentration. The graphene dispersion stability in base oil follows according to this sequence PE>TMP>NPG which also indicates the amount of oleate chain can affect the graphene dispersion.
2. The frictional performance of the bio-based lubricant was affected when graphene was added. It was found that graphene is not compatible with NPG ester as the friction increase significant for most concentration whereas PE ester exhibit decreased friction. Based on the wear result, it can be said that graphene was more prominent as an anti-wear additive compared to friction modifier for polyol esters. After one month, it can be seen that sample with poor dispersion stability experienced a negative effect on the tribological properties of the lubricant. The utilization of graphene was very beneficial towards the tribological performance of bio-based lubricant however its dispersion stability needs to be considered.
3. It was seen that by adding a suitable surfactant, the dispersion stability of graphene in bio-based lubricant can be significantly improved. Triton X-100, a

non-ionic surfactant, did not have significant effect on the dispersion stability of graphene. Anionic surfactant on the other hand, is more suitable to be dispersed along with graphene in bio-based lubricant. Ionic liquid, being a solvent to graphene, is a remarkable surfactant to stabilized graphene suspension as stable dispersion can be seen throughout the observation period. The synergy between graphene and ionic liquid was studied. It was found that ionic liquid does not only significantly stabilize the dispersion of graphene but also plays a role in protecting the contacting surface.

5.2 Recommendations

There are some recommendations that can be made in order to gain a more in-depth knowledge regarding this topic such as;

1. Extensive study needs to be carried out to study the compatibility between a wider selection of commercial surfactant with bio-based lubricant to increase graphene stability in bio-based lubricant.
2. Another route to counter this problem is to implement modification on graphene structure and study the dispersion of modified graphene in bio-based lubricant.
3. Further study on higher graphene concentration is needed to fully observe the performance and dispersion stability of graphene at higher concentration.
4. Other methods to blended graphene and base oil can be considered such as ultrasonic agitation to reduce agglomeration. To fully analyse the agglomeration of graphene, dynamic light scattering can be used to measure dispersion stability.

REFERENCE

Agarwal, A. K. (2007). Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Progress in Energy and Combustion Science, 33*(3), 233-271.

Akbulut, M. (2012). Nanoparticle-Based Lubrication Systems. *Journal of Powder Metallurgy and Mining, 01*(01), 1-3.

Arumugam, S., & Sriram, G. (2014). Synthesis and characterization of rapeseed oil bio-lubricant dispersed with nano copper oxide: Its effect on wear and frictional behavior of piston ring–cylinder liner combination. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology, 228*(11), 1308-1318.

Arwin, G. Z., & Rashmi, G. W. (2013). Tribological Evaluation of Nano Graphene Platelets as an Additive to Biolubricant Base Fluid. *Proceedings of the EURECA 2013*.

Asadauskas, S., Perez, J. M., & Duda, J. L. (1997). Lubrication properties of castor oil - Potential basestock for biodegradable lubricants©. *Lubrication Engineering, 53*(12), 35-40.

Atif, R., & Inam, F. (2016). Reasons and remedies for the agglomeration of multilayered graphene and carbon nanotubes in polymers. *Beilstein journal of nanotechnology, 7*, 1174-1196.

Azman, N., Syahrullail, S., & Rahim, E. (2018). Preparation and dispersion stability of graphite nanoparticles in palm oil. *Jurnal Tribologi, 19*, 132-141.

Azman, S., Zulkifli, N., & Masjuki, H. (2015). *Graphene nanoplatelets in bio-based lubricant.* Paper presented at the Proceedings of Malaysian International Tribology Conference 2015.

Azman, S. S. N., Zulkifli, N. W. M., Masjuki, H., Gulzar, M., & Zahid, R. (2016). Study of tribological properties of lubricating oil blend added with graphene nanoplatelets. *Journal of Materials Research, 31*(13), 1932-1938.

Bartz, W. J. (1998). Lubricants and the environment. *Tribology International, 31*(1), 35-47.

Battez, A. H., González, R., Viesca, J. L., Fernández, J. E., Díaz Fernández, J. M., Machado, A., . . . Riba, J. (2008). *Wear, 256*, 422-428.

Berman, D., Erdemir, A., & Sumant, A. V. (2013a). Few layer graphene to reduce wear and friction on sliding steel surfaces. *Carbon, 54*, 454-459.

Berman, D., Erdemir, A., & Sumant, A. V. (2013b). Reduced wear and friction enabled by graphene layers on sliding steel surfaces in dry nitrogen. *Carbon, 59*, 167-175.

Berman, D., Erdemir, A., & Sumant, A. V. (2014). Graphene: a new emerging lubricant. *Materials Today, 17*(1), 31-42.

Black, M., & Rawlins, J. W. (2009). Thiol–ene UV-curable coatings using vegetable oil macromonomers. *European Polymer Journal, 45*(5), 1433-1441.

Boroojeni, K. G., Amini, M. H., Nejadpak, A., Iyengar, S., Hoseinzadeh, B., & Bak, C. L. (2016). *A theoretical bilevel control scheme for power networks with large-scale penetration of distributed renewable resources.* Paper presented at the Electro Information Technology (EIT), 2016 IEEE International Conference on.

Campanella, A., Rustoy, E., Baldessari, A., & Baltanás, M. A. (2010). Lubricants from chemically modified vegetable oils. *Bioresource Technology, 101*(1), 245-254.

Carr, D. D., & DeGeorge, N. (1989). United States Patent No. 4,826,633. U. S. Patent.

Chauhan, S. R. (2013). Effect of microsize particulates on tribological characteristics of vinylester composites under dry and lubricated conditions. *Materials Science and Engineering, 2*(1), 2-7.

Chen, L., Wang, L., Zeng, Z., & Zhang, J. (2006). Effect of surfactant on the electrodeposition and wear resistance of Ni–Al2O3 composite coatings. *Materials Science and Engineering: A, 434*(1), 319-325.

Chilliard, Y., Ferlay, A., & Doreau, M. (2001). Effect of different types of forages, animal fat or marine oils in cow's diet on milk fat secretion and composition, especially conjugated linoleic acid (CLA) and polyunsaturated fatty acids. *Livestock Production Science, 70*(1), 31-48.

Chou, R., Battez, A. H., Cabello, J. J., Viesca, J. L., Osorio, A., & Sagastume, A. (2010). Tribological behavior of polyalphaolefin with the addition of nickel nanoparticles. *Tribology International, 43*(12), 2327-2332.

Choudhary, S., Mungse, H. P., & Khatri, O. P. (2012). Dispersion of alkylated graphene in organic solvents and its potential for lubrication applications. *Journal of Materials Chemistry, 22*(39), 21032-21039.

Demirbaş, A. (2002). Biodiesel from vegetable oils via transesterification in supercritical methanol. *Energy Conversion and Management, 43*(17), 2349-2356.

Doll, K. M., Moser, B. R., & Erhan, S. Z. (2007). Surface tension studies of alkyl esters and epoxidized alkyl esters relevant to oleochemically based fuel additives. *Energy & Fuels, 21*(5), 3044-3048.

Dou, X., Koltonow, A. R., He, X., Jang, H. D., Wang, Q., Chung, Y.-W., & Huang, J. (2016). Self-dispersed crumpled graphene balls in oil for friction and wear reduction. *Proceedings of the National Academy of Sciences, 113*(6), 1528-1533.

Dresel, W. (2007). *Lubricants and lubrication*: John Wiley & Sons.

Emtsev, K. V., Bostwick, A., Horn, K., Jobst, J., Kellogg, G. L., Ley, L., . . . Seyller, T. (2009). Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide. *Nature Materials, 8*(3), 203-207.

Eswaraiah, V., Sankaranarayanan, V., & Ramaprabhu, S. (2011). Graphene-Based Engine Oil Nanofluids for Tribological Applications. *ACS Applied Materials & Interfaces, 3*(11), 4221-4227.

Fan, X., & Wang, L. (2015). High-performance lubricant additives based on modified graphene oxide by ionic liquids. *Journal of Colloid and Interface Science, 452*, 98-108.

Fan, X., Xia, Y., Wang, L., & Li, W. (2014). Multilayer Graphene as a Lubricating Additive in Bentone Grease. *Tribology Letters, 55*(3), 455-464.

Fandiño, O., Lugo, L., Comuñas, M. J. P., López, E. R., & Fernández, J. (2010). Temperature and pressure dependences of volumetric properties of two poly(propylene glycol) dimethyl ether lubricants. *The Journal of Chemical Thermodynamics, 42*(1), 84-89.

Fertier, L., Koleilat, H., Stemmelen, M., Giani, O., Joly-Duhamel, C., Lapinte, V., & Robin, J.-J. (2013). The use of renewable feedstock in UV-curable materials – A new age for polymers and green chemistry. *Progress in Polymer Science, 38*(6), 932-962.

Frost, R. L., Martens, W., Williams, P. A., & Kloprogge, J. T. (2002). Raman and infrared spectroscopic study of the vivianite-group phosphates vivianite, baricite and bobierrite. *Mineralogical Magazine, 66*(6), 1063-1073.

Fukuhara, M., & Tsubouchi, T. (2003). Naphthenic hydrocarbon oils transmissible for transverse waves. *Chemical Physics Letters, 371*(1), 184-188.

Gao, T., Li, C., Zhang, Y., Yang, M., Jia, D., Jin, T., . . . Li, R. (2019). Dispersing mechanism and tribological performance of vegetable oil-based CNT nanofluids with different surfactants. *Tribology International, 131*, 51-63.

Georgakilas, V., Otyepka, M., Bourlinos, A. B., Chandra, V., Kim, N., Kemp, K. C., . . . Kim, K. S. (2012). Functionalization of graphene: covalent and non-covalent approaches, derivatives and applications. *Chemical reviews, 112*(11), 6156-6214.

Gibson, R. A., Muhlhausler, B., & Makrides, M. (2011). Conversion of linoleic acid and alpha-linolenic acid to long-chain polyunsaturated fatty acids (LCPUFAs), with a focus on pregnancy, lactation and the first 2 years of life. *Maternal & Child Nutrition, 7*(s2), 17-26.

Gnanasekaran, D., & Chavidi, V. P. (2018). Biodegradable, Renewable, and Eco-friendly Vegetable Oil: Lubricants *Vegetable Oil based Bio-lubricants and Transformer Fluids* (pp. 29-47).

González, R., Bartolomé, M., Blanco, D., Viesca, J. L., Fernández-González, A., & Battez, A. H. (2016). Effectiveness of phosphonium cation-based ionic liquids as lubricant additive. *Tribology International, 98*, 82-93.

Gryglewicz, S., Muszyński, M., & Nowicki, J. (2013). Enzymatic synthesis of rapeseed oil-based lubricants. *Industrial Crops and Products, 45*, 25-29.

Gulzar, M. (2017). *Tribological Study of nanoparticles enriched bio-based lubricants for engine piston ring-cylinder interaction.* University Of Malaya, Kuala Lumpur.

Guo, Y.-B., & Zhang, S.-W. (2016). The Tribological Properties of Multi-Layered Graphene as Additives of PAO2 Oil in Steel–Steel Contacts. *Lubricants, 4*(3), 30-42.

Hamid, H. A., Yunus, R., Rashid, U., Choong, T. S. Y., & Al-Muhtaseb, A. a. H. (2012). Synthesis of palm oil-based trimethylolpropane ester as potential biolubricant: Chemical kinetics modeling. *Chemical Engineering Journal, 200-202*, 532-540.

Harding, K. G., Dennis, J. S., von Blottnitz, H., & Harrison, S. T. L. (2007). Environmental analysis of plastic production processes: Comparing petroleum-based polypropylene and polyethylene with biologically-based poly-β-hydroxybutyric acid using life cycle analysis. *Journal of Biotechnology, 130*(1), 57-66.

Harrington, K. J. (1986). Chemical and Physical-Properties of Vegetable Oil Esters and Their Effect on Diesel Fuel Performance. *Biomass, 9*(1), 1-17.

Heidlebaugh, S. J., Domenech, T., Iasella, S. V., & Velankar, S. S. (2014). Aggregation and Separation in Ternary Particle/Oil/Water Systems with Fully Wettable Particles. *Langmuir, 30*(1), 63-74.

Hernandez, Y., Lotya, M., Rickard, D., Bergin, S. D., & Coleman, J. N. (2009). Measurement of multicomponent solubility parameters for graphene facilitates solvent discovery. *Langmuir, 26*(5), 3208-3213.

Hisham, S., Kadirgama, K., Ramasamy, D., Noor, M. M., Amirruddin, A. K., Najafi, G., & Rahman, M. M. (2017). Waste cooking oil blended with the engine oil for reduction of friction and wear on piston skirt. *Fuel, 205*, 247-261.

Huang, H. D., Tu, J. P., Gan, L. P., & Li, C. Z. (2006). An investigation on tribological properties of graphite nanosheets as oil additive. *Wear, 261*(2), 140-144.

Hwang, H.-S., & Erhan, S. Z. (2006). Synthetic lubricant basestocks from epoxidized soybean oil and Guerbet alcohols. *Industrial Crops and Products, 23*(3), 311-317.

Jayadas, N. H., & Nair, K. P. (2006). Coconut oil as base oil for industrial lubricants—evaluation and modification of thermal, oxidative and low temperature properties. *Tribology International, 39*(9), 873-878.

Jayadas, N. H., Prabhakaran Nair, K., & G, A. (2007). Tribological evaluation of coconut oil as an environment-friendly lubricant. *Tribology International, 40*(2), 350-354.

Ji, H., Wang, B., Zhang, X., & Tan, T. (2015). Synthesis of levulinic acid-based polyol ester and its influence on tribological behavior as a potential lubricant. *RSC Advances, 5*(122), 100443-100451.

Johnson, D. W., Dobson, B. P., & Coleman, K. S. (2015). A manufacturing perspective on graphene dispersions. *Current Opinion in Colloid & Interface Science, 20*(5–6), 367-382.

Khan, Z. H., Kermany, A. R., Ochsner, A., & Iacopi, F. (2017). Mechanical and electromechanical properties of graphene and their potential application in MEMS. *Journal of Physics D-Applied Physics, 50*(5), 1 - 24.

Kim, J., Mistry, K., Matsumoto, N., Sista, V., Eryilmaz, O., & Erdemir, A. (2012). Effect of surfactant on tribological performance and tribochemistry of boric acid based colloidal lubricants. *Tribology-Materials, Surfaces & Interfaces, 6*(3), 134-141.

Kinoshita, H., Nishina, Y., Alias, A. A., & Fujii, M. (2014). Tribological properties of monolayer graphene oxide sheets as water-based lubricant additives. *Carbon, 66*, 720-723.

Knothe, G., & Steidley, K. R. (2005). Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components. *Fuel, 84*(9), 1059-1065.

Lawal, S. A., Choudhury, I. A., & Nukman, Y. (2012). Application of vegetable oil-based metalworking fluids in machining ferrous metals—A review. *International Journal of Machine Tools and Manufacture, 52*(1), 1-12.

Lhermerout, R., Diederichs, C., & Perkin, S. (2018). Are Ionic Liquids Good Boundary Lubricants? A Molecular Perspective. *Lubricants, 6*(1), 9-21.

Li, X., Cao, Z., Zhang, Z., & Dang, H. (2006). Surface-modification in situ of nano-SiO2 and its structure and tribological properties. *Applied Surface Science, 252*(22), 7856-7861.

Liang, K.-Y., & Yang, W.-D. (2018). Prediction the concentration of graphite direct exfoliation by liquid solution with solubility parameters map. *AIP Advances, 8*(1), 015018.

Liang, S., Shen, Z., Yi, M., Liu, L., Zhang, X., & Ma, S. (2016). In-situ exfoliated graphene for high-performance water-based lubricants. *Carbon, 96*, 1181-1190.

Lin, J., Wang, L., & Chen, G. (2011). Modification of Graphene Platelets and their Tribological Properties as a Lubricant Additive. *Tribology Letters, 41*(1), 209-215.

Lorenzini, R., Fiselier, K., Biedermann, M., Barbanera, M., Braschi, I., & Grob, K. (2010). Saturated and aromatic mineral oil hydrocarbons from paperboard food packaging: estimation of long-term migration from contents in the paperboard and data on boxes from the market. *Food Additives & Contaminants: Part A, 27*(12), 1765-1774.

M.D. Avilés, N. S., J Sanes, T. Espinosa, F.J. Carrión, M.D. Bermúdez. (2017). *Graphene as a lubricant additive. Effect of the base oil, contact materials and sliding conditions*. Paper presented at the IX Iberian Conference on Tribology, University of Minho, Guimarães, Portugal.

Maleque, M. A., Masjuki, H. H., & Sapuan, S. M. (2003). Vegetable-based biodegradable lubricating oil additives. *Industrial Lubrication and Tribology, 55*(3), 137-143.

Masjuki, H. H., Maleque, M. A., Kubo, A., & Nonaka, T. (1999). Palm oil and mineral oil based lubricants—their tribological and emission performance. *Tribology International, 32*(6), 305-314.

Masson, J. F., Polomark, G. M., Bundalo-Perc, S., & Collins, P. (2006). Melting and glass transitions in paraffinic and naphthenic oils. *Thermochimica Acta, 440*(2), 132-140.

Masudi, A., & Muraza, O. (2018). Vegetable Oil to Biolubricants: Review on Advanced Porous Catalysts. *Energy & Fuels, 32*(10), 10295-10310.

Mekonnen, T., Mussone, P., Khalil, H., & Bressler, D. (2013). Progress in bio-based plastics and plasticizing modifications. *Journal of Materials Chemistry A, 1*(43), 13379-13398.

Mobarak, H. M., Niza Mohamad, E., Masjuki, H. H., Kalam, M. A., Al Mahmud, K. A. H., Habibullah, M., & Ashraful, A. M. (2014). The prospects of biolubricants as alternatives in automotive applications. *Renewable and sustainable energy reviews, 33*, 34-43.

Mohan, V. B., Lau, K.-t., Hui, D., & Bhattacharyya, D. (2018). Graphene-based materials and their composites: A review on production, applications and product limitations. *Composites Part B: Engineering, 142*, 200-220.

Mungse, H. P., & Khatri, O. P. (2014). Chemically functionalized reduced graphene oxide as a novel material for reduction of friction and wear. *The Journal of Physical Chemistry C, 118*(26), 14394-14402.

Mungse, H. P., Kumar, N., & Khatri, O. P. (2015). Synthesis, dispersion and lubrication potential of basal plane functionalized alkylated graphene nanosheets. *RSC Advances, 5*(32), 25565-25571.

Nagendramma, P., & Kaul, S. (2012). Development of ecofriendly/biodegradable lubricants: An overview. *Renewable and sustainable energy reviews, 16*(1), 764-774.

Noorawzi, N., & Samion, S. (2016). Tribological Effects of Vegetable Oil as Alternative Lubricant: A Pin-on-Disk Tribometer and Wear Study. *Tribology Transactions, 59*(5), 831-837.

O'Rourke, D., & Connolly, S. (2003). Just oil? The distribution of environmental and social impacts of oil production and consumption. *Annual Review of Environment and Resources 28*(1), 587-617.

Ota, J., Hait, S., Sastry, M., & Ramakumar, S. (2015). Graphene dispersion in hydrocarbon medium and its application in lubricant technology. *RSC Advances, 5*(66), 53326-53332.

Padgurskas, J., Rukuiza, R., Prosyčevas, I., & Kreivaitis, R. (2013). Tribological properties of lubricant additives of Fe, Cu and Co nanoparticles. *Tribology International, 60*, 224-232.

Paul, G., Hirani, H., Kuila, T., & Murmu, N. C. (2019). Nanolubricants dispersed with graphene and its derivatives: an assessment and review of the tribological performance. *Nanoscale, 11*(8), 3458-3483.

Peña-Parás, L., Taha-Tijerina, J., Garza, L., Maldonado-Cortés, D., Michalczewski, R., & Lapray, C. (2015). Effect of CuO and Al2O3 nanoparticle additives on the tribological behavior of fully formulated oils. *Wear, 332-333*, 1256-1261.

Policandriotes, T., & Filip, P. (2011). Effects of selected nanoadditives on the friction and wear performance of carbon–carbon aircraft brake composites. *Wear, 271*(9-10), 2280-2289.

Qu, J., Bansal, D. G., Yu, B., Howe, J. Y., Luo, H., Dai, S., . . . Mordukhovich, G. (2012). Antiwear performance and mechanism of an oil-miscible ionic liquid as a lubricant additive. *ACS Applied Materials & Interfaces, 4*(2), 997-1002.

Quinn, T. (1962). Role of oxidation in the mild wear of steel. *British Journal of Applied Physics, 13*(1), 33-37.

Randles, S., Singler, R., Hamid, S., Henderson, H., Navarrini, F., Wallfahrer, U., . . . Short, G. (2005). *Synthetics, Mineral Oils, and Bio-Based Lubricants* (1st Edition ed.). Boca Raton.

Saidur, R., Abdelaziz, E., Demirbas, A., Hossain, M., & Mekhilef, S. (2011). A review on biomass as a fuel for boilers. *Renewable and sustainable energy reviews, 15*(5), 2262-2289.

Salimon, J., Salih, N., & Yousif, E. (2010). Biolubricants: raw materials, chemical modifications and environmental benefits. *European journal of lipid science and technology, 112*(5), 519-530.

Salimon, J., Salih, N., & Yousif, E. (2012). Improvement of pour point and oxidative stability of synthetic ester basestocks for biolubricant applications. *Arabian Journal of Chemistry, 5*(2), 193-200.

Sanes, J., Avilés, M.-D., Saurín, N., Espinosa, T., Carrión, F.-J., & Bermúdez, M.-D. (2017). Synergy between graphene and ionic liquid lubricant additives. *Tribology International, 116*, 371-382.

Schneider, M. P. (2006). Plant-oil-based lubricants and hydraulic fluids. *Journal of the Science of Food and Agriculture, 86*(12), 1769-1780.

Schuepfer, D. B., Badaczewski, F., Guerra-Castro, J. M., Hofmann, D. M., Heiliger, C., Smarsly, B., & Klar, P. J. (2020). Assessing the structural properties of graphitic and non-graphitic carbons by Raman spectroscopy. *Carbon, 161*, 359-372.

Senatore, A., D'Agostino, V., Petrone, V., Ciambelli, P., & Sarno, M. (2013). Graphene oxide nanosheets as effective friction modifier for oil lubricant: materials, methods, and tribological results. *ISRN Tribology, 2013*.

Shahnazar, S., Bagheri, S., & Abd Hamid, S. B. (2016). Enhancing lubricant properties by nanoparticle additives. *International Journal of Hydrogen Energy, 41*(4), 3153-3170.

Sharma, A., & Murugan, S. (2017). Durability analysis of a single cylinder DI diesel engine operating with a non-petroleum fuel. *Fuel, 191*, 393-402.

Sharma, B. K., Adhvaryu, A., Liu, Z., & Erhan, S. Z. (2006). Chemical modification of vegetable oils for lubricant applications. *Journal of the American Oil Chemists' Society, 83*(2), 129-136.

Shebanova, O. N., & Lazor, P. (2003). Raman spectroscopic study of magnetite (FeFe2O4): a new assignment for the vibrational spectrum. *Journal of Solid State Chemistry, 174*(2), 424-430.

Shih, C.-J., Lin, S., Strano, M. S., & Blankschtein, D. (2010). Understanding the stabilization of liquid-phase-exfoliated graphene in polar solvents: molecular dynamics simulations and kinetic theory of colloid aggregation. *Journal of the American Chemical Society, 132*(41), 14638-14648.

Singh, A. K. (2011). Castor oil-based lubricant reduces smoke emission in two-stroke engines. *Industrial Crops and Products, 33*(2), 287-295.

Singh, Y. (2015). Tribological behavior as lubricant additive and physiochemical characterization of Jatropha oil blends. *Friction, 3*(4), 320-332.

Song, H.-J., & Li, N. (2011). Frictional behavior of oxide graphene nanosheets as water-base lubricant additive. *Applied Physics, 105*(4), 827-832.

Stephen Sie Kiong, K., Yusup, S., Vui Soon, C., Arpin, T., Samion, S., & Nik Mohamad Kamil, R. (2017). Tribological Investigation of Graphene as Lubricant Additive in Vegetable Oil. *Journal of Physical Science, 28*(Suppl. 1), 257-267.

Sumeet, A. D., & Pavankumar, R. S. (2016). Investigation of the Tribological Properties of Journal Bearing under Wear Test. *International Educational Scientific Research Journal, 2*(9), 61-63.

Sun, J. W. (1998). Changes in energy consumption and energy intensity: A complete decomposition model. *Energy Economics, 20*(1), 85-100.

Syahir, A., Zulkifli, N., Masjuki, H., Kalam, M., Harith, M., Yusoff, M., . . . Jamshaid, M. (2020). Tribological Improvement Using Ionic Liquids as Additives in Synthetic and Bio-Based Lubricants for Steel–Steel Contacts. *Tribology Transactions, 63*(2), 235-250.

Syahir, A. Z., Zulkifli, N. W. M., Masjuki, H. H., Kalam, M. A., Alabdulkarem, A., Gulzar, M., . . . Harith, M. H. (2017). A review on bio-based lubricants and their applications. *Journal of Cleaner Production, 168*, 997-1016.

Tantra, R., Schulze, P., & Quincey, P. (2010). Effect of nanoparticle concentration on zeta-potential measurement results and reproducibility. *Particuology, 8*(3), 279-285.

Ting, C.-C., & Chen, C.-C. (2011). Viscosity and working efficiency analysis of soybean oil based bio-lubricants. *Measurement, 44*(8), 1337-1341.

Van der Waal, G. (1985). The relationship between the chemical structure of ester base fluids and their influence on elastomer seals, and wear characteristics. *Lubrication Science, 1*(4), 280-301.

Wang, H., Lu, S., Zhang, Y., Lan, F., Lu, X., & Xiang, Y. (2015). Pristine graphene dispersion in solvents and its application as a catalyst support: a combined theoretical and experimental study. *Journal of Materials Chemistry A, 3*(12), 6282-6285.

Wang, J., Chu, H., & Li, Y. (2008). Why single-walled carbon nanotubes can be dispersed in imidazolium-based ionic liquids. *ACS nano, 2*(12), 2540-2546.

Wang, Y., Li, Y., Tang, L., Lu, J., & Li, J. (2009). Application of graphene-modified electrode for selective detection of dopamine. *Electrochemistry Communications, 11*(4), 889-892.

Warshel, A., & Levitt, M. (1976). Theoretical studies of enzymic reactions: Dielectric, electrostatic and steric stabilization of the carbonium ion in the reaction of lysozyme. *Journal of Molecular Biology, 103*(2), 227-249.

Yu, W., & Xie, H. (2012). A review on nanofluids: preparation, stability mechanisms, and applications. *Journal of nanomaterials, 2012*, 1.

Yusoff, M., Zulkifli, N., Masum, B., & Masjuki, H. (2015). Feasibility of bioethanol and biobutanol as transportation fuel in spark-ignition engine: a review. *RSC Advances, 5*(121), 100184-100211.

Yusoff, M. N. A. M., Zulkifli, N. W. M., Masum, B. M., & Masjuki, H. H. (2015). Feasibility of bioethanol and biobutanol as transportation fuel in spark-ignition engine: a review. *RSC Advances, 5*(121), 100184-100211.

Zhang, B., Ning, W., Zhang, J., Qiao, X., Zhang, J., He, J., & Liu, C.-Y. (2010). Stable dispersions of reduced graphene oxide in ionic liquids. *Journal of Materials Chemistry, 20*(26), 5401-5403.

Zhang, C., Li, F., Yang, Z., Wang, X., Chen, G., Lu, Z., . . . Cai, M. (2021). Comparing tribology properties of halogen-free ionic liquid, halogen-containing ionic liquid, and PAO 10 lubricants for steel–Al2024 friction contact at room temperature and high temperature. *Journal of Molecular Liquids, 323*, 115041-115061.

Zhang, W., Zhou, M., Zhu, H. W., Tian, Y., Wang, K. L., Wei, J. Q., . . . Wu, D. H. (2011). Tribological properties of oleic acid-modified graphene as lubricant oil additives. *Journal of Physics D-Applied Physics, 44*(20), 205303-205313.

Zheng, D., Cai, Z.-b., Shen, M.-x., Li, Z.-y., & Zhu, M.-h. (2016). Investigation of the tribology behaviour of the graphene nanosheets as oil additives on textured alloy cast iron surface. *Applied Surface Science, 387*, 66-75.

Zhou, Y., Leonard, D. N., Guo, W., & Qu, J. (2017). Understanding tribofilm formation mechanisms in ionic liquid lubrication. *Scientific reports, 7*(1), 1-8.

Zin, V., Barison, S., Agresti, F., Colla, L., Pagura, C., & Fabrizio, M. (2016). Improved tribological and thermal properties of lubricants by graphene based nano-additives. *RSC Advances, 6*(64), 59477-59486.

Zulkifli, N. W. M., Azman, S. S. N., Kalam, M. A., Masjuki, H. H., Yunus, R., & Gulzar, M. (2016). Lubricity of bio-based lubricant derived from different chemically modified fatty acid methyl ester. *Tribology International, 93*, 555-562.

Zulkifli, N. W. M., Kalam, M. A., Masjuki, H. H., Shahabuddin, M., & Yunus, R. (2013). Wear prevention characteristics of a palm oil-based TMP (trimethylolpropane) ester as an engine lubricant. *Energy, 54*, 167-173.

PUBLICATION AND PAPER PRESENTED

Journal Article

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Conference Paper

i. M.H. Harith, N.W.M. Zulkifli, H.H. Masjuki, M.N.A.M. Yusoff, A.Z. Syahir, T. M. Ibrahim, Z.M. Zulfattah, Influence of graphene nanoplatelet on the tribological performance of various bio-based lubricant, Asia International Conference on Tribology, 2018, Sarawak, Malaysia

ii. NWM Zulkifli, M. H. Harith, MNAM Nurun. Synergistic Effect of Ionic Liquid and Graphene on the Lubricant Behaviour Contained in Bio-Based Oil. Paper presented at the International Tribology Conference, 2019, Sendai, Japan.

iii. NWM Zulkifli, MH Harith, HH Masjuki, TM Ibrahim, AZ Syahir, MNAM Yusoff, ZM Zulfattah, and NA Zainal, Dispersion of Graphene in Various Bio-Based Lubricant and Its Effect on Tribological Properties, 2nd International Conference on Tribology, 2018, Istanbul, Turkey.

iv. M.H. Harith, NSM Aishah, N.W.M. Zulkifli, H.H. Masjuki, M.N.A.M. Yusoff, A.Z. Syahir, Z.M. Zulfattah, Tribological behaviour of 2D–2D and 2D–3D nanocomposites in biobased lubricant, Malaysia-Singapore Research Symposium 2019, 2019, National University of Singapore, Singapore