



University of Crete  
Department of Chemistry



Hellenic Mediterranean University  
Department of Electrical &  
Computer Engineering

Diploma Thesis

# **Synthesis of reduced graphene oxide and study of its tribological behavior as an additive in engine oil**

Michael Stella

**Supervisor:** Prof. Athanasios G. Coutsolelos

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## **Abstract**

Since it was first isolated, graphene has attracted enormous interest by the scientists due to its unique optical, electrical and mechanical properties. It is considered the hardest material in nature, due to its special mechanical properties, while at the same time it is very light, weighing only 0.77 mg per square meter.[1] Also, the thermal conductivity of graphene is one of its very important properties, on which this diploma thesis was based and in combination with its excellent tribological properties make it ideal to be used as a lubricant and as an additive in engine oil. It is commonly used in scientific fields, such as supercapacitors, biosensors, photovoltaics, and touch panels. In the present diploma thesis, rGO was used as additive in a commercialized synthetic engine oil (Shell 5W-40). As engine oil, it is an important type of lubricants and coolants, it serves to eliminate friction in moving parts of an engine as well as to cool them. More specifically, samples of different concentration (0.01%w/w, 0.02%w/w, 0.04%w/w, 0.06%w/w, 0.08%w/w, 0.1%w/w and 0.2%w/w) of rGO, SWCNTs, rGO+SWCNTs and MWCNTs dispersions in engine oil (5W-40) were studied. The twenty-five samples were established by turbidimetry method and the tribological behavior of the most favourable ones, was determined through a reciprocating tribometer, using steel ball (100 CR6 or 52100) on special cut steel blocks (Sverker 21-AISI D2) to investigate their wear and friction behavior. The best results obtained, concerned the dispersions of rGO in engine oil with concentrations 0.02%w/w and 0.04%w/w, where the friction data was decreasing. Further experiments were performed for examining the viscosity of rGO, in engine oil, since it gave out the best results during the study of the tribological behavior, under various temperatures and concentrations. The experiments were carried out initially at the temperature 20 oC and then at 80 oC for the concentrations 0%w/w, 0.01%w/w, 0.02%w/w, 0.04%w/w and 0.06%w/w. The results revealed that the viscosity decreases by increasing the temperature and increases by increasing the concentration. The best additive in engine oil which gives out the best results is 0.06% w/w rGO, since viscosity is more similar to the plain oil.

## Περίληψη

Από τότε που απομονώθηκε για πρώτη φορά, το γραφένιο απέσπασε τεράστιο ενδιαφέρον από τους επιστήμονες, λόγω των μοναδικών οπτικών, ηλεκτρικών και μηχανικών του ιδιοτήτων. Παρουσιάζει μηχανικές ιδιότητες, καθώς θεωρείται το πιο σκληρό υλικό στη φύση, ενώ ταυτόχρονα είναι πολύ ελαφρύ, ζυγίζοντας μόνο 0.77 mg ανά τετραγωνικό μέτρο. [1]Επίσης, η θερμική αγωγιμότητα που εμφανίζει το γραφένιο είναι μια από τις πολύ σημαντικές ιδιότητές του, στις οποίες στηρίχτηκε η παρούσα διπλωματική εργασία, η οποία σε συνδυασμό με τις εξαιρετικές τριβολογικές ιδιότητες του, το καθιστούν ιδανικό για τη χρήση του ως λιπαντικό και ως πρόσθετο σε λάδι μηχανής. Βρίσκει εφαρμογές σε διάφορους τομείς, όπως στους υπερπυκνωτές, βιοαισθητήρες, φωτοβολταϊκά και πάνελ αφής. Στην παρούσα διπλωματική εργασία, το rGO χρησιμοποιείται σαν πρόσθετο σε λάδι μηχανής (5W-40). Καθώς το λάδι μηχανής αποτελεί επίσης ένα είδος λιπαντικής και ψυκτικής ουσίας, χρησιμοποιείται για μείωση των τριβών στα κινούμενα μέλη μιας μηχανής, καθώς και για την ψύξη της. Πιο συγκεκριμένα, μελετήθηκαν δείγματα διαφορετικών συγκεντρώσεων (0.01% w/w, 0.02% w/w, 0.04% w/w, 0.06% w/w, 0.08% w/w, 0.1% w/w και 0.2% w/w) των εναιωρημάτων σε λάδι μηχανής των rGO, SWCNTs, rGO+SWCNTs και MWCNTs. Τα εικοσιπέντε δείγματα προσδιορίστηκαν μέσω νεφελομετρίας, καθώς επίσης μελετήθηκε η τριβολογική συμπεριφορά των πιο ιδανικών δειγμάτων, μέσω ενός παλινδρομικού τριβομέτρου, με χαλύβδινη σφαίρα (100 CR6 ή 52100) σε ειδικά τεμάχια χάλυβα κοπής (Sverker 21-AISI D2), για τη διερεύνηση της συμπεριφορά τους ως προς τη φθορά και την τριβή. Τα βέλτιστα αποτελέσματα αφορούσαν τα εναιωρήματα του rGO συγκεντρώσεων 0.02%w/w και 0.04%w/w, όπου τα δεδομένα τριβής ήταν μειωμένα. Περαιτέρω πειράματα έγιναν για εξέταση του ιξώδους των εναιωρημάτων του rGO σε λάδι μηχανής, εφόσον αυτό ήταν που έδωσε τα καλύτερα αποτελέσματα κατά τη μελέτη της τριβολογικής συμπεριφοράς, κάτω από συνθήκες διαφορετικών συγκεντρώσεων και θερμοκρασίας. Τα πειράματα πραγματοποιήθηκαν αρχικά στους 20°C και στη συνέχεια στους 80°C για τις συγκεντρώσεις 0%w/w, 0.01%w/w, 0.02%w/w, 0.04%w/w και 0.06%w/w. Τα αποτελέσματα έδειξαν ότι το ιξώδες μειώνεται με αύξηση της θερμοκρασίας και αυξάνεται με αύξηση της συγκέντρωσης. Ως καλύτερο πρόσθετο σε λάδι μηχανής αποδείχθηκε ότι είναι το 0.06 % w/w rGO σε λάδι μηχανής εφόσον δίνει τις πιο παραπλήσιες τιμές ιξώδους με το καθαρό λάδι.

## Abbreviations

<b>GO</b>	Graphene Oxide
<b>rGO</b>	Reduced Graphene Oxide
<b>SWCNTs</b>	Single Walled Carbon Nanotubes
<b>MWCNTs</b>	Multi Walled Carbon Nanotubes
<b>VC</b>	Vitamin C (Ascorbic Acid)
<b>AcOH</b>	Acetic Acid
<b>HI</b>	Hydroiodic Acid
<b>H<sub>2</sub>SO<sub>4</sub></b>	Sulphuric Acid
<b>NaNO<sub>3</sub></b>	Sodium nitrate
<b>HNO<sub>3</sub></b>	Nitric Acid
<b>KMNO<sub>4</sub></b>	Potassium permanganate
<b>NaHCO<sub>3</sub></b>	Sodium Bicarbonate
<b>DI H<sub>2</sub>O</b>	Deionized Water
<b>H<sub>2</sub>O<sub>2</sub></b>	Hydrogen peroxide

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## Chapter 1: Introduction - Lubricants

### 1.1 Lubricants

Lubricants are chemical substances, used to lower wear and friction between surfaces in contact. As a result, the heat produced during their movement is also reduced. Consequently, lubricants are also used as coolants. [2]

Lubricants have not only industrial applications, but they are also used for other purposes, such as cooking and bio-applications. [2] They are mostly used in machines and in vehicles.

They are divided in two categories:

- Monotype lubricants, which refer to the ones with simple liquidity and concern old-technology vehicles.
- Polytype lubricants, which refer to the ones with multi-liquidity and concern new technology vehicles.

Polytype lubricants are subdivided in three main categories: [2]

- Semi-synthetic lubricants
- Synthetic lubricants
- Mineral based lubricants

Mineral based lubricants, or in other words mineral oils, are produced from crude oil, which has undergone some refining processes.

Synthetic lubricants occur during the chemical treatment of some of the ingredients of the mineral oils and they are known as the best lubricants nowadays. For their production the following are used [3]:

- Esters
- Synthetic hydrocarbons, polyolefins, produced from ethylene, taken from the crude oil.

Semi-synthetic lubricants are produced by mixing mineral oils and synthetic lubricants with a ratio of 70-80% and 20-30% respectively.

Comparing synthetic lubricants and mineral oils, synthetic lubricants are more expensive, although their quality is much better, providing great protection to engine parts.

## 1.2 Properties of lubricants

The properties of lubricants are assessed by various laboratory tests, reported in the publications of the American Society for Testing and Materials (ASTM) and the Institute of Petroleum (IP). They are standard methods, easily modified and internationally accepted. Most of their properties are analytically explained below. [4]

### 1.2.1 Lubricating ability

It is a complex property associated with the lubricant's ability to create and maintain a continuous lubrication/protection interfacial membrane, between two surfaces. This property is the one that reduces friction and consequently engine's wear.

#### 1.2.1.1 Viscosity

Viscosity is a physical quantity that characterizes the internal friction of a fluid and shows resistance, that the fluid presents, during its flow. Higher viscosity corresponds to higher fluid resistance (e.g. mineral oil), while low viscosity results in low resistance (e.g. gasoline). The units of the viscosity are shown in Table 1:

Quantity	International System (SI)	CGS System
Dynamic viscosity $\eta$	$N*s/m^2=Pa*s$	$gr*cm/s=P(\text{poise})$
Kinematic viscosity $\nu$	$m^2/s$	$cm^2/s=St (\text{stokes})$
Density $\rho$	$Kg/m^3=(Ns^2/m)/m^3=N*s^2/m^4$	$gr/cm^3$

Table 1: Viscosity Units

### Viscosity and temperature

The viscosity depends on temperature variations. So, we can't refer to viscosity without mentioning its determination temperature. As the temperature of an oil increases, its viscosity decreases, and the oil becomes thinner. By lowering its temperature, the viscosity increases, and the oil becomes more viscous.

### Viscosity and pressure

When increased pressure is applied to an oil, viscosity also increases. Under the influence of very high pressure, the oil solidifies.

### **1.2.1.2 Viscosity Index (VI)**

The Viscosity Index of an oil is a number without units, indicating the oil's resistance to viscosity change during temperature variations. The smaller this number is, the easier it is to change the oil's fluidity, while changing the temperature. The higher VI is, the more stable the oil is while changing the temperature. In this case, the oil resists becoming more viscous at low temperatures and thinner at high temperatures.

### **1.2.2 The cooling ability**

It is the property of the lubricant to remove heat from friction points of metal parts and to act as a deterrent towards temperature increase. The cooling capacity of a lubricant is a function of its specific heat and its thermal conductivity.[4]

### **1.2.3 Chemical Stability**

It is the property of the lubricant to resist to its deterioration by the atmospheric air, water and metals, that gets in contact with. Deterioration of the lubricant implies the appearance of mud and tar components, while due to its oxidation it acquires corrosive properties. [4]

#### **1.2.3.1 Oxidation Resistance**

Oils' oxidation occurs during operation, due to high temperatures and the presence of air. Oxidation occurs when spraying devices are used for lubrication or when metal particles exist. The degree of oils' oxidation varies, since it is influenced depending on the operating conditions.

The synthetic lubricants show excellent resistance to oxidation and have greater lifespan than mineral oils.

The operating temperature of mineral oils must be around 50-70 °C. With a single increase of 10 °C, the oxidation rate is doubled, and the life of the oil is reduced by half. Synthetic lubricants have much longer life because they exhibit higher oxidation resistance. Their operating temperature is 90-140 °C. This is the reason that synthetic lubricants are most commonly used. [5]

#### **1.2.3.2 Antiperspirant property**

It is the property that enables oil not to form foam, something that causes the following unpleasant phenomena:

- It affects the operation of the oil pump (risk of cavitation).
- Errors occur while measuring the oil level in the tank.

- The amount of oil that reaches the lubrication points is less than the required one.
- The lubricating membrane between friction surfaces becomes compressed and destroyed, since the foam includes air.

### **1.2.3.3 Anti-Corruption Protection**

Oxidation of iron surfaces is a chemical reaction, that begins during the exposure to air or moisture. In order the oils to form a protective layer, they have to exhibit a good adhesion to the rubbed metallic surfaces.

#### **Colour:**

The term colour means the colour we see, when we place a bottle of oil in the passing light, between the light source and our eyes. Colour may varies, depending on the origin of the oil, but should not affect the oil's quality or behavior at all. However, it has an effect on consumers, who usually prefer light colours. During oil's operation, its colour becomes darker. This means that the oil has been oxidized, contaminated or finally mixed with another darker oil. [5]

### **1.2.3.4 Corrosive behavior**

The meaning of this term is the complete absence or avoidance of corrosive substances, which could contaminate metal surfaces, which the lubricant comes into contact with. In addition, the mission of the lubricant is to protect the lubricated metal surfaces from corrosion.

### **1.2.4 Thermal Stability**

It is the property that enables oil to resist against its decomposition when exposed to high temperatures. A material is considered as thermally stable when it does not decompose under the influence of temperature.

### **1.2.5 Acidity-Alkalinity**

- TAN acidity (Total Acid Number) is the number of milligrams of KOH required to neutralize 1 g of acidic oil. In other words, it is the number that explains the state of the oil in relation to the acids contained in it. Acids exist due to the products of engine combustion or the oxidation of oil.
- TBN alkalinity (Total Base Number) is the number of milligrams of KOH required to neutralize 1 g of alkaline oil. In other words, it is the number that shows the effectiveness of additives, contained in an oil. When TBN number is lower than the

normal one, then the additives have been consumed to treat the oxidation products and so the oil does not properly protect the machine's metals. As a result, TBN number decreases upon the use of oil.

- Normal values for unused oils are: TAN <0.05 mg KOH / g, TBN = 6/18 mg KOH / g for vehicle oils, TBN = 20/70 mg KOH / g for shipping oils.

### 1.2.6 Demulsification number

The presence of water in the oil creates an emulsion that erodes the lubricated surfaces. This phenomenon is observed during the lubrication of steam engines, steam turbines, bearings on steel mills or paper mills and generally in any case the oil may come in contact with water. Therefore, in all these applications, the oil must be able to be demulsified, in other words, to easily and quickly be separated from water in the lubrication circuit.

### 1.2.7 Ashes

The ash is created from the metal elements present in the additives and from the residues (oxides, dust, metal fragments) created by the use of oils.

### 1.2.8 Specific Weight

An amount of oil can be measured by volume or weight, so it's important to know its density.

However, a term called "specific weight" is often used. The specific weight of an oil is defined as the ratio of the weight of a given volume of oil (at a certain temperature) divided by the weight of an equal volume of distilled water (at the same temperature), as explained in the equation below:

$$\text{specific weight} = \frac{W_{oil} (T_i)}{W_{DH_2O} (T_i)}$$

Where:

- $W_{oil} (T_i)$  is the weight of a specific volume of oil at a temperature of  $T_i$  and
- $W_{DH_2O} (T_i)$  is the weight of equal volume of distilled water at a temperature of  $T_i$

The specific weight of oils usually ranges between 0.84 kg/L and 0.98 kg/L. Since specific weight changes upon temperature changes, the instant measurement temperature is vital.

### **1.2.9 Ignition Point - Combustion Point - Self-ignition Point:**

- The ignition point is the lowest temperature at which a heated oil at a certain heating rate produces vapors that can instantly ignite in the presence of a flame. Paraffin oils have a higher ignition point than naphthenic oils. The volatile components (e.g. traces of gasoline) contained in an oil reduce the ignition point, even when they exist in very small proportion. In terms of safety, the ignition point is very important for transport and storage of oils, because products with low ignition point are flammable.
- The combustion point is a temperature higher than the ignition point. It is defined as the temperature at which the oil vapours ignite in the presence of a flame and the resulting combustion is maintained at least for five seconds.
- Self-ignition point is the lowest temperature at which an oil ignites, in the presence of air or oxygen, but without flame. Self-ignition point is much higher than the ignition point.

### **1.2.10 Cloud point – Pour point**

Cloud and pour points are two empirical specifications for predicting the temperature ranges, which create flow problems. To determine these temperature ranges, a quantity of lubricant is transferred to a standard glass tube, cooled at a certain rate and examined periodically. First, the temperature at which the first blur (nebula) appears is recorded. This temperature is called as the cloud point. The appearance of nebulas in the lubricant is caused by the presence of paraffinic hydrocarbons. As the temperature drops, the number of nebulas within the oil increases. As the cooling of the oil goes on, its ability to flow decreases. The lowest temperature at which the lubricant still flows is called as the flow point.

### **1.2 Main Functions of lubricants**

Lubrication aims to reduce the coefficient of friction ( $\mu$ ) and the wear of metals, which is a result of friction of the metal parts that touch each other. When the lubrication is insufficient or generally bad, the following phenomena are presented:

- Increased engine's fuel consumption
- Increased wear on the engine parts, which are rubbed. This results in a premature replacement of these parts.

Thus, depending on the ever-increasing cost of manufacturing that engines and technical work require to replace them, reducing engine wear to a minimum is the main goal of

lubrication. Conclusively, for the lubrication of each engine, no random lubricant must be used, but the most suitable one, depending on the characteristics of the engine. This improves the engine's performance, reduces unavoidable friction as much as possible, and contributes to better engine maintenance. In addition, proper lubrication also contributes to:

- removal of increasing heat due to friction
- sealing of the combustion chamber by crankshaft of the internal combustion engines
- protection of lubricated metal surfaces from corrosion

### **1.3 Additives in Lubricants**

Lubricants' Additives are chemicals that either improve their properties, by providing them new and improved properties or eliminate undesirable characteristics. Some of the main properties of these additives are:

- Reduction of the viscosity dependence on temperature.
- Reduction of the freezing point.
- Reduction of the corrosion.
- Reduction of the oxidation and therefore the oil aging.
- Increase of the strength of the oil layer.
- Providing protection against dirt deposits.
- Providing protection against the formation of foam during pumping the oil.

Different types of lubricants require different additives depending on the properties that are to be enhanced or the characteristics that are to be minimized, as is further explained in this chapter. The additives significantly increase the production cost of lubricants, but this extra charge can be balanced by the benefits given to the engine. The additives prolong the lifetime of lubricants and provide a better performance to engines. As a result, wear, and cost to maintain the engine are lower.

#### **1.3.1 Types of Additives**

There are many types of lubricants' additives, which are categorized based on their properties and the way of modification. The main types are expanded below: [6], [7]



- Viscosity Index Improvers: They are polymers that avert the lubricant from becoming thin while the temperature increases. They also provide the lubricant a better flow at low temperatures and as a result they reduce wear. They are added at a ratio of 2-10%.
- Pour Point Depressants: They lower pour point, the lowest temperature at which the oil (lubricant) can flow. As a result, they play an important role in the circulation of lubricant in the engine lubrication network. They are added at a ratio of 0.1-1%.
- Anti-Pollution additives: They are meant to prevent the engine's pistons from being polluted. They surround the pollutants, forming a thin membrane, preventing them from settling on the inner walls of the cylinders.
- Corrosion Inhibitors: They prevent metals' corrosion, caused by water or oil's oxidation products. This fact is a result of high polar attraction of the additives, towards metal surfaces. A continuous cohesive layer is formed, preventing direct contact of the corrosive agents with the metals.
- Anti-wear agents: These additives are used for limiting wear from friction and protects the engine's parts. They are polar and react chemically with the metal surfaces when they are in contact with.
- Antioxidant additives: They slow down or even completely block oxidation of the lubricant, which would destroy its lubricating abilities by acting corrosively on metal surfaces, using the acids produced by oxidation. They are added at a ratio of 0.5-2%.

## Chapter 2: Carbon

### 2.1 Carbon

Carbon (chemical symbol C) is a nonmetallic chemical element with atomic number  $Z=6$ . It is placed in the 14<sup>th</sup> group (IV) and 2<sup>nd</sup> period in the periodic table. In nature, it is found in crystalline form, but also in amorphous one, as it is the main constituent of organic compounds. It is a four-valent element, that forms four chemical covalent bonds, since its electronic arrangement is  $1s^2 2s^2 2p^2$ . From this electronic arrangement, it would be expected that carbon may form only two chemical bonds, but due to hybridization it forms four chemical bonds. Due to smaller energy difference between the 2s and 2p atomic orbitals compared to the energy of the chemical bond, an electron is promoted from the 2s to 2p<sub>z</sub> orbital. As a result, the electron wave-functions of the four orbitals are combined, providing the electronic structure  $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$ . [8],[9]

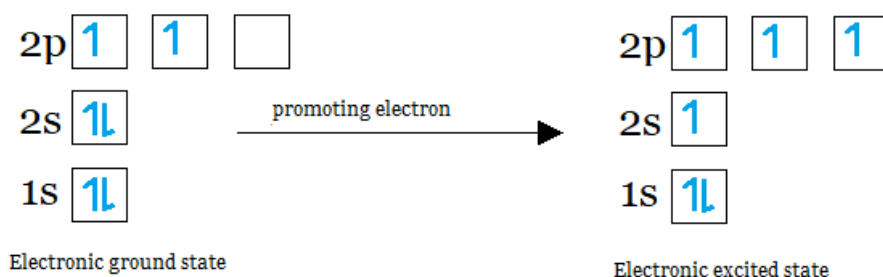


Figure 1: Promoting electron mechanism

The hybridized orbitals overlap even more, during the formation process of the molecule, so that a lower energy state is produced (i.e. molecule). There are three possible overlapping ways, which are presented in detail in Figure 2.

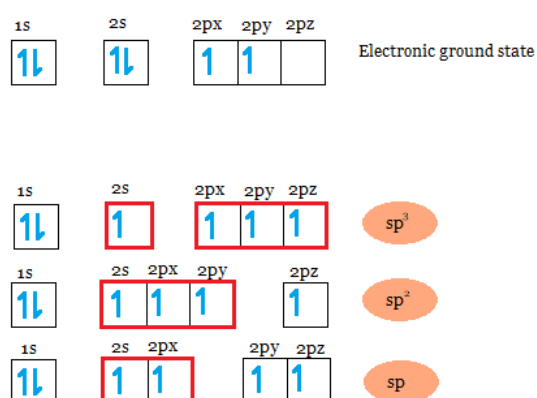


Figure 2: Carbon hybridized orbitals

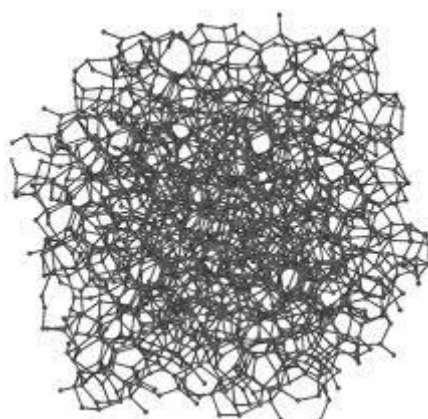
The combination of one s and three p orbitals leads to the formation of four  $sp^3$  hybrid orbitals. For example, in alkanes the carbon atom has four  $sp^3$  hybridized orbitals. Similarly, the combination of one s and two p orbitals leads to the formation of three  $sp^2$  hybridized orbitals, which are found in alkenes. Finally, the combination of one s and one p orbitals leads to the formation of two  $sp$  hybridized orbitals, as found in alkynes. More specifically,  $sp$  hybridization gives chain structures,  $sp^2$  resulting in planar structures while  $sp^3$  leads to tetrahedral structures. [9]

## 2.2 Allotropic forms of carbon

Carbon has the ability to form bonds, not only with other chemical elements, but also with other carbon atoms. Due to this property, various structures can be formed, which are called allotropic forms of carbon. These forms have different physical and chemical behaviours. An example is the difference between diamond and graphite, even both forms consist only of carbon atoms. Carbon allotropes are categorised into crystalline and amorphous forms. [10]

### 2.2.1 Amorphous carbon

This category concerns on carbon compounds which are found free in nature and do not have any crystalline structure. Their name is related to the irregularity of their structure and to the fact that they do not actually have any particular shape. This means they are amorphous. The absence of a specific structure is attributed to their thermodynamic instability. In this form of carbon, most bonds are either  $sp^2$  or  $sp^3$  hybridized and no  $sp$  hybridized bonds are found. [11]



*Figure 3: Amorphous carbon structure*

Amorphous carbon is found in the form of anthracite, lignite and peat. [10] They are solid minerals with differences in their properties and in carbon content. The carbon content of each structure is shown in Table 2 : [12]

Amorphous carbon structure	Carbon content
Anthracite	90%
Lignite	60-70%
Peat	50%

Table 2: Carbon content of amorphous carbon structures

## 2.2.2 Crystalline forms of Carbon

These carbon forms have thermodynamically stable forms. Graphite, diamond, glassy carbon, nanofoam carbon, fullerenes, carbon nanotubes and graphene belong to this category. The four more prominent crystalline forms of carbon are discussed further below.

### 2.2.2.1 Diamond

At high pressures, carbon atoms form the crystalline structure which called diamond, a very hard material. More specifically, its name comes from the ancient Greek word “adamas”, which means invincible. In the past, very hard stones, that could not be treated, were called diamonds. In the diamond structure, four carbon to carbon covalent bonds are formed by each carbon atom, with  $sp^3$  hybridization. As a result, diamonds display a tetrahedral structure. These covalent bonds are simple bonds, with a length of 1.56 Å. A three-dimensional network of six membered rings of atoms is formed. Because of its cubic crystalline structure and of the high strength of the carbon-carbon bonds, diamond is considered as the toughest known material in nature. Its boiling point is 4827 °C and its melting point 3550°C. [13], [14]

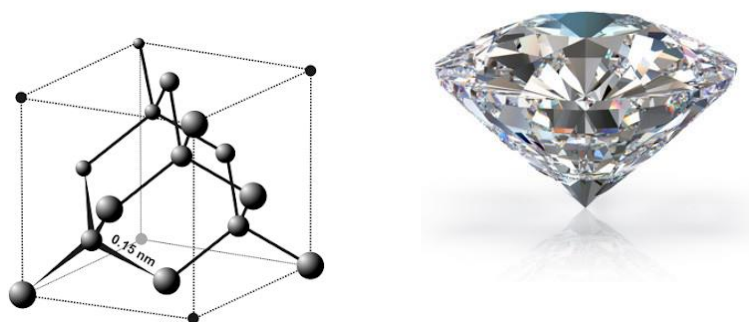
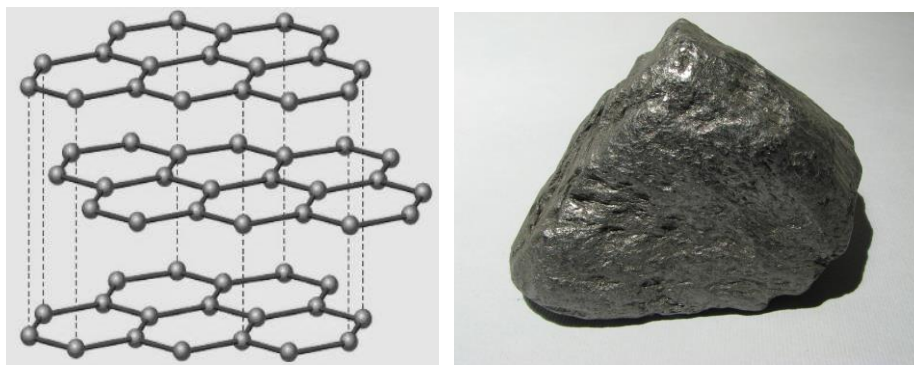


Figure 4: Diamond

### 2.2.2.2 Graphite

Graphite is a three-dimensional black mineral; whose name derives from “gráfin” which means “writing” in ancient Greek. It got this name thanks to the ability to be transferred on a soft surface when it’s rubbed on it. Carbon atoms in graphite, are covalently bonded with each carbon atom forming three covalent bonds with other carbon atoms, with  $sp^2$  hybridization. As a result, a flat structure of six-membered rings is formed, giving the vision of a “honeycomb”. Since graphite has many strong covalent bonds, a large amount of energy is required to break them. Due to this fact, graphite has high melting and boiling points. The hexagonal rings are in “layers”. There are no covalent bonds between the layers, but they are attached with weak van der Waals forces ( $2 \text{ eV/nm}^2$ ). Because of the low energy amount of the van der Waals forces, the “layers” can slide over one another, which makes graphite slippery. As a result, graphite is soft and the “layers” can be easily isolated. [15] Another important property of graphite is its excellent electrical and thermal conductivity. The carbon atoms have four valence electrons as described in *section 2.1*. Since in graphite each carbon atom forms only three covalent bonds, there’s a remaining single electron in its outer energy level, that’s not in a covalent bond. These electrons are released from the carbon atoms and are called delocalized electrons. The delocalized electrons can move between the layers and can conduct thermal energy (heat) and electricity.

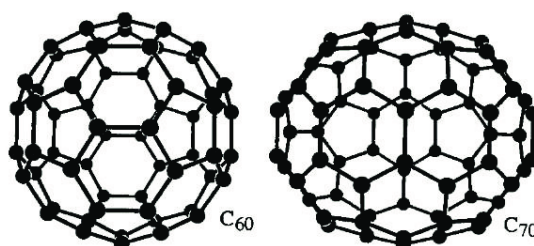
Graphite is based on carbon. However, it is similar to metals, as both graphite and metals are good conductors of heat and electricity. That’s because both have delocalized electrons that can be moved. [16], [17].



*Figure 5: Graphite*

### 2.2.2.3 Fullerenes

Fullerenes were discovered in the mid-1980s by Kroto (from the United Kingdom) and Heath, Brien, Curl and Smalley (from the United States of America). Due to the fullerenes' toxicity professor Harry Kroto was diagnosed with cancer and died in 2016. The discovery of fullerenes was performed during the laser vaporisation of graphite, in He atmosphere. Then, very stable molecules were formed, consisting of 36-350 carbon atoms, with a diameter range of 0.7-1.5 nm. Fullerenes are molecules of carbon atoms with hollow shapes. They usually consist of hexagonal rings of carbon atoms, but in some cases, they can also have rings with five or seven carbon atoms. The first Fullerene molecule discovered, is called Buckminsterfullerene ( $C_{60}$ ). It contains 60 carbon atoms arranged in a hollow sphere. Carbon atoms form either six- or five-membered rings. Since its discovery [18],  $FC_{60}$  has received considerable attention in various fields [19], and nowadays it has many important commercial and industrial applications, including drug delivery, electronics, superconductors, and cosmetics [20],[21]. Finally, they can be used as catalysts to speed up chemical reactions. [9],[22]



*Figure 6: Fullerene*

### 2.2.2.4 Nanotubes

Carbon nanotubes are also allotropic forms of carbon, discovered by Sumio Iijima in 1991 [8]. They are one-dimensional materials, with diameter to length ratio, greater than 1000, forming cylindrical tubes that consist entirely of six carbon atoms rings. The carbon atoms of which they consist of are  $sp^2$  hybridized similarly to fullerenes. These cylindrical molecules have excellent properties, such as mechanical strength and elasticity, electrical and thermal conductivity and expansion. Their structure, geometry and properties allows them to have various applications in nanotechnology, electronics, optics and materials' science.

They are categorized as Single Walled Carbon Nanotubes (SWCNTs) and Multi Walled Carbon Nanotube (MWCNTs).

The differences between SWCNTs and MWCNTs are shown in Table 3: [23]

SWCNTs	MWCNTs
Have only a one-wall tube	Have 6 to 25 or more wall tubes in concentric cylinders
Diameter of 0.5-1.5 nm.	Diameter of more than 100 nm

Table 3: Differences between SWCNTs and MWCNTs

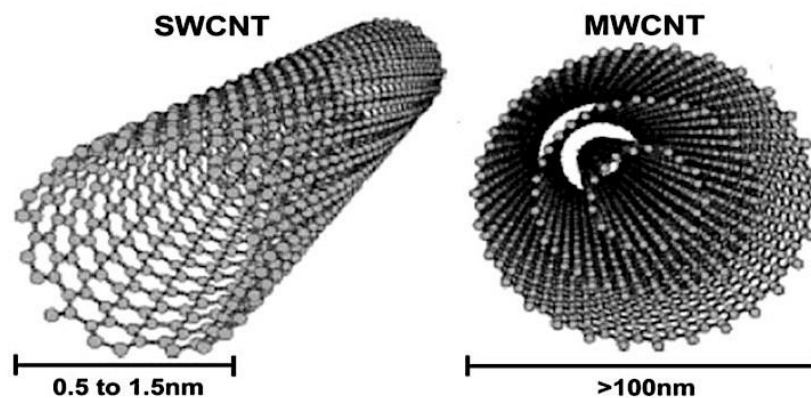


Figure 7: a) SWCNTs (left), b) MWCNTs (right)

## Chapter 3: Graphene and its derivatives

### 3.1 Graphene

Graphene was first isolated in 2004 by Geim and Novoselov, who awarded in 2010 the Nobel Prize in Physics. [24] The method used for graphene's isolation was the mechanical exfoliation of graphite using an adhesive tape. Nowadays, various preparation methods and techniques towards the isolation of graphene have been developed. Graphene has remarkable mechanical, electrical, thermal and optical properties. As a result, it has attracted the interest of the global scientific community while it is estimated to be able to find practical applications in various categories of materials.

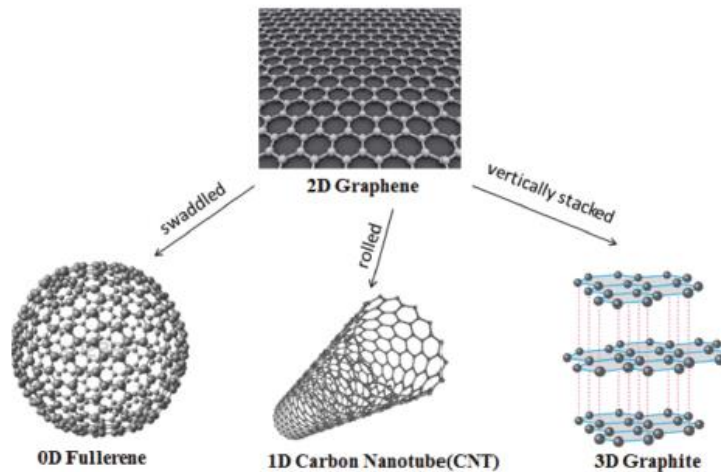
Graphene is a thin single layer of graphite (*section 2.2.2.2*), in which carbon atoms form a two-dimensional lattice. It can be also enwrapped, forming other allotropic forms of carbon. In case of graphene, the 2s atomic orbitals interact with the 2p<sub>x</sub> and 2p<sub>y</sub> orbitals forming three sp<sup>2</sup> hybrid orbitals. This interaction results in the formation of three strong σ-bonds between the carbon atoms, in which the electrons are located along the plane. This results in graphene's excellent mechanical properties [25].

The π electrons in the 2p<sub>z</sub> are weakly attached to the core of the carbon atoms and are therefore delocalized. These delocalized π electrons exhibit high electron mobility and serve as charge carriers, making graphene an excellent conductor of electricity and are therefore responsible for its electronic properties. In fact, graphene is a semi-metal, meaning that there is virtually no overlap between the valence band and the conduction band, making the energy bandgap practically zero. The band gap is an energy range of a solid material, where no electronic states can exist. It refers to the requires energy, needed to promote a valence electron bound to an atom, to become a conduction electron. The fact that graphene has a zero-band gap means that electrons can flow easily from the top of the valence band to the bottom of the conduction band, similarly to a metal conductor.

#### 3.1.1 Graphene production

Graphene production is a very cost effective and easy procedure. Various methods for graphene production have been developed over the last decade. Some of these methods are still used to date, while others have been abandoned due to high cost or impracticality. The main methods used today are explained in the following sections in details.





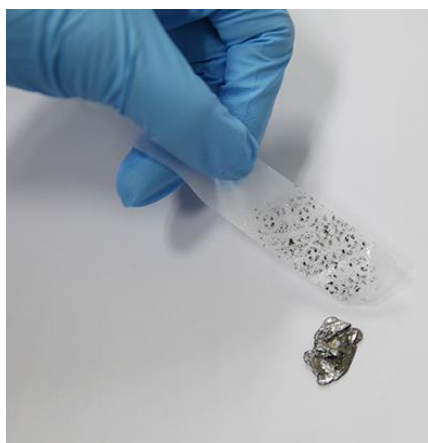
*Figure 8: Graphene as the building block for many other carbon allotropes.*

### 3.1.1.1 Mechanical exfoliation

The method of micromechanical exfoliation was first applied for the isolation of monolayer graphene. According to this method, a piece of an adhesive tape was repeatedly attached on a graphite crystal, to break the van der Waals interactions between its layers and isolate them.

Using this method, a problem occurred. The problem was that the crystals of graphene were hidden in "Haystacks" made of thick Graphite sheets [8]. This problem was solved, since graphene is visible under an optical microscope when it's placed on a silicon substrate. In this way, monolayer Graphene could be detected between the multilayer regions. The thickness of the substrate has been carefully selected.

To observe Graphene under the microscope, the adhesive tape with the optically transparent Graphene sheets was immersed in acetone solution to dissolve the tape. Graphene flakes are then transferred onto a silicon oxide ( $\text{SiO}_2$ ) substrate. Graphene flakes are then visible with the optical microscope, where different graphene thicknesses appeared with different colors.[26] One year later, scientists simplified the technique, using dry deposition of graphene, while skipping the step where acetone is required. As a result, Graphene crystallites with diameter larger than 1 mm were obtained, visible even to the naked eye. [27]



*Figure 9: Mechanical exfoliation method*

### **3.1.1.2 Epitaxial growth on silicon carbides**

According to this method, graphene is produced by heating silicon carbide (SiC), at a temperature above 1100 °C and at low pressures in the range of  $10^{-6}$  Torr. This method produces epitaxial Graphene with dimensions, depending on the size of the SiC substrate [1].

### **3.1.1.3 Epitaxial growth via Chemical Vapour Deposition on metallic substrates**

To perform this method, a carbon source and a metal substrate with a suitable atomic structure are required. Through Chemical Vapor Deposition (CVD) high quality laminated graphene with a surface area of  $1 \text{ cm}^2$  has been produced, on thin nickel or copper films used as a carbon source. If this procedure is carried out at low pressure conditions, then monolayer graphene can be produced. The replacement of methane, which has a carbon atom, with ethane or propane, can lead to the production of two-layer graphene. Finally, after the completion of graphene's deposition, the metal substrate is removed using appropriate chemical processes. [1]

## **3.2 Graphene Oxide**

The synthesis of graphene by chemical processes involves the initial preparation of graphite oxide (GO) using the Hummers - Offeman method. This method follows the mixing of graphite with a solution of sulphuric acid ( $\text{H}_2\text{SO}_4$ ), sodium nitrate ( $\text{NaNO}_3$ ) and potassium permanganate ( $\text{KMnO}_4$ ). Graphite oxide's surface is strongly modified with hydroxyl groups on the  $\text{sp}^3$  hybridized carbon lattice and with carbonyl and carboxyl groups attached to the ends of the  $\text{sp}^2$  carbon atoms. As a result, graphite oxide is highly hydrophilic which upon an appropriate modification, can lead to the formation of graphene oxide. Although graphite oxide and graphene oxide have similar chemical properties, due to their surface-bound

groups, their structures significantly differ. Graphene oxide (GO) is a monolayer material, derived from the exfoliation of graphite oxide. The liquid phase exfoliation of graphite oxide via ultrasonication results in more homogenous and stable colloidal systems i.e., graphene oxide dispersions. [28]

The presence of oxygen containing groups on the graphitic lattice of GO disrupts the  $sp^2$  hybridised system and drastically decreases the conductivity. GO is considered as an insulating material due to its wide band gap [29]. However, the  $sp^2$  hybridised system can be partially recovered to restore the conductivity of this graphene-based material, as will be further explained in chapter 3.3. Partial removal of the oxygen functional groups during reduction makes graphene oxide more conductive and less hydrophilic [30]. The result of reduction is the development of a new graphene-based material known as reduced graphene oxide (rGO), which is further discussed in chapter 3.3.

### **3.3 Reduced Graphene Oxide**

As previously mentioned, due to the presence of oxygen groups in GO, a disruption of the  $sp^2$  hybridized system occurs. In order the  $\pi$  network to be recovered, corresponding to graphene, GO must undergo reduction. Thanks to reduction, oxygen functional groups are partially removed and the  $sp^2$  hybrid system is partially recovered, resulting in the production of a highly conductive rGO. Due to this material high conductivity, it can be used in various applications, such as to serve as a conductive scaffold for the development of electrocatalysts. In the present work, the role of rGO as an additive in lubricants is described. There are many reduction methods, such as chemical, thermal, and electrochemical processes. During the oxidation of Graphite to produce Graphite oxide, many defective sites are created, which are stable even after the reduction process [31].

#### **3.3.1 Reduction Strategies**

##### **3.3.1.1 Thermal annealing**

GO can be reduced by heat treatment, using a rapid heating ( $>2000$  °C/min). The rapid increase of temperature causes decomposition of the oxygen functional groups and leads to the release of gases. Consequently, high pressure occurs between the GO layers. Applied pressure of 2.5 MPa is adequate to separate two stacked GO layers. It is evident that the

rapid heating method has two functions. On one hand, exfoliation of graphite oxide can be achieved, while on other hand the individual GO sheets undergo reduction via the decomposition of oxygen containing groups. This process is used to produce small size graphene flakes that exhibit wrinkles. The reason that small and deformed graphene flakes occur is that along with the oxygen atoms, carbon atoms are also removed from the layers of GO leading to a structural damage [32].

### **3.3.1.2 Reduction by Hydrazine**

The reduction with chemical reagents can be carried out at room temperature or under moderate heating. One of the most common chemical reduction methods is the use of hydrazine as a potent reducing agent. This method of reduction was used before the discovery of Graphene [33]. This reductant can be effectively used in aqueous dispersions of GO, as it does not react with water. Heat-assisted hydrazine reduction of GO suspensions results in rGO nanosheets. When dried, an electrically conductive black powder with C/O ratio of around 10 can be obtained. Hydrazine's derivatives, such as hydrazine hydrate or dimethylhydrazine, can also effectively produce rGO from GO.

### **3.3.1.3 Reduction by Ascorbic acid (Vitamin C)**

Ascorbic acid is a non-toxic, biocompatible reducing agent for GO, which is considered as an ideal substitute of hydrazine, and therefore it can be used for further applications. When GO is reduced by ascorbic acid (Vit C) the sheet resistance achieved is similar to the respective taken using hydrazine under the same conditions. Furthermore, the reduction with Vit C does not cause any aggregation of rGO layers as occurred after the use of hydrazine [32].

### 3.3.1.4 Reduction by Hydroiodic acid HI

Another widely used as reducing agent, for the preparation of rGO, is the hydroiodic acid (HI). During this process, the rGO produced exhibits improved flexibility and even tensile strength, while the hydrazine assisted one is too rigid to be rolled. This occurs, due to the fact that the rGO structure produced by HI consists of less defects than the one produced by hydrazine, also exhibiting improved mechanical properties [32]. Furthermore, using this reduction method, higher conductivity can be achieved.

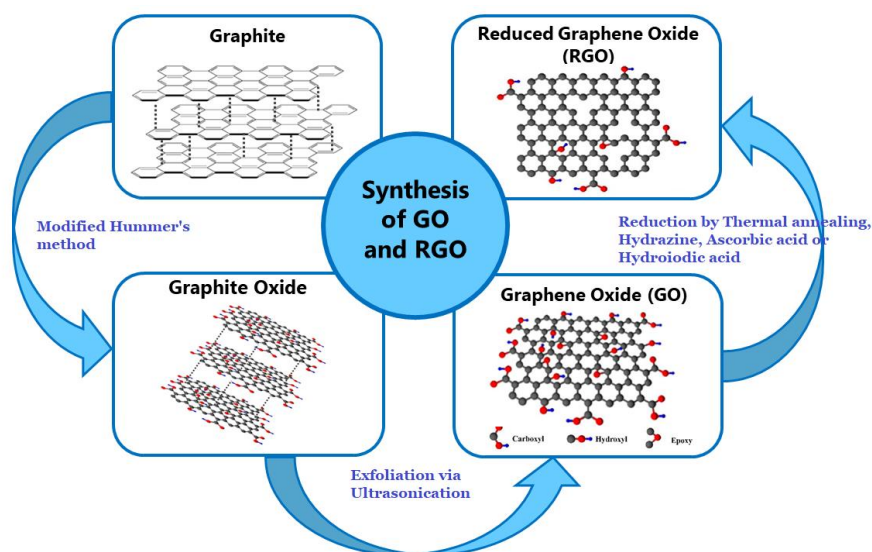


Figure 10: Summary of processes for the synthesis of GO and RGO.

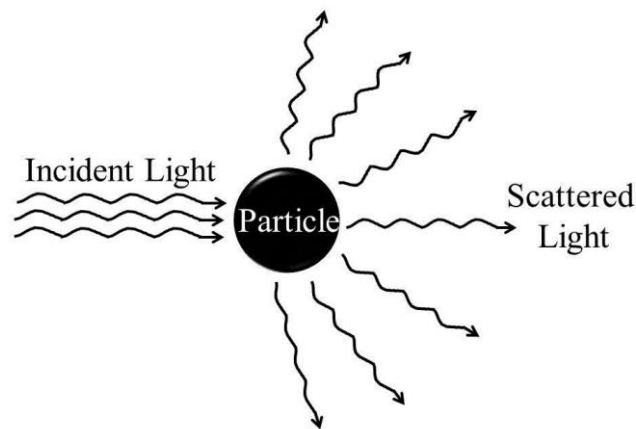
## Chapter 4: Experimental Methodologies - Theory

### 4.1 Nephelometry – Turbidimetry

When a light beam encounters an object, it interacts with it and various optical phenomena occur. These phenomena are referred as the basic properties of light. Some of these properties are the following:

- light reflection
- light diffusion
- light refraction
- light scattering
- light absorption

Light scattering is a visual phenomenon, in which the light changes its direction in a range of angles when they interreact with a material that has a granular, fibrous or rough surface. As a result, a part of light is absorbed by the material, while the rest is scattered [34]. Continuous scattering (course changes) of light leads to its diffusion.



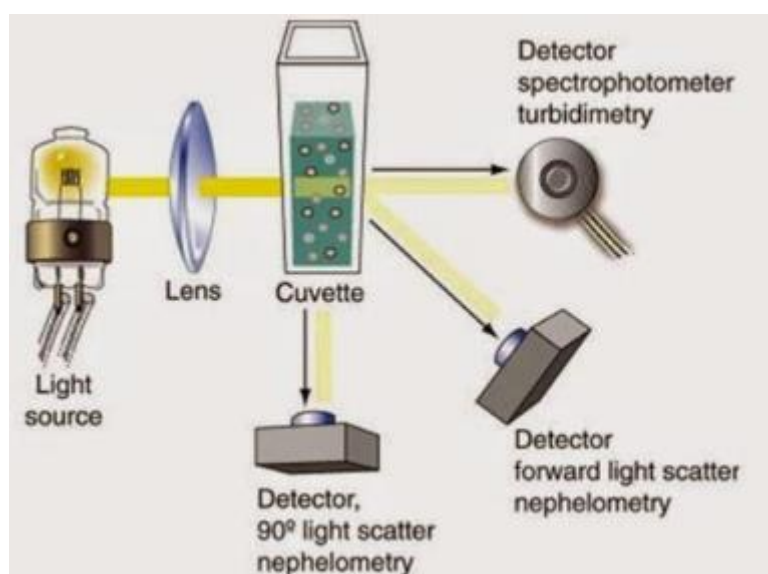
*Figure 11: Light Scattering*

Nephelometry and Turbidimetry are two related techniques and are commonly used in clinical laboratories. Both are based on the measurement of the diffused beam of the excited particles. When the light passes through a solution containing inactivated particles, a part of light is scattered, another is absorbed while the rest is transmitted through the liquid. In nephelometry the intensity of the scattered light is measured, while in turbidimetry is

measured the intensity of the transmitted one through the sample. This interaction serves to measure the concentration of particles into a dispersion, by counting light transmission (turbidimetry), or diffusion of light (nephelometry) [35].

More specifically, turbidimetry is the measurement of the light's intensity reduction, which passes through a dispersion, with the incoming beam having the same direction as the outgoing one. Nephelometry is the measurement of light intensity, scattered at an angle of  $90^\circ$  when it passes through a dispersion [36].

For example, immunoassays involving nephelometry and turbidimetry are widely used to measure the concentrations of specific proteins. The turbidity produced by the precipitation of proteins with sulfosalicylic acid has been used for many years as a non-specific method for determining the amount of protein in urine and cerebrospinal fluid. Higher light diffusion is produced when acetyl-pyridine chloride is added to urine containing mucopolysaccharides, as another certified use of turbidimetry [36].



*Figure 12: Nephelometry and Turbidimetry*

#### **4.1.1 Turbidimeters**

Theoretically, turbidity can be measured in any common photometer or spectrophotometer. Since, a small change in the emitted light is measured by the presence of a strong background signal, instruments that provide a small signal-to-noise ratio are desirable [37].

Using short light wavelengths leads to the advantage of increased diffusion and expected higher signal, but in biological solutions light absorption also increases.

#### **4.1.2 Nephelometers**

Nephelometers, usually consist of a light source, an incident light filter, a cuvette and a detector placed at a specific angle to avoid direct light emission. The supplied filters (or monochromators) for incident or emitted light are set at the same wavelength, as in case of fluorescents, in which the diffused light is measured at. Tungsten or quartz lamps are commonly used. Alternative sources are Xenon lamps, Mercury arcs, light emitting diodes and laser devices. The detector must be well shielded, in order to minimize the interference from scattering light.

Generally, nephelometry has greater sensitivity and therefore yields faster results than turbidimetry. On other hand, turbidimetry does not require specialized instruments and can be applied to the most existing automatic clinical analyzers, or to an instrument that combines both techniques [35].

#### **4.2 Tribological behavior study – Tribometry**

Tribometry is the measurement and determination of wear and friction. They are determined by a tribometer. Tribometers are used for the evaluation of tribological properties, namely friction, wear, adhesion, hardness etc. [38].

Friction is the force of resistance manifested against any movement of parts of the same body or in the relative motion of two bodies whose surfaces are in contact. In first case, internal friction occurs, where the second case is known as external friction. The direction of friction is always opposite to that of motion [39]. Friction force is categorised as static friction when bodies are balanced and as sliding friction when bodies are moving. Frictional force is due to electrostatic forces between the molecules of the two surfaces [40].

Static friction is the force that prevents a body from moving while the body is still in balance. Its measure is equal to that of the applied force tending to move the body and can take values from 0 N to a maximum value equal to  $\mu_s \cdot F_N$ , where  $\mu_s$  is a dimensionless quantity called static friction coefficient and depends on the roughness of the surface and  $F_N$  is the force applied between bodies in contact. [41]

The friction factor is experimentally calculated. When the external force exceeds the above value ( $\mu_s \cdot F_N$ ) then the body begins to slip and then sliding friction is exerted on it. Sliding friction is slightly less than the maximum of static friction because when the body gains



speed, friction forces slightly decrease. The general relationship of static friction is:  $F_f \leq \mu_s \cdot F_N$

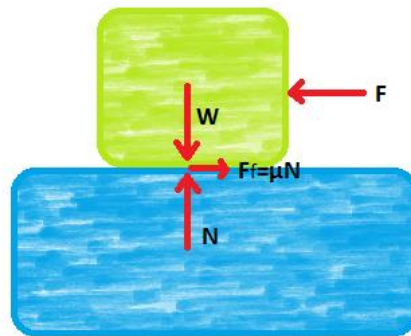


Figure 13: Friction force  $F_f$

Sliding friction is the force that resists the motion of bodies in contact. It is also called kinetic friction. It has the opposite direction of the motion and a measure given by the following relation:

$$F_K = \mu_K \cdot F_N$$

Where  $\mu_K$  is the sliding friction factor. This factor is slightly smaller than the static friction factor for all surfaces except from very smooth ones. Tribology, as an autonomous scientific and technological branch, investigating friction and wear of materials, as well as ways, methods and forms of lubrication. The term tribology comes from the Greek words friction and speech, which mean the study of friction. Applied tribology or tribotechnology is mainly related to machine maintenance, lubrication and elimination of energy losses through friction and environmental protection, associated with lubrication.

The role of tribology is to reduce friction and wear during the movement of two bodies in contact in order to save energy and allowing machines to run at lower cost through lubrication. In order to fulfill these goals, knowledge in Chemistry, Metallurgy and Mechanical Engineering is required.

#### 4.2.1 Tribometers

The devices used for the determination of tribological quantities are called tribometers. There are many types of tribometers, which are often referred to by the specific contact arrangement they stimulate or by the original equipment developer.

#### **4.2.1.1 Bouncing ball tribometer**

It consists of a ball, that crashes at an angle, against a surface. The ball slides along a line until it crashes on the surface and the bounces off of it. Frictional Force is determined by measuring the rotational speed of the ball, or by measuring the force on the horizontal surface.

#### **4.2.1.2 Pin on disc tribometer**

It consists of a stationary pin, loaded on a rotating disk. The disk can have any shape, for a specific contact area. The coefficient of friction is determined by the ratio of the frictional force to the loading force on the pin.

#### **4.2.1.3 Reciprocating Tribometer**

A steel ball is loaded on a stationary steel plate. The plate is fully immersed into the liquid to be tested. During the measuring process, the ball is oscillating with a certain frequency and is in constant contact with the steel plate. A load is applied on the specimen where the steel ball is applied. The changes of the friction coefficient over the testing time are measured. After the test the abraded area on the ball is evaluated by means of an optical.

### **4.3 Viscometry**

Viscometry refers to a set of techniques that measure the viscosity of various fluids and are often used in the chemistry of polymers, food and lubricants. By using these techniques, it is possible to characterize a polymer by determining the viscosity of its solutions or tinctures. Viscometers are used in polymer solutions as an easy and simple way to estimate their molecular weight [42].

#### **4.3.1 Viscometer**

The devices used for the experimental determination of viscosity are called viscometers. A viscometer is the instrument used to measure the viscosity of a liquid. In simple viscometers, the time required for a certain amount of liquid to flow through a constant sized opening, is measured. Other types of viscometers are based on measuring the time it takes for a metal sphere to sink through a container filled with liquid, and others on the speed of damping the oscillations of a disk hovering in the liquid. Finally, other viscometers measure the force required to rotate a cylinder inside liquid. The most well-known types of viscometers are:

##### **4.3.1.1 The Hoppler viscometer:**

It measures the time required for a bullet to be sunk through a tube filled with the solution of interest. The tube is surrounded by a second tube that contains water at a constant temperature. In this manner the absolute viscosity is determined.

#### 4.3.1.2 The Ostwald viscometer:

This type of viscometer measures the flow time of a certain amount of solution in a capillary tube of known diameter and length. The measurement is carried out at constant temperature. As a result, the relative viscosity with water is determined.

#### 4.3.1.2 The Brookfield viscometer:

The rotational torque of a disc rotating in the solution at a constant temperature is measured.



*Figure 16: Hoppler Viscometer*



*Figure 15: Brookfield Viscometer*



*Figure 14: Ostwald Viscometer*

## **Chapter 5: Experimental Procedure**

In order to synthesize rGO and to investigate its tribological behavior as additive in engine oil, a two-step sample preparation and further characterization study was performed. Firstly, rGO samples were prepared and then dispersed in engine oil (5W-40). Further preparation of three samples was also performed, to compare their properties with the rGO containing ones. However, only rGO samples were tribologically characterized. The tribological characterization of the other three samples will be performed in future. The prepared samples were namely as SWCNTs, rGO + SWCNTs and MWCNTs. Then, they were also dispersed in engine oil (5W-40). Secondly, the tribological behavior of the samples containing rGO was investigated through a reciprocating tribometer, using steel ball (100 CR6 or 52100) on special cut steel blocks (Sverkel 21-AISI D2), in order to estimate their wear and friction behavior. Further, turbidity measurements were performed. During the third part, using the dispersions, where the best results were given, viscometry measurements was performed, for the determination of the most favorable material, suitable to be used as additive in engine oils.

### **5.1 Part One: rGO production and sample preparation**

#### **5.1.1 rGO Production**

rGO was prepared in-house through a typical procedure, including the preparation of graphite oxide, following by a HI assisted reduction procedure. More specifically, first graphite oxide was produced by oxidizing Graphite via a modified Hummer's method and then the yield was reduced to prepare reduced graphite oxide using hydroiodic acid (HI) and acetic acid (AcOH) as reducing agents.

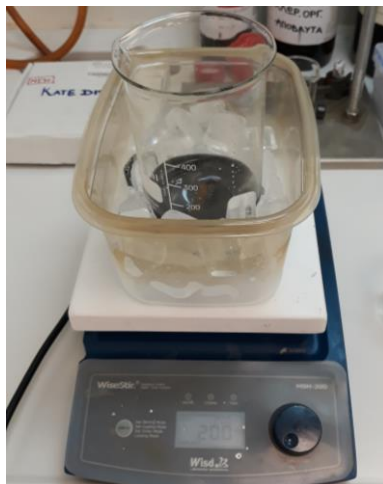
##### **5.1.1.1 Modified Hummer's method and Reduction by Hydroiodic acid**

###### **Modified Hummer's method:**

Graphite powder (1g) and sulphuric acid  $H_2SO_4$  95-98 %w/w (46 mL) were placed in a beaker (600mL) under magnetic stirring. Due to the fact the reaction is highly exothermic the setup was placed in an ice bath. The mixture was left stirring for 20 minutes.

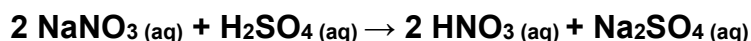


*Figure 17: Graphite powder*



*Figure 18: The addition of H<sub>2</sub>SO<sub>4</sub>*

This step was followed by the addition of NaNO<sub>3</sub> (1g), which was performed slowly and in small amounts at a time. The mixture was left stirring for 1 h. The reaction that took place is:



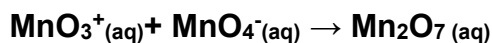
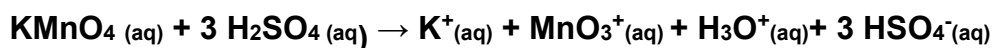
NaNO<sub>3</sub> was used to assist the intercalation of graphite by H<sub>2</sub>SO<sub>4</sub>, since it cannot take place without an oxidizing agent. The oxidizing agent is HNO<sub>3</sub>, produced by the reaction between H<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub> [43].

After stirring for 1h, KMnO<sub>4</sub> (6g) was added very slowly and in small doses, since the reaction is highly exothermic. The reaction between H<sub>2</sub>SO<sub>4</sub> and KMnO<sub>4</sub> leads to the production of Mn<sub>2</sub>O<sub>7</sub>, which is highly reactive and known to combust at temperatures higher than 55 °C. After the addition of KMnO<sub>4</sub>, a thick green solution was observed.



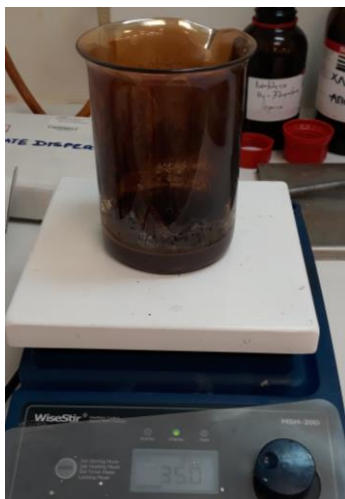
*Figure 19: The addition of KMnO<sub>4</sub>*

The reactions that took place are:



**GIC: graphite intercalated by H<sub>2</sub>SO<sub>4</sub>**

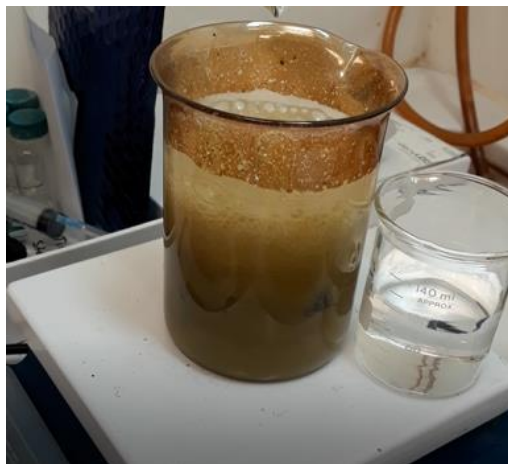
The mixture was left stirring for 24 h. After the 24 h had passed, the mixture was left stirring at 35 °C for 100 min and the color turned to dark brown.



*Figure 20: 24 hours later*

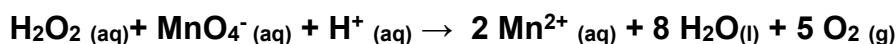
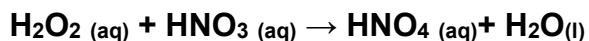
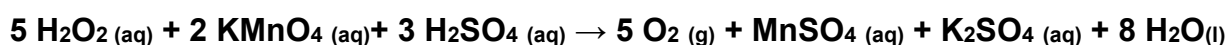
After 100 min, the heat was turned up to 90 °C and deionised H<sub>2</sub>O (80 mL) were slowly added. The mixture was further left stirring for 40 minutes. The reaction was then removed from the hotplate and deionised H<sub>2</sub>O (200 mL) were added. The next step was the addition of H<sub>2</sub>O<sub>2</sub> 30% (20 mL), which was added slowly and carefully. The addition of H<sub>2</sub>O further contributes in graphite layers exfoliation. H<sub>2</sub>O<sub>2</sub> was added to stop the oxidation reaction and additionally to remove any excess of KMnO<sub>4</sub>. Generally, H<sub>2</sub>O<sub>2</sub> is an oxidizing agent, but in this reaction, it has reducing properties [44]. In an acidic environment (H<sub>2</sub>SO<sub>4</sub>), it reduces

Mn<sup>7+</sup> to Mn<sup>2+</sup> while H<sub>2</sub>O<sub>2</sub> itself is oxidized, producing O<sub>2</sub>, therefore preventing further oxidation of Graphite oxide.



*Figure 21: The addition of H<sub>2</sub>O<sub>2</sub> (left) warming water until 65°C (right)*

The reactions that took place upon the addition of H<sub>2</sub>O<sub>2</sub> are:



After the addition of H<sub>2</sub>O<sub>2</sub>, the mixture's colour turned to green-brown. The mixture was then left stirring until it reached room temperature. The final colour was yellow-brown. Finally, the entire mixture was centrifuged at 4200 rpm for 20 minutes for the isolation of graphite oxide (sediment) and the supernatant liquid was disposed of.



*Figure 22: Centrifugation*

The sediment was first washed with warm deionized H<sub>2</sub>O (200 mL) at the temperature of 65 °C and then with deionised H<sub>2</sub>O at room temperature, until the supernatant reached neutral pH (7). Litmus paper was used to determine the pH.



*Figure 23: Washing the sediment*



*Figure 24: Drying the sediment*



*Figure 25: Pulverising the solid to powder*

### **Reduction by Hydroiodic acid:**

The previously prepared Graphite oxide (1g) was added to a centrifugation tube followed by glacial AcOH (37 mL). The mixture was then placed in an ultrasonication bath for 10 minutes to be homogenized. The following step was the addition of HI 55% (2 mL), followed by further ultrasonication for 5 minutes. A magnetic stirrer was then added to the tube, which was placed in a silicone oil bath (60 °C) and left stirring for 48 h.

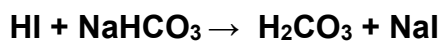
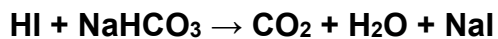




*Figure 26: The tube in a silicone bath*

When 48 h passed, the mixture was centrifuged at 4200 rpm for 20 minutes. The supernatant liquid, which contains of HI, was discarded. The sediment was washed 5 times with saturated  $\text{NaHCO}_3$  solution, for the neutralization of the excess HI.

The reactions that took place are:

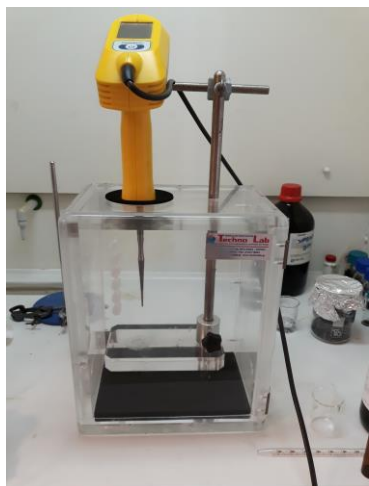


The sediment was washed with acetone until the disappearance of the yellow colour of the supernatant. The colour change from yellow to colorless indicates the removal of HI traces. The sediment was then placed in an oven at 60 °C and left to dry for several days. The prepared reduced graphite oxide was finally pulverized into a fine powder.

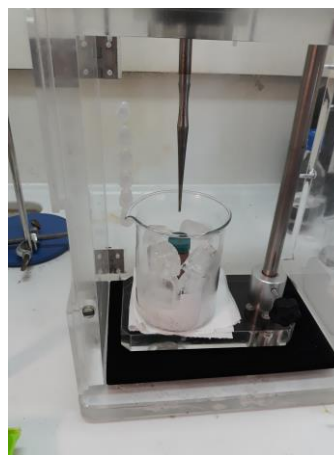
#### **5.1.1.2 rGO samples preparation**

For the preparation of the samples, different contents of rGO were added to the engine oil, in order to produce different additive/oil ratios. The amount of engine oil used each time was 20 ml with only the amount of the additive changing. The additive/oil ratios are listed in detail in Table 4. Each sample underwent ultrasonication using an ultrasonic probe set at 26 KHz for 30 min. The shear force produced by the high frequencies emitted from the probe caused

the particle agglomerates to break apart. A Hielscher UP200Ht ultrasonication was used to disperse reduced graphite oxide into the engine oil. The vial containing oil and reduced graphite oxide was placed in an ice-bath during the ultrasonication, to prevent the system's overheating, due to high-energy frequencies of the probe.



*Figure 27: Ultrasonication probe (Hielscher)*



*Figure 28: Vial in ice-bath*

The prepared samples were then centrifugated for 30 min at 4200 rpms, for the separation of the larger particles of the dispersion. The supernatant, which is the final form of the dispersion, was transferred to a new vial. The centrifuge machine used was Hettich Universal 320 R.



*Figure 29: Centrifugation*

The amounts (mg) of each substance added in the vials are shown in the Tables below:

<b>rGO + engine oil</b>			
<i>Vial</i>	<b>Concentration (%w/w)</b>	<b>Engine oil (mL)</b>	<b>rGO (mg)</b>
1	0.2	20	20
2	0.1	20	10
3	0.08	20	8
4	0.06	20	6
5	0.04	20	4
6	0.02	20	2
7	0.01	20	1

*Table 4: rGO in engine oil Vials*

### 5.1.2 Preparation of SWCNT's +rGO, SWCNT's and MWCNT's samples

For the preparation of the samples, different contents of each material were added to the engine oil, in order to produce different additive/oil ratios. The same procedure used for rGO samples' preparation was followed. The additive/oil ratios are listed in detail in Tables 5,6,7.

<i>SWCNTs in engine oil</i>			
<i>Vial</i>	<i>Concentration(%w/w)</i>	<i>Engine oil (mL)</i>	<i>SWCNTs (mg)</i>
8	0.2	20	20
9	0.1	20	10
10	0.08	20	8
11	0.06	20	6
12	0.04	20	4
13	0.02	20	2
14	0.01	20	1

*Table 5: SWCNTs in engine oil vials*

rGO +SWCNTs in engine oil				
<i>Vial</i>	Concentration (%w/w)	Engin oil (mL)	SWCNTs (mg)	rGO (mg)
15	0.2	20	10	10
16	0.1	20	5	5
17	0.08	20	4	4
18	0.06	20	3	3
19	0.04	20	2	2
20	0.02	20	1	1
21	0.01	20	0.5	0.5

Table 6: rGO +SWCNTs in engine oil vials

MWCNTs in engine oil			
Vial	Concentration (%w/w)	Engin oil (mL)	MWCNTs (mg)
22	0.06	20	6
23	0.04	20	4
24	0.02	20	2
25	0.01	20	1

Table 7: MWCNTs in engine oil vials



Figure 31: rGO Vials 1,2,3,4,5,6 from right to left (bottom view)



Figure 30: rGO Vials 1,2,3,4,5,6 from right to left (front view)



Figure 32: rGO Vials 1,2,3,4,5,6 from right to left (upside down view)

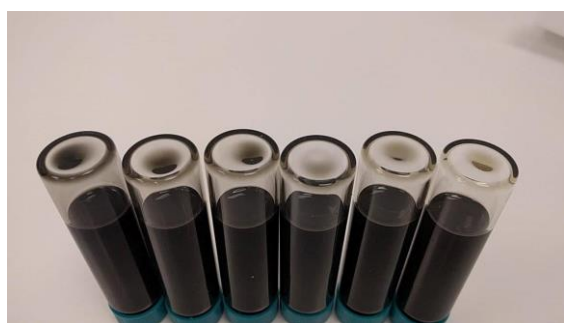


Figure 34: SWCNTs Vials 8,9,10,11,12,13 from right to left (bottom view)

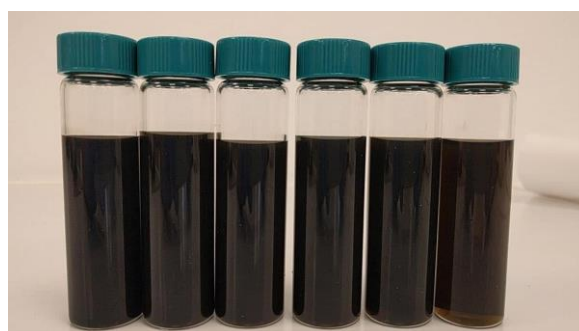


Figure 33: SWCNTs Vials 8,9,10,11,12,13 from right to left (front view)

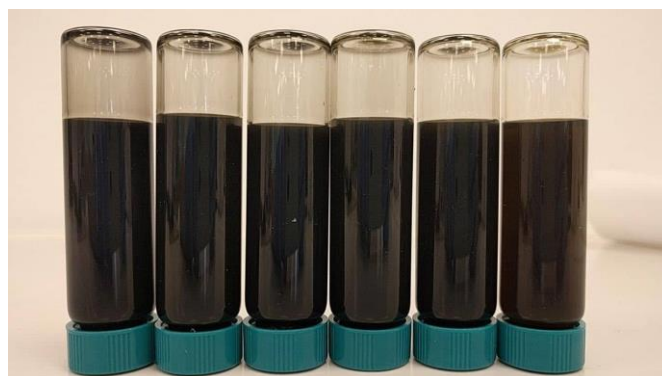


Figure 35: SWCNTs Vials 8,9,10,11,12,13 from right to left (upside down view)

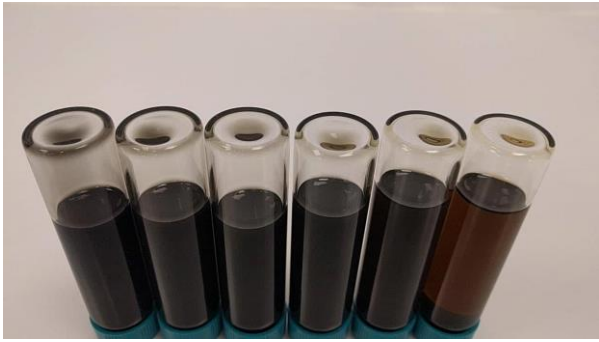


Figure 37: rGO + SWCNTs Vials  
15,16,17,18,19,20 from right to left (bottom view)

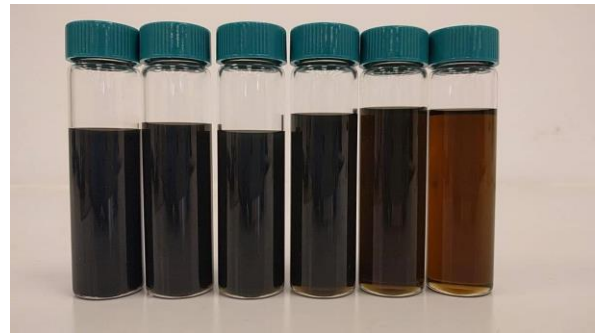


Figure 36: rGO + SWCNTs Vials  
15,16,17,18,19,20 from right to left (front view)



Figure 38: rGO + SWCNTs Vials  
15,16,17,18,19,20 from right to left (upside down view)



Figure 39: MWCNTs Vials 22,23,24,25 from right to left (front view)



Figure 40: Vials 7,21,14,25 from left to right

The Lubricant's properties are shown in the table below:

5W-40 fully synthetic multigrade engine oil			
<b>TBN</b>	11.28mg KOH/gr	<i>Elements Contained</i>	Ca, Zn, P, S and Mg
<b>Flash point</b>	217°C		
<b>Viscosity (100°C)</b>	13.59 cSt		
<b>Viscosity (40°C)</b>	84.27cSt		

Table 8: Lubricant's properties

## 5.2 Part Two: Characterization study

### 5.2.1 Turbidity measurements – Tribological characterization

#### 5.2.1.1 Turbidimetry

It was necessary to perform turbidimetry tests, in order to monitor the stability of the prepared samples. The champion sample is chosen for further characterizations.

Stability measurements were carried out using a Tribometer, in which the light passes through the probe at 0 ° in relation to the direction of incident light. The obtained data was stored and processed using OriginLab 9.0.

Concentration	Turbidity			
	rGO	SWCNTs	rGO + SWCNTs	MWCNTs
<b>0.2</b>	56	0	0	-
<b>0.1</b>	53	0	0	-
<b>0.08</b>	48.72	0	0	-
<b>0.06</b>	43.96	0	3.78	17.65
<b>0.04</b>	43.35	0	21.38	29.9
<b>0.02</b>	27.25	12.8	46.24	24.26
<b>0.01</b>	13.5	48.47	44.42	17.69



### 5.2.1.2 Tribological Characterization

rGO in engine oil at different ratios were further investigated with tribological characterizations.

Seven different contents of rGO were incorporated in the 5W-40 engine oil and the prepared samples were investigated using a custom made reciprocating tribometer. The tests were carried out under boundary and mixed lubrication conditions at 100°C. The normal load during the tribometry tests was set to 60.5 N. The sliding speed and stroke were 0.055 m/s and 8 mm, respectively. The temperature of the cylinder liner was set to 100 °C, using a heater equipped with a digital controller mounted on the tribotester. Three drops of the reference oil and rGO dispersed in engine were dropped on the surface of steel block. All tribometry tests were performed for a total time of 20 minutes.

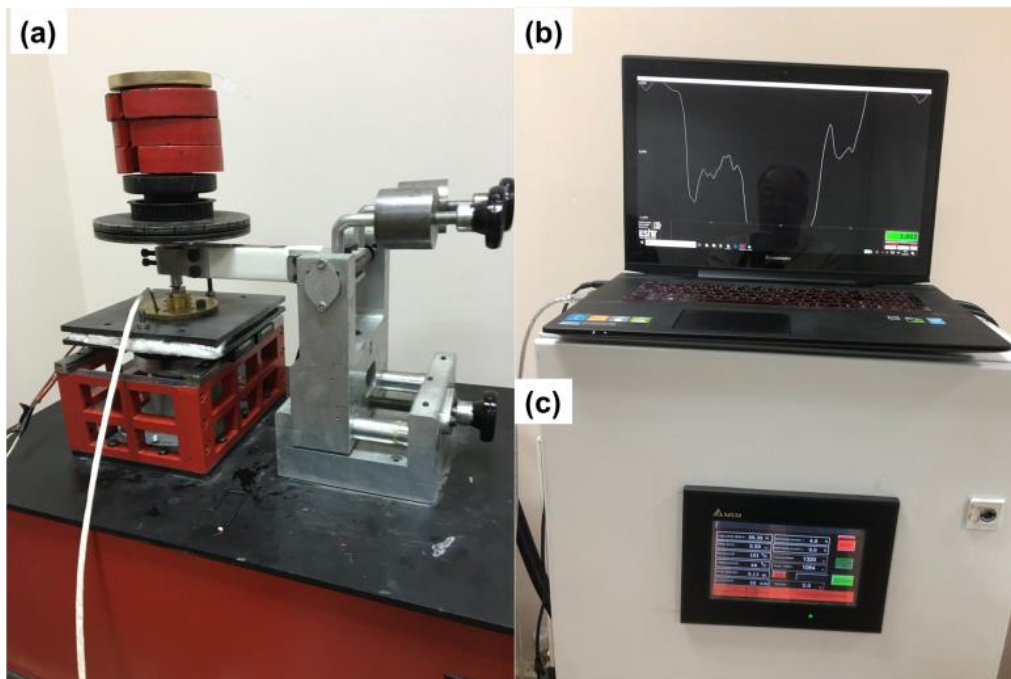


Figure 41: Reciprocating tribotest rig, (a) general view, (b) specimens mounted in the test rig, (c) heating control and temperature measurements.

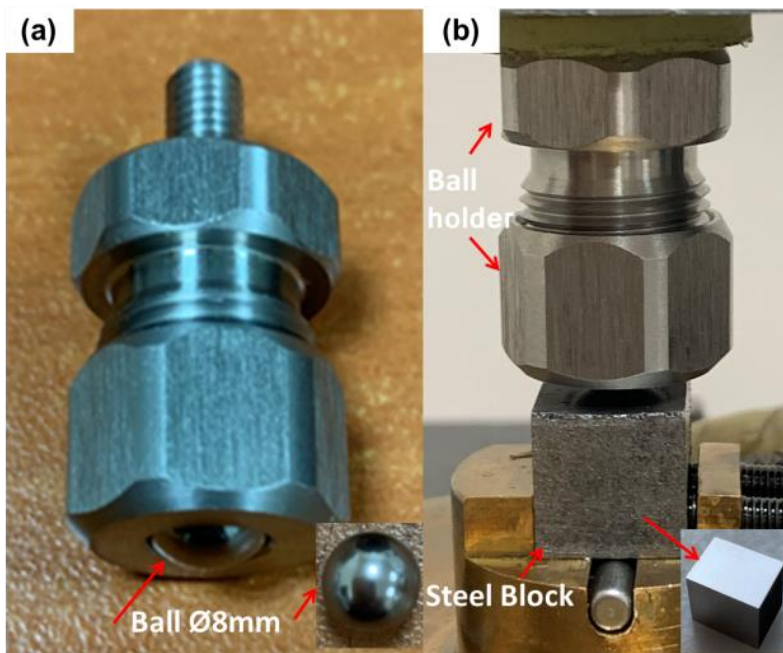


Figure 42: Ball and block specimens: (a) Ball placed in holder, (b) Steel Block and ball holder configuration

### 5.2.2 Viscometry measurements

Further study was performed to examine the viscosity of rGO in engine oil since it yielded the best results during tribological characterization. The experiments were carried out initially at 20 °C and then at 80 °C for rGO concentrations of 0 %w/w, 0.01 %w/w, 0.02 %w/w, 0.04 %w/w and 0.06 %w/w.

To perform viscosity measurements, a 600 mL beaker was first filled with plain engine oil. Then, it was placed on a hotplate at a controlled temperature of 20 °C. The viscometer's probe was submerged in the dispersion and the viscosity was measured. The increase of the temperature at 80 °C followed and the viscosity was measured once more. This method was repeated for all rGO-Engine oil dispersions.

## Chapter 6: Results and Discussion

### 6.1 Examining Turbidimetry results

As mentioned in chapter 5, the first characterization method performed was Turbidimetry for the determination of the samples' stability according to the concentration of the prepared dispersions, in order to extract some conclusions about their quality. The acquired results are listed in Table 9.

Concentration	Turbidity			
	rGO	SWCNTs	rGO + SWCNTs	MWCNTs
0.2	56	0	0	-
0.1	53	0	0	-
0.08	48.72	0	0	-
0.06	43.96	0	3.78	17.65
0.04	43.35	0	21.38	29.9
0.02	27.25	12.8	46.24	24.26
0.01	13.5	48.47	44.42	17.69

Table 9: Turbidity of rGO, SWCNTs, rGO and SWCNTs and MWCNTs in engine oil (5W-40)

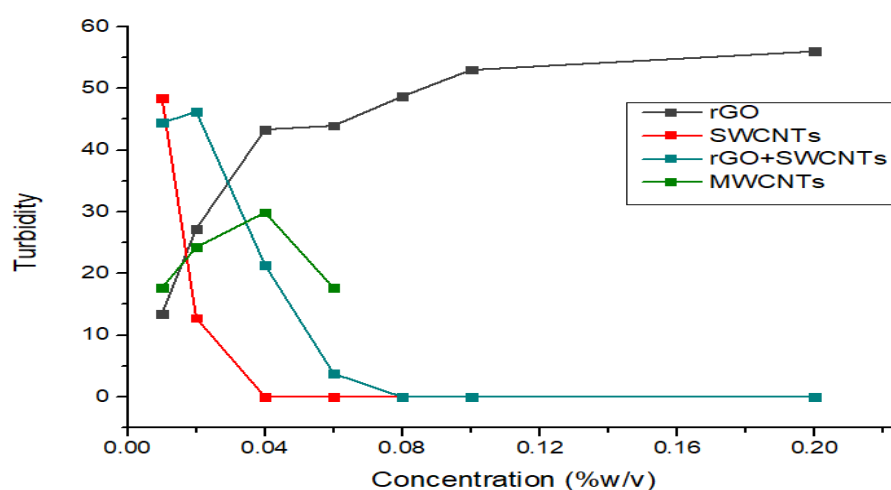


Figure 42: Turbidity to Concentration diagram of rGO (black), SWCNTs (red), rGO and SWCNTs (blue) and MWCNTs (green) in engine oil (5W-40)

A cloudy oil is due to the presence high concentration, that block the transmission of light. The turbidity values were then plotted as a function of rGO concentration (Figure 42). The diagram shows that rGO is the most stable additive in engine oil and as a result it's the most suitable for further examination. It is also evident that the samples rGO + SWCNTs and MWCNTs in engine oil, upon the increase of the additive concentration, turbidity was slightly increased and then suddenly decreased. For the sample incorporating SWCNTs, the turbidity decreases with the increase in SWCNTs concentration. On the other hand, rGO in engine oil gives different results. During the increase of the concentration, turbidity increases. Conclusively, engine oil accepts higher concentrations of rGO compared to the other additives.

### 6.2 Examining Tribological characterization results

The results of tribological characterization of rGO in engine oil are presented in the form of a bar graph in Figure 43, which shows that the coefficient of friction (COF) decreases as rGO concentration decreases. Since a small COF is desired, the most favorable concentrations of rGO as an additive in engine oil were 0.02 and 0.04%w/w.

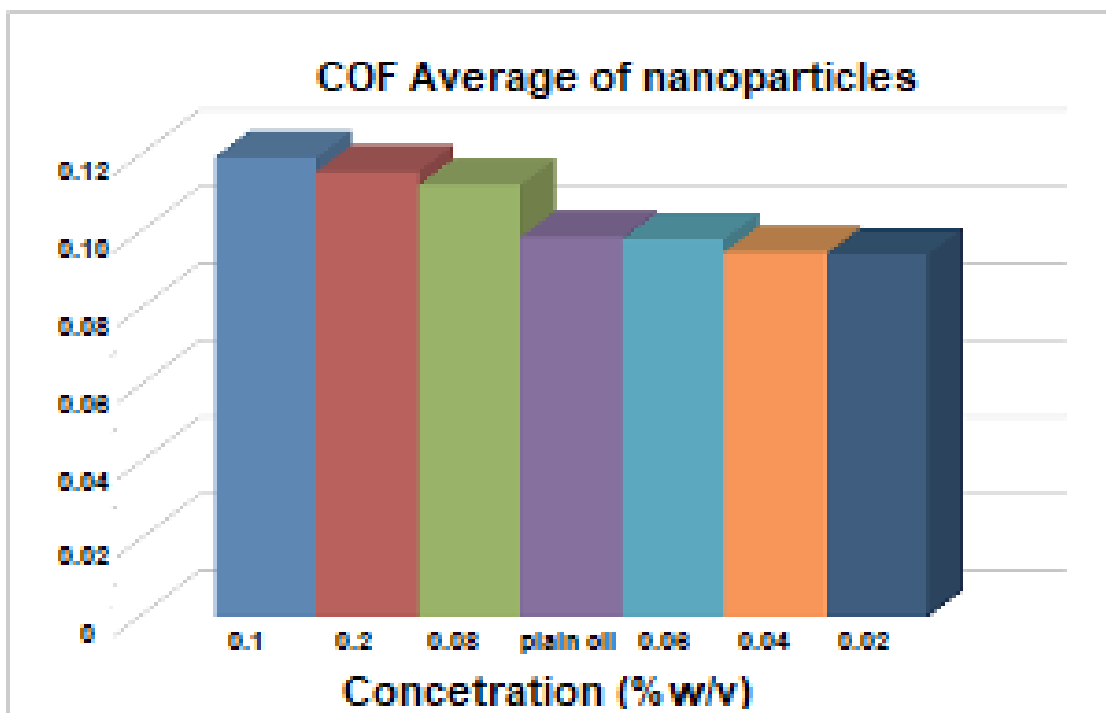


Figure 43: Coefficient of Friction of nanoparticles

### 6.3 Examining Viscometry results

Viscometry measurement were also performed for the samples of rGO in engine oil. The results of this study are presented in Table 10. The resulting viscosity values were also plotted as a function of rGO concentration, as seen in Figure 44 and Figure 45. The results showed that rGO 0.06% at 20°C and rGO 0.06% at 80°C had the closest viscosity values to than of plain engine oil at the same temperatures. It is important that the additive did not drastically change the engine oil's viscosity. Therefore, rGO at 0.06% concentration is the most suitable additive in terms of maintaining viscosity.

Concentration %w/w	Viscosity (mPa/s) at 20°C	Viscosity (mPa/s) at 80°C
0 (plain oil)	179.20	67.2
0.01	291.84	58.62
0.02	311.25	51.37
0.04	317.74	79.47
0.06	287.10	61.85

Table 10: Viscosity measurements at 20°C and 80°C of rGO in engine oil.

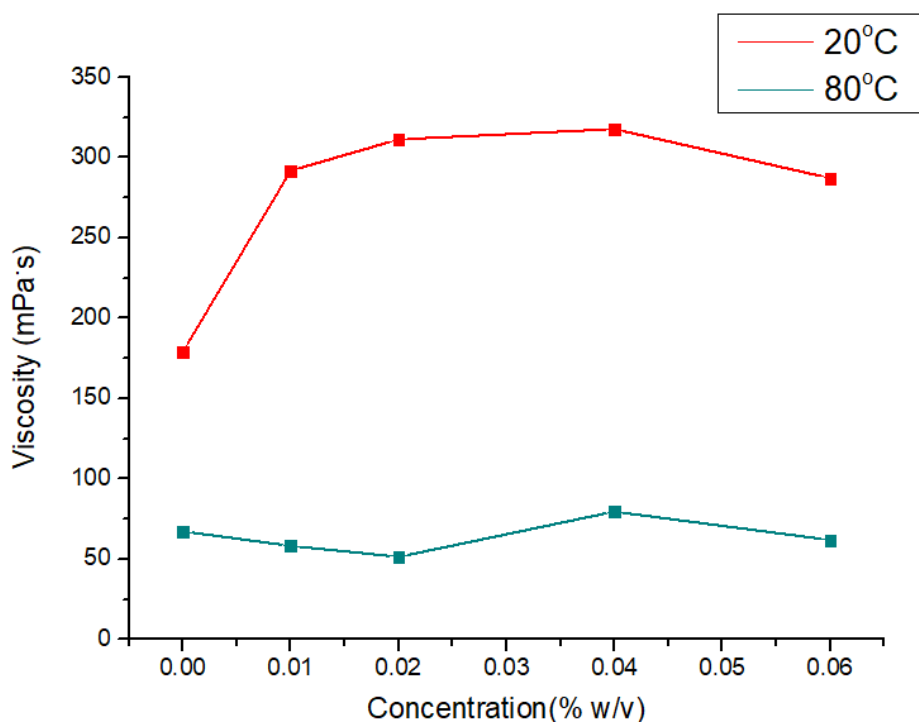
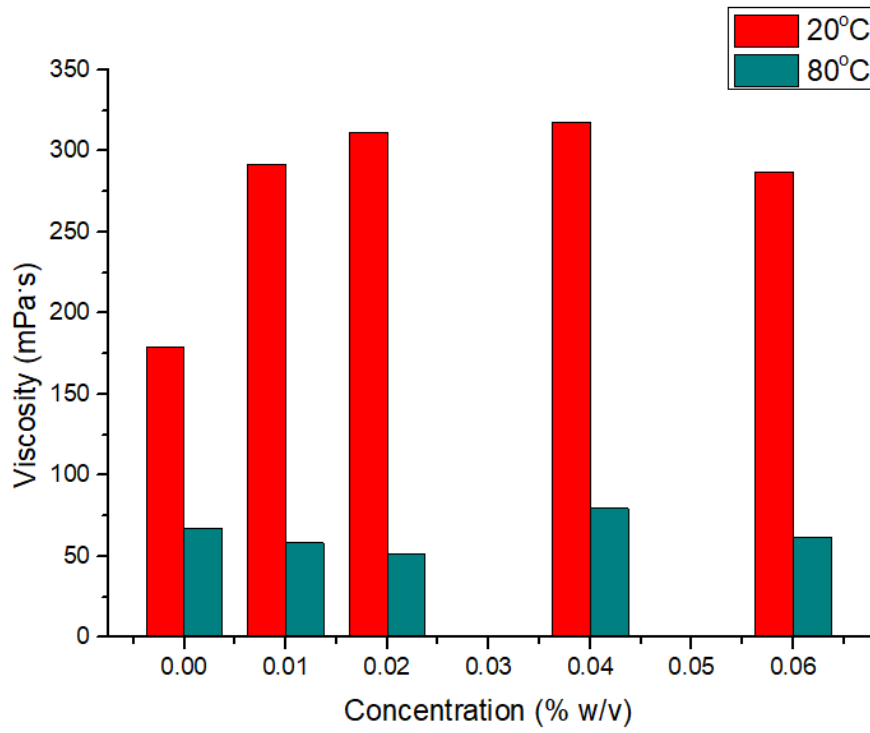


Figure 44: Viscosity over concentration of rGO in engine oil at 20°C and 80°C .



*Figure 45: Viscosity over concentration of rGO in engine oil at 20°C and 80°C.*

## Conclusions

In the present diploma thesis it was examined the behavior of different graphene-based additives in engine oil by investigating wear and friction. Samples of rGO, SWCNTs, SWCNTs + rGO and MWCNTs were added in 5W-40 engine oil at different ratios. The samples were first evaluated by turbidimetry method, which showed that rGO yielded the best results, since the increase in rGO concentration caused an increase in turbidity, without the presence of sediment. This means that engine oil accepts higher concentrations of rGO compared to the other additives. The tribological behavior of rGO in engine oil was also examined with results showing that optima rGO concentrations were 0.02 %w/w and 0.04 %w/w, for which the data showed decreased friction values. Finally, viscosity of rGO in oil was studied at 20 °C and 80 °C. The results revealed that the sample with closer viscosity to that of plain oil was the sample with 0.06% w/w rGO concentration. Considering the results in this diploma thesis, the main conclusion that can be drawn is that out of the examined additives, the most suitable additive in engine oil is rGO 0.06%w/w.

## Future Work

In order to promote the application of graphene-based materials as additives in engine oil, further research should be conducted in the following aspects. First, a clarification of the microscopic mechanisms with which the materials enhance the performance of engine oil. For example, in this work, hydroiodic acid assisted rGO was the champion additive in terms of enhancing the tribological properties and viscosity. It would be of great interest to study the role of rGO in chemical enhanced oil recovery and the mechanisms that take place during the interaction of rGO and the oil. The understanding of these mechanisms may prove to be a valuable tool in the research of engine oil additives. With advanced knowledge, researchers can more intently produce rGO based oil additives by focusing on the mechanism which is known to yield the most desired results. Moreover, by revealing the compatibility of rGO with other additives, such as surfactants within the engine oil it could expand the range of oils which can be improved in the future using rGO-based additives. It is also important to include a variety of rGO samples, i.e. different reduction degrees, different applied reducing agent etc. in this type of studies. This will not only aid in fully investigating the correlation between the rGO's structure and properties and the improvement in oil performance, but also to promote the discovery of the optimum rGO oil additive. Finally, putting forward the performance requirements of rGO, such as the fine-tuning of its properties via chemical functionalization, we could expand the range of effects this advanced nanomaterial provides on the enhancement of the engine oil performance.



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