Tarnish resistance of silver reinforced with carbon material to artificial sweat and hydrogen sulfide.

Miss Kunthida Chanthaban

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ความต้านทานการหมองของโลหะเงินที่เสริมด้วยวัสดุคาร์บอน ต่อเหงื่อเทียมและไฮโดรเจนซัลไฟด์

น.ส.กุลธิดา จันทะบาล

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By	Miss Kunthida Chanthaban
Field of Study	Chemical Engineering
Thesis Advisor	Professor JOONGJAI PANPRANOT, Ph.D.

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.... Dean of the FACULTY OF ENGINEERING
(Professor SUPOT TEACHAVORASINSKUN, D.Eng.)

THESIS COMMITTEE

.... Chairman
(Professor PAISAN KITTISUPAKORN, Ph.D.)
.... Thesis Advisor
(Professor JOONGJAI PANPRANOT, Ph.D.)
.... Examiner
(Professor ARTIWAN SHOTIPRUK, Ph.D.)
.... External Examiner
(Assistant Professor Patcharaporn Weerachawanasak, D.Eng.)

กุลธิดา จันทะบาล : ความต้านทานการหมองของโลหะเงินที่เสริมด้วยวัสดุคาร์บอนต่อเหงื่อเทียมและไฮโดรเจนซัลไฟด์. (Tarnish resistance of silver reinforced with carbon material to artificial sweat and hydrogen sulfide.) อ.ที่ปรึกษาหลัก : ศ.จูงใจ ปั้นประณต

เครื่องประดับเงินได้รับความนิยมเป็นอย่างมากจึงเป็นสินค้าที่น่าสนใจและมีการพัฒนามาอย่างต่อเนื่อง การเสื่อมสภาพของพื้นผิวของโลหะเงิน (การหมอง) ยังเป็นปัญหาที่สำคัญที่สุดของเครื่องประดับเงินคณะผู้วิจัยจึงได้ทำการศึกษาลักษณะของโลหะเงินที่เสริมด้วยวัสดุคาร์บอนโดยใช้วิธีการขึ้นรูปเหรียญ (Coin) และนำไปทดสอบความต้านทานการหมองของสีของโลหะเงินต่อเหงื่อเทียมและแก๊สไฮโดรเจนซัลไฟด์ ผลของตัวอย่างที่เติมวัสดุคาร์บอนหลังทดสอบเหงื่อเทียม พบว่าการเติมคาร์บอนที่มีกระจายตัวมากช่วยในเรื่องของการลดความหมองจากเหงื่อเทียมได้ดีกว่าเนื่องจากเมื่อเติม คาร์บอน (C) เข้าไปกระจายตัวในซิลเวอร์ (Ag) ทำให้พื้นที่ของซิลเวอร์ (Ag) น้อยลงส่งผลให้ลดการเกิดซิลเวอร์คลอไรด์ จะเห็นได้ว่ากลุ่มที่ 1 ให้ผลลัพธ์ที่ดีที่สุด เนื่องจากยิ่งมีหมู่ฟังก์ชันมากจึงช่วยในการกระจายตัวได้ดี และผลของตัวอย่างที่เติมวัสดุคาร์บอนหลังการทดสอบแก๊สไฮโดรเจนซัลไฟด์ พบว่าการเติมวัสดุคาร์บอนช่วยในเรื่องของการลดความดำจากแก๊สไฮโดรเจนซัลไฟด์ได้ดีกว่าการที่ไม่เติมโดยสารตัวเติมยิ่งมีปริมาณคาร์บอนมากยิ่งช่วยให้ลดความหมองได้มาก เนื่องจากเมื่อเติมวัสดุคาร์บอนเข้าไปแล้วคาร์บอน (C) จะไปช่วยสร้างพันธะกับซัลเฟอร์ (S) มากกว่าที่จะไปสร้างพันธะกับซิลเวอร์ (Ag) จึงทำให้ความหมองที่เกิดจากซิลเวอร์ซัลไฟด์ (Ag_2S) ลดน้อยลง

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....

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Due to its immense popularity, silver jewelry has undergone continual development, it an intriguing product. The most significant issue with silver jewelry is the tarnish of the silver metal's surface. Therefore, using a coin making technique, the study team evaluated the properties of silver metal reinforced by carbon materials. To evaluate the silver's to sweat and hydrogen sulfide tarnishing. Effects of adding carbon to samples after performing an artificial sweat test. It was discovered that the use of highly scattered carbon improved the ability to remove tarnish from fake sweat because it reduced the surface area of the silver (Ag) dispersion. to reduce silver chloride formation, It is evident that group 1 produces the best outcomes. The more functional group the groups, the better the distribution. Effects of samples with carbon after testing for hydrogen sulfide. It has been discovered that adding carbon materials in reducing tarnish from hydrogen sulfide better. Since carbon (C) helps from reaction with sulfur (S) rather than silver (Ag) when carbon material is added, the tarnish brought on by silver sulfide (Ag_2S) is reduced.

Field of Study:	Chemical Engineering	Student's Signature ....
Academic Year:	2023	Advisor's Signature ....

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The researcher would like to express his deepest gratitude here. Finally, the researcher hopes that this research will be useful for relevant agencies. and those interested in further study.

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CHAPTER I

INTRODUCTION

1.1 Introduction

The jewelry industry, such as gold, silver, platinum, etc., is an industry that adds value to the economy. According to statistics, exports of gems and jewelry excluding gold in 2022 were valued at 7,987.50 million in USD. An increase of 29.54% compared to the year 2021, where Thailand has exported jewelry ranked among the top in the world, with gold jewelry having the highest export rate. followed by silver jewelry Silver jewelry is an interesting product in terms of export value with a continuous growth rate. In 2022, silver jewelry exports were valued at 1,736.27 million in USD. 1.18% increase compared to 2021[1]

Silver jewelry is very popular and therefore an interesting product that has been continuously developed. Good quality silver must be 99.99% pure silver, but the commonly used to make jewelry is at 92.5%, known as 925 silver (Sterling Sliver), which is an international standard in the industry. Silver jewelry and the remaining 7.5% are other metals or alloys in silver. This is because pure silver is too soft and not as strong as it should be. Therefore, it is not popular to use pure silver in the production of jewelry. The most popular metal to mix with silver is copper because it helps to transform silver into a hardened property. and also makes the work piece more resistant to scratches It also results in the resulting silver having a shiny white appearance as well. But due to the properties of silver, when exposed to air containing sulfur will cause the surface of silver jewelry to become dull over time.

With that being said, silver surface deterioration or tarnishing is the most important problem of silver jewelry. Because it is greatly affected when exposed to air. In this respect, many studies have been conducted to examine the corrosion of silver upon exposure to air. And it is well known that when silver metal is exposed to air, which Sulfur (S) is an element. These substances when in contact with silver metal. will react and form a new substance called Silver sulfide (Ag_2S) is coated on the surface of silver metal. And since silver sulfide is a brown-black substance thus causing the silver to become tarnished Not as shiny as before. Silver sulfide In addition to being found in the air can also occur in humid conditions high salt as well Another factor found is that the copper added to increase the hardness of the silver when exposed to air causes a reaction to form a new substance. Copper oxide (Cu_2O), which is a reddish-brown substance. As a result, silver jewelry becomes tarnished as well. Currently, high concentrations of corrosive gases such as CO_2, H_2S and SO_2 are present in the environment as a result of environmental polluting activities. This makes silver more susceptible to corrosion when exposed to air. Therefore, it is important to find effective ways to resist tarnishing of silver. Currently, a number of solutions have been studied focusing on alloying silver with other metals such as Al, Ge, Si, Zn, Cd and P to prevent oxidation and tarnishing. The addition of germanium was found to slow down the tarnishing rate of silver. However, this method takes longer and requires higher temperatures which can lead to silver loss.[2, 3] In addition to the addition of germanium, rhodium is also used in silver jewelry to prevent tarnishing and increase luster, but rhodium is quite expensive. Studies have also shown that the lower cost nickel plating also provides good anti-tarnishing and gloss-enhancing properties as rhodium. But nickel in contact with skin can be harmful. It can cause redness or skin irritation, so it is not commonly used.[4] As mentioned above, reducing tarnishing by adding metal or metal coating still has a high cost and some metals also have side effects on human skin. Therefore, researchers are interested in developing fillers to reduce tarnishing of silver jewelry to have better efficiency and reduce production costs.

According to the research [5], it was found that the synthesis of graphene on silver foil by chemical vapor deposition (CVD) method inhibited the formation of silver sulfide. can prevent tarnishing due to Graphene reacts with sulfur better than silver. The research team therefore studied the characteristics of carbon-reinforced silver by using a coin forming method and tested the tarnishing resistance of silver to artificial sweat and hydrogen sulfide.

1.2 Objectives of the Research

To study the effect of type of carbon material on the tarnish resistance of silver reinforced with carbon material to artificial sweat and hydrogen sulfide.

1.3 Scopes of the Research

1. Filler powder CL-1, CL-2, CL-3, Graphene Oxide, Graphene, Graphene Rod, Carbon Black and Activated Carbon were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), thermogravimetric Analysis (TGA) and Fourier transform Infrared Spectroscopy (FTIR)

2. 500 mg Ag-301 powder (110 °C overnight) and Filler were mixed by grinding method, the concentration of Filler in the media was set to 0%, 0.5%, 0.7% and 1%. Then powder mixture was compressed by a hydraulic machine at a pressure of 100 kg/cm^2 for 30 seconds.

3.The fillers used in this study were Group 1 CL-1, CL-2 and CL-3 are classified as Carbon Synthetic with an average carbon content of approximately 42 Wt% and oxygen 15 Wt%., Group 2 Graphene Oxide classified as Carbon Oxide The average carbon content of approximately 60 Wt% and oxygen 36 Wt%., Group 3 Graphene, Graphene Rod, Carbon Black and Activated Carbon classified as Pure Carbon with an average carbon content of approximately 90 Wt% and oxygen 8 Wt%.

4.Sample Coin added CL-1, CL-2, CL-3, Graphene Oxide, Graphene, Graphene Rod, Carbon Black and Activated Carbon in the media was set to 0%, 0.5%, 0.7% and 1%. before tarnish tests were characterized by Colorimeter.

5.Sample Coin added carbon Group 1, Group 2 and Group 3 before tarnish test were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

6. Take the molded sample coin to tests for identification of silver tarnishing by Hydrogen Sulfide (H_2S), Place the sample so that the H_2S gas covers the area to be tested for 15 seconds.

7. Take the molded sample coin to tests for identification of silver tarnishing by Sweat, Put the sample under 20 mL of media to be tested for 15 seconds.

8. Sample Coin added CL-1, CL-2, CL-3, Graphene Oxide, Graphene, Graphene Rod, Carbon Black and Activated Carbon in the media was set to 0%, 0.5%, 0.7% and 1%. After tarnish tests were characterized by Colorimeter.

9.Sample Coin added carbon Group 1, Group 2 and Group 3 after tarnish test were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

CHAPTER II

BACKGROUND AND LITERAURE REVIEWS

2.1 Properties of silver

2.1.1 Physical Properties

Silver displays brilliant metallic luster and it can be well polished to refine the shiny appearance. Its shine is so well recognized that a colour itself is named after the element. Silver is a soft transition metal. It is ductile and malleable. The thermal conductivity of silver is highest of all materials and the electrical conductivity of silver is highest among all metals. With the following qualifications:

- Silver has two stables naturally occurring isotopes; silver-107 and silver-109. Both are found in almost equal quantities in nature with silver-107 being only slightly more abundant.
- The atomic mass of silver is 107.87
- The melting point of silver is 962°C
- The boiling point of silver is 2212°C
- The density of silver is 10500 in S.I. units at 20°C

2.1.1 Chemical Properties

Silver is quite an unreactive metal. The first ionization energy of silver is lowest compared to all other elements in group-11. The silver reacts with sulfur and its compounds, the silver metal is attacked by strong oxidizers. Most common oxidation states of silver are +1 and +2. The state of +3 is also observed rarely. [6]

2.2 Parameters of silver tarnish

The reactions of sulfureted compounds with other elements can even turn out to be on a greater scale than those of sulfide compounds with silver. A list of the main reactions between silver alloys and chemical agents present in the environment is shown in Table 1.

Table 1 List of the main chemical reactions involved in the tarnishing processes. [7]

Reaction	**Equilibrium constant (K, 25°C)**	**Compound name**	**Color**[24]
$2Ag+H_2S+0.5O_2 \rightarrow Ag_2S+H_2O$	6.117×10^{42}	silver sulfide	black, grey-black
$2Cu + H_2S +0.5O_2 \rightarrow Cu_2S + H_2O$	6.568×10^{50}	copper sulfide	blue-black
$Cu_2O + H_2S \rightarrow Cu_2S + H_2O$	8.197×10^{24}	copper sulfide	blue-black
$GeO_2 + 2H_2S \rightarrow GeS_2 + 2H_2O$	19.36	germanium sulfide	black
$SnO + H_2S \rightarrow SnS + H2O$	2.89×10^{10}	stannic sulfide	brown-black, grey
$ZnO + H_2S \rightarrow ZnS + H_2O$	2.292×10^{14}	zinc sulfide	white
$SiO_2 + 2H_2S \rightarrow SiS_2 + 2H_2O$	6.840×10^{-35}	silicon sulfide	white or grey
$B_2O_3 + 3H_2S \rightarrow B_2S_3 + 3H_2O$	1.761×10^{-59}	boron sulfide	white-yellow
$Cu + O_2 + 2NO_2 \rightarrow Cu(NO_3)_2$	2.736×10^{37}	copper nitrate	blue
$Ag + NO_2 \rightarrow AgNO_2$	6.426×10^{5}	silver nitrite	yellow-grey
$Ag + 0.5SO_2 + 0.25O_2 \rightarrow 0.5Ag_2SO_3$	5.682×10^{9}	silver sulfite	---
$Cu + 0.5SO_2 + 0.5O_2 \rightarrow 0.5Cu2SO_4$	1.117×10^{31}	copper sulfate	green
$2Ag + Cl_2 \rightarrow 2AgCl$	---	silver chloride	white
$SiO_2 + 2H_2S \rightarrow SiS_2 + 2H_2O$	6.840×10^{-35}	silicon sulfide	white or grey

Note: The second column shows an equilibrium constant, which indicates the tendency of the reaction to occur at a temperature of 25°C. A value of the equilibrium constant that is greater than 1 indicates that the reaction takes place spontaneously. High values of K indicate a high tendency for the reaction to occur. Vice-versa, values of the equilibrium constant below 1 show that the reaction does not tend to occur spontaneously.

2.3 Hydrogen sulfide removal by Carbon

Hydrogen sulfide (H_2S) is one of the factors that cause silver to tarnish. Currently, the removal of hydrogen sulfide by carbon has attracted increasing attention. Among many materials, carbon is considered a good hydrogen sulfide remover. Carbon absorbs sulfur (C−S) as shown in Figure 1. From the above, the researchers hypothesized that adding carbon to carbon (C) in silver jewelry will absorb sulfur (S) reduces the formation of silver sulfide (Ag_2S) that has a black brown colour, which causes silver to become dull.

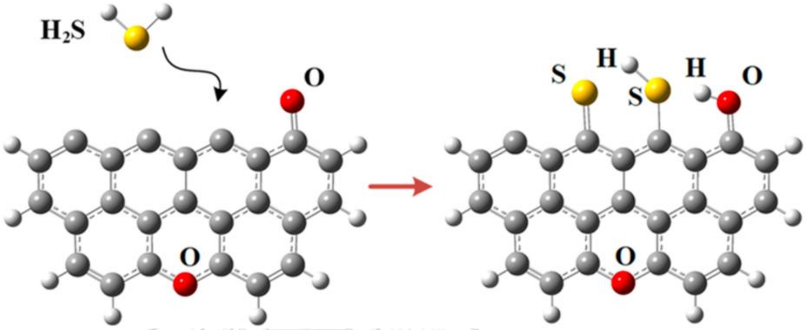


Figure 1 Removal of hydrogen sulfide using carbon.[8]

2.4 Tarnish Test

Most of the silver was found to be tarnished. Sulfidation, or the corrosion of sulfur-containing metals, is what causes tarnishing [3]. It creates brown-black silver sulfide (Ag_2S). Due to the process that tarnishes silver in the atmosphere, the test uses sulfur-tarnishing test samples such hydrogen sulphide (H_2S). containing H_2S, or hydrogen sulfide at below

$$2Ag + H_2S + 1/2O_2 \dashrightarrow Ag_2S + H_2O$$

The electronics industries in Japan, Europe, and the USA have all established a number of standards for corrosion testing. The majority of these standards specify the fuming process and require for sulfur concentrations between 400 and 30,000 ppb. Contrarily, it's unexpected that the jewelry business demands sulfur concentrations as high as 4 million ppb. When studies are conducted to compare corrosion test results with actual usage, such intense concentration could result in incorrect conclusions. The tarnishing tests was based on a fuming test in a closed environment with exposure to 0.4% H2S atmosphere. There are many pathways to achieving such atmospheric conditions. In our experiment, the H_2S atmosphere was achieved by reacting 0.21 grams of potassium sulfide (K_2S) with 21 ml of hydrochloric acid (HCl) at 1 Molar concentration. The reaction is governed by the following equation: [9]

$$K_2S_{(s)} + 2HCl_{(aq)} \rightarrow 2KCl_{(s)} + H_2S_{(g)}$$

Silver jewelry was placed in a sack for six months to test it. Silver jewelry was discovered to be tarnished, and upon examination, a little quantity of sulfur was discovered. This suggests that oxygen may also contribute to the corrosion of silver jewelry [9]. In an oxygen environment, silver tarnishes as a result of the process that produces the dark substance silver oxide (Ag_2O). Reaction at below

$$4Ag + O_2 \text{--->} 2Ag_2O$$

There are also other variables that can tarnish money, such as the user's sweat, which may be exposed to sulfur from their daily diet. Many pungent vegetables, such as broccoli, cabbage, and peanuts, are known to be high in sulfur. causing a high concentration of sulfur in sweat as well May result in making more money tarnished In addition, the acidity and alkalinity of sweat had a great influence on silver tarnishing.

The pH of human sweat is generally around 6-7. The artificial sweat used in this test was prepared according to EN 1811:2011 by mixing urea (0.1 wt%), sodium chloride (0.5 wt%) and lactic acid (0.1 wt%) in deionized water yielded a solution pH of 6.5 ± 0.05 [10]

2.5 Colour measurement techniques by Colorimeter

Colour is an optical property that characterizes the appearance of products and is taken as one of the parameters in product standardization. The colour measurement process by the eyes of ordinary people may have high discrepancies. To reduce colour measurement errors due to eyes and light sources, the International Commission on Illumination (CIE) has established a sample colour difference measurement against a standard sample. which can be obtained from the difference between brightness, red-green and the yellow-blue colour as shown in Figure 2.

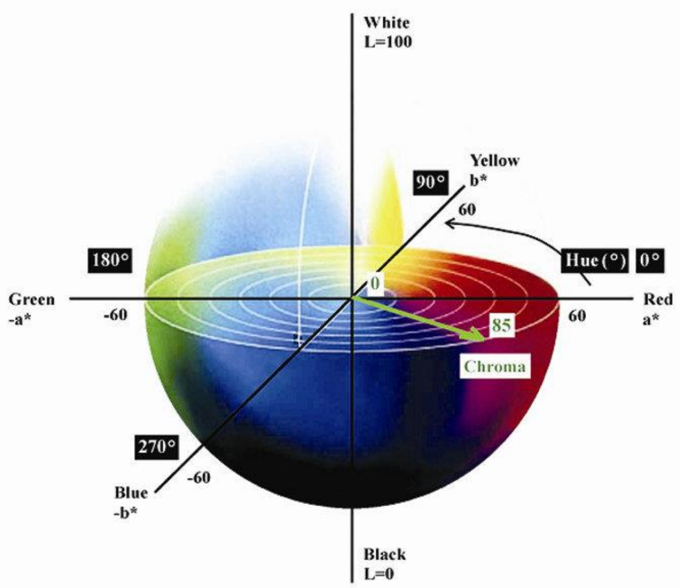


Figure 2 L*a*b* colour Chart by International Commission on Illumination (CIE) [11]

L^* is represents Lightness

a^* is represents the Redness/Greenness axis

b^* is represents the yellowness/blueness axis

ΔE is used to express Delta Error, the total colour difference computed using a colour difference equation. The colour difference is generally calculated as the square root of the combined squares of the chromaticity differences, Δa^* and Δb^*, and the Lightness difference, ΔL.

The colour difference between the sample and the standard sample can be found as the equation.

$$\Delta L^* = L^* \text{of the standard sample} - L^* \text{of the sample} \tag{1}$$

$$\Delta a^* = a^* \text{of the standard sample} - a^* \text{of sample} \tag{2}$$

$$\Delta b^* = b^* \text{ of the standard sample} - b^* \text{ of sample} \tag{3}$$

If ΔL^* is small, it means that there is little change from the original colour.

Δa^* is positive means very green, Δa^* is negative means very red.

Δb^* is positive means very blue, Δb^* is negative means very blue.

In addition to telling the difference by ΔL^*, Δa^*, Δb^*, it can tell the total colour difference between the sample and the standard sample (total colour difference) ΔE when

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \tag{4}$$

CHAPTER III

MATERIALS AND METHODS

3.1 Materials

Table 2 Chemicals used as filler.

NO.	Filler	Element CK (Wt%)	 NK (Wt%)	 OK (Wt%)	 SK (Wt%)	Suppliers
1	CL-1	40.05	21.61	22.69	15.66	Crystallyte co., ltd.
2	CL-2	43.00	14.27	17.55	25.19	Crystallyte co., ltd.
3	CL-3	42.92	15.94	13.04	28.10	Crystallyte co., ltd.
4	Graphene Oxide	59.72	1.90	35.66	2.71	Luoyang Tongrun Nano Technology
5	Graphene	89.00	2.58	7.77	0.65	Sigma Aldrich
6	Graphene Rod	86.46	2.85	9.94	0.75	Alfa Aesar, Thermo Fisher Scientific
7	Carbon Black	91.93	1.63	6.23	0.22	Alfa Aesar, Thermo Fisher Scientific
8	Activated Carbon	89.69	2.21	7.28	0.81	-

Note: Group 1 CL-1, CL-2 and CL-3 are classified as Carbon Synthetic with an average carbon content of approximately 42 Wt% and oxygen 15 Wt%.

Group 2 Graphene Oxide classified as Carbon Oxide The average carbon content of approximately 60 Wt% and oxygen 36 Wt%.

Group 3 Graphene, Graphene Rod, Carbon Black and Activated Carbon classified as Pure Carbon with an average carbon content of approximately 90 Wt% and oxygen 8 Wt%.

Table 3 Chemical used as the experiment.

NO.	Name	Formula	Suppliers
1	Silver Nano Powder	Ag-301	Prime Nanotechnology Co.,Ltd.
2	Potassium sulfide	K_2S	KemAus
3	Hydrochloric Acid	HCl	KemAus
4	Sodium Chloride	NaCl	Loba Chemie Pvt. Ltd.
5	Lactic acid	$C_3H_6O_3$	Chemipan Corporation Co., Ltd.
6	Urea	CH_4N_2O	Market

3.2 Preparation of silver coin sample.

500 mg Ag-301 powder (110 °C overnight) and Filler were mixed by grinding method, the concentration of Filler (CL-1, CL-2, CL-3, Graphene Oxide, Graphene, Graphene Rod, Carbon Black and Activated Carbon) in the media was set to 0%, 0.5%, 0.7% and 1%. Then powder mixture was compressed by a hydraulic machine at a pressure of 100 kg/cm^2 for 30 seconds.

3.3 Comparative tests for identification of silver tarnishing.

3.3.1 Hydrogen Sulfide (H_2S) Tarnish.

210 mg of Potassium sulfide, and 21 mL Hydrochloric Acid 1N were added on beaker. Place the sample so that the gas covers the area to be tested for 15 seconds. After that sample were characterization with in 24 hours.

3.3.2 Sweat Tarnish.

Media solution 20 mL were generated for 1 sample by adding 100 mg of Sodium chloride, 20 mg of Lactic acid and 20 mg Urea to 19.56 mL of DI water. Put the sample under 20 mL of media to be tested for 15 seconds. After that sample were characterization with in 5 minutes.

3.4 Characterization

3.4.1 Colorimeter

Sample the Coin added CL-1, CL-2, CL-3, Graphene Oxide, Graphene, Graphene Rod, Carbon Black and Activated Carbon in the media was set to 0%, 0.5%, 0.7% and 1%. were characterized by Colorimeter of UltraScan VIS-USVIS2143 to standard colour difference measurements will be taken. to make a comparison with the colour of the sample to be used to assess the quality of the sample.

3.4.2 Scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX).

Sample the Coin added carbon Group 1, Group 2 and Group 3 were characterized by scanning electron microscopy (SEM) of Hitachi mode S-3400N and energy dispersive X-ray spectroscopy (EDX) to investigate the morphology of the surface and the bulk composition, respectively.

3.4.3 Thermogravimetric Analysis (TGA)

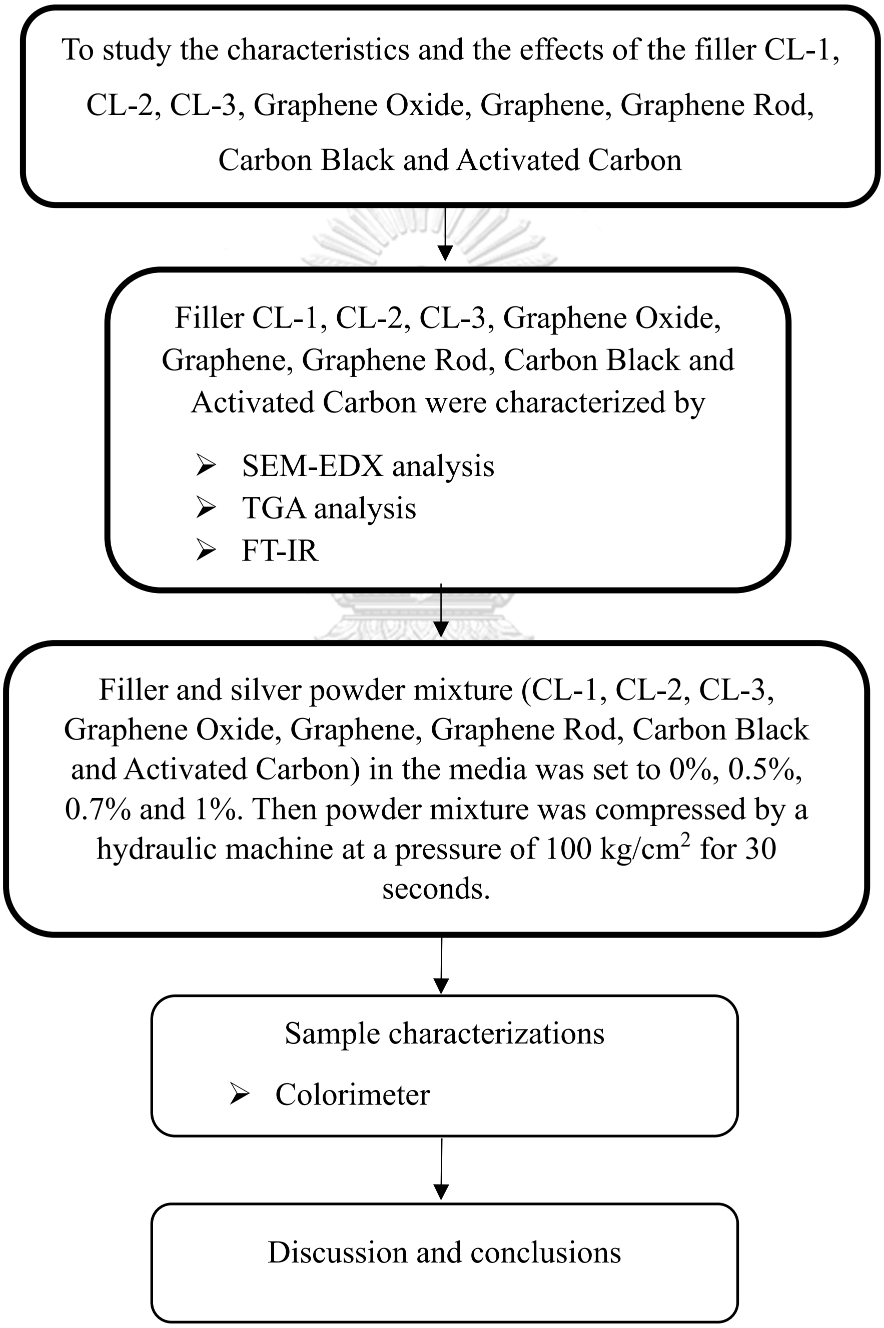
Sample the Coin added carbon Group 1, Group 2 and Group 3 were characterized by thermogravimetric analysis (TGA) of 1000 °C under nitrogen to determine the filler powder lost weight when the temperature change.

3.4.4 Fourier transform Infrared Spectroscopy (FTIR)

Sample the Coin added carbon Group 1, Group 2 and Group 3 were characterized by Fourier transform Infrared Spectroscopy (FTIR) to determine the function group of filler.

3.5 Research methodology

Part I. To study the characteristics of filler and the effect of the amount of carbon material added per default colour of silver.



To study the characteristics and the effects of the filler CL-1, CL-2, CL-3, Graphene Oxide, Graphene, Graphene Rod, Carbon Black and Activated Carbon

Filler CL-1, CL-2, CL-3, Graphene Oxide, Graphene, Graphene Rod, Carbon Black and Activated Carbon were characterized by

- SEM-EDX analysis
- TGA analysis
- FT-IR

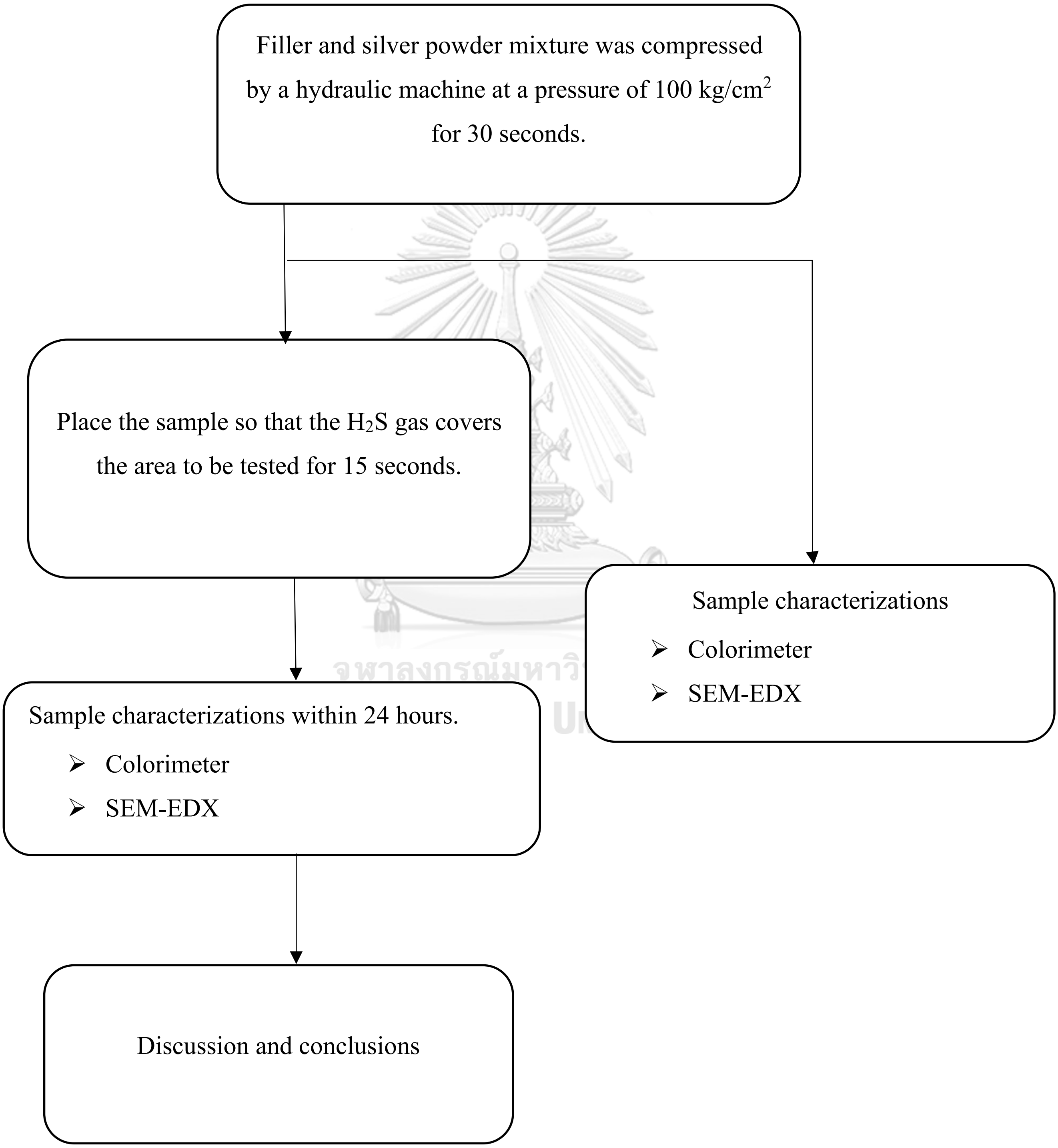
Filler and silver powder mixture (CL-1, CL-2, CL-3, Graphene Oxide, Graphene, Graphene Rod, Carbon Black and Activated Carbon) in the media was set to 0%, 0.5%, 0.7% and 1%. Then powder mixture was compressed by a hydraulic machine at a pressure of 100 kg/cm^2 for 30 seconds.

Sample characterizations

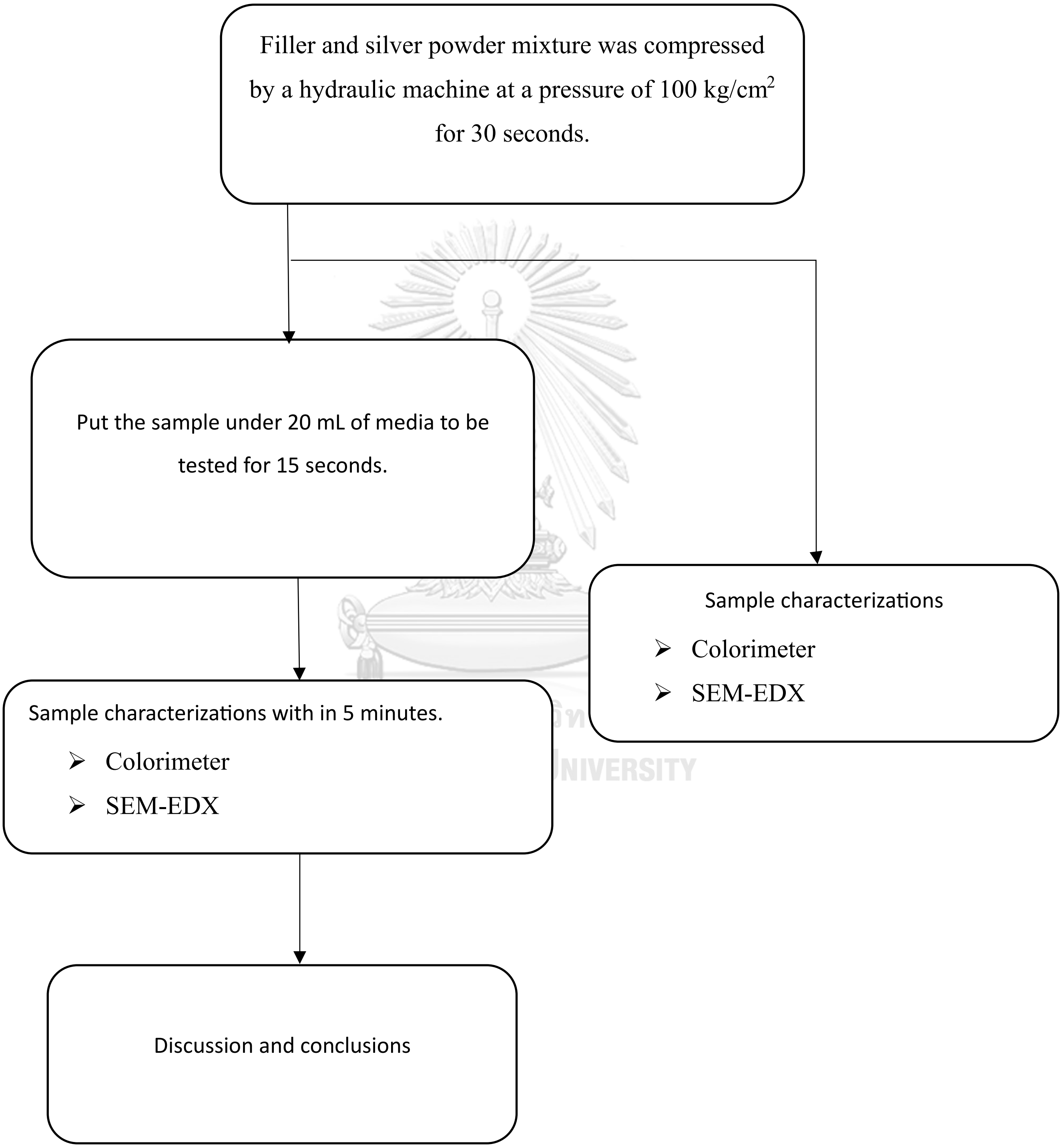
- Colorimeter

Discussion and conclusions

Part II. To compare the colour difference of the sample before and after tarnish and characteristic by SEM-EDX to be used to assess the quality of the sample passed H_2S tarnish method.



Part III. To compare the colour difference of the sample before and after tarnish and characteristic by SEM-EDX to be used to assess the quality of the sample passed sweat tarnish method



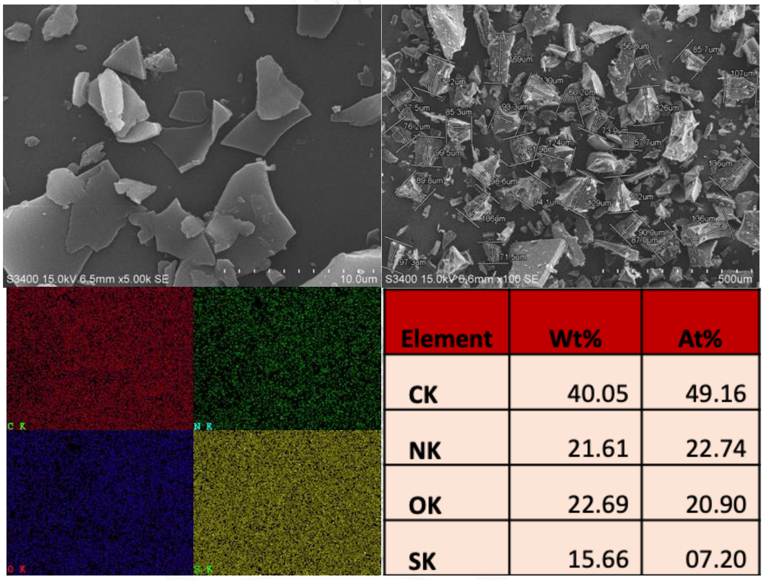
CHAPTER IV

RESULTS AND DISCUSSION

Part I. To study the characteristics of filler and the effect of the amount of carbon material added per default color of silver.

4.1 Characterization of filler.

4.1.1 Scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX), Thermogravimetric analysis (TGA) of CL-1 filler.



Element	Wt%	At%
CK	40.05	49.16
NK	21.61	22.74
OK	22.69	20.90
SK	15.66	07.20

Figure 3 SEM-EDX images of CL-1 filler.

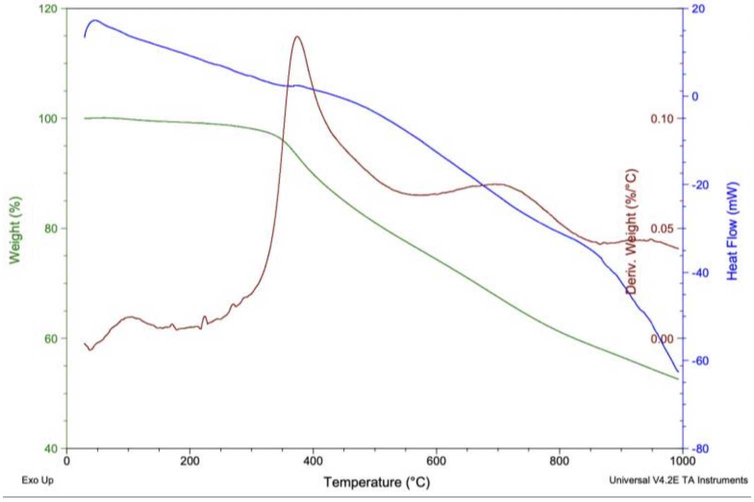
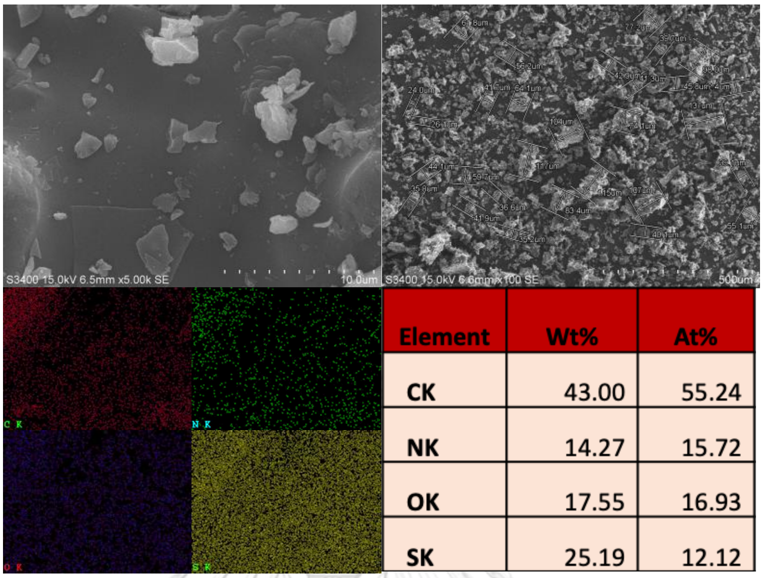


Figure 4 TGA images of CL-1 filler

4.1.2 Scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX), Thermogravimetric analysis (TGA) of CL-2 filler.



Element	Wt%	At%
CK	43.00	55.24
NK	14.27	15.72
OK	17.55	16.93
SK	25.19	12.12

Figure 5 SEM-EDX images of CL-2 filler.

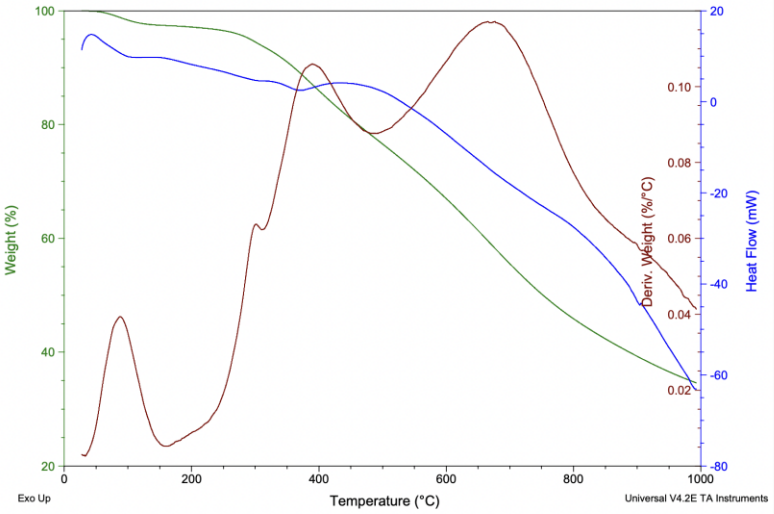
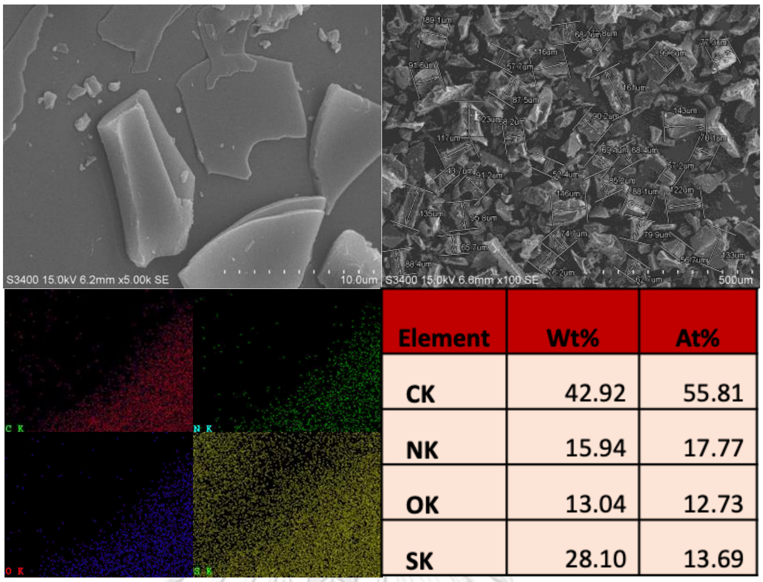


Figure 6 TGA images of CL-2 filler

4.1.3 Scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX), Thermogravimetric analysis (TGA) of <u>CL-3 filler.</u>



Element	Wt%	At%
CK	42.92	55.81
NK	15.94	17.77
OK	13.04	12.73
SK	28.10	13.69

Figure 7 SEM-EDX images of CL-3 filler.

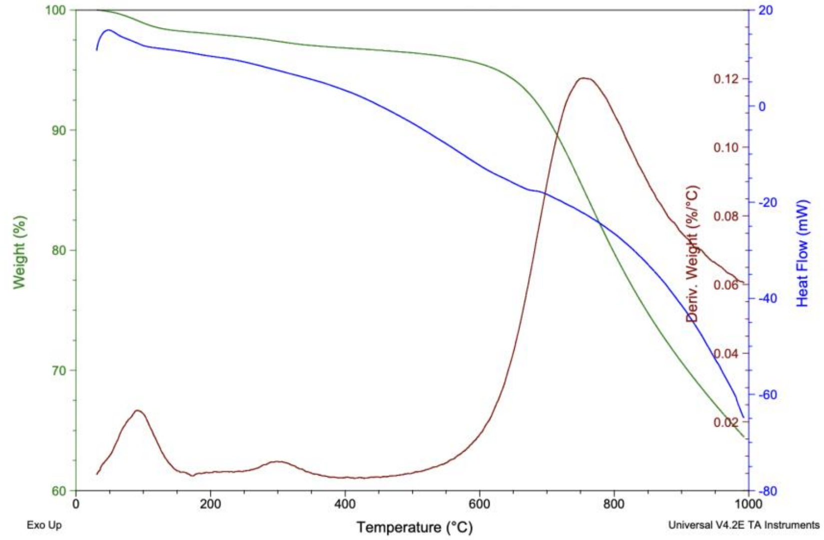
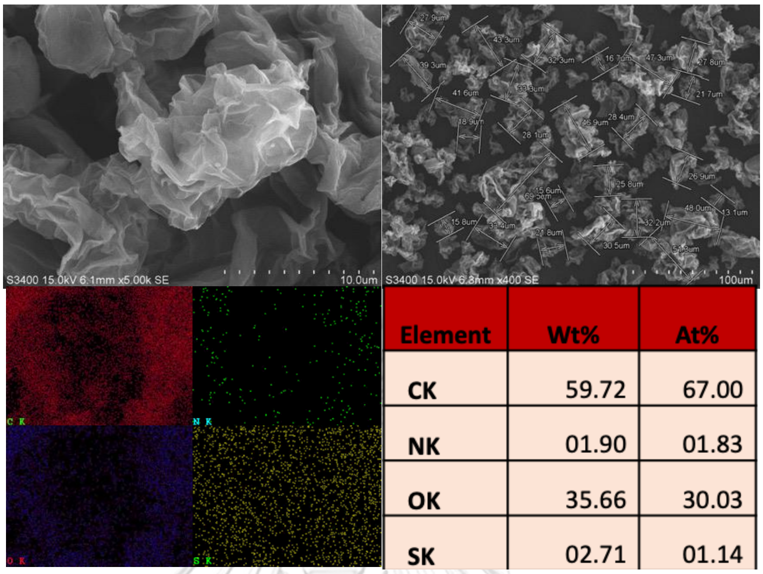


Figure 8 TGA images of CL-3 filler

4.1.4 Scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX), Thermogravimetric analysis (TGA) of Graphene Oxide filler.



Element	Wt%	At%
CK	59.72	67.00
NK	01.90	01.83
OK	35.66	30.03
SK	02.71	01.14

Figure 9 SEM-EDX images of Graphene Oxide filler

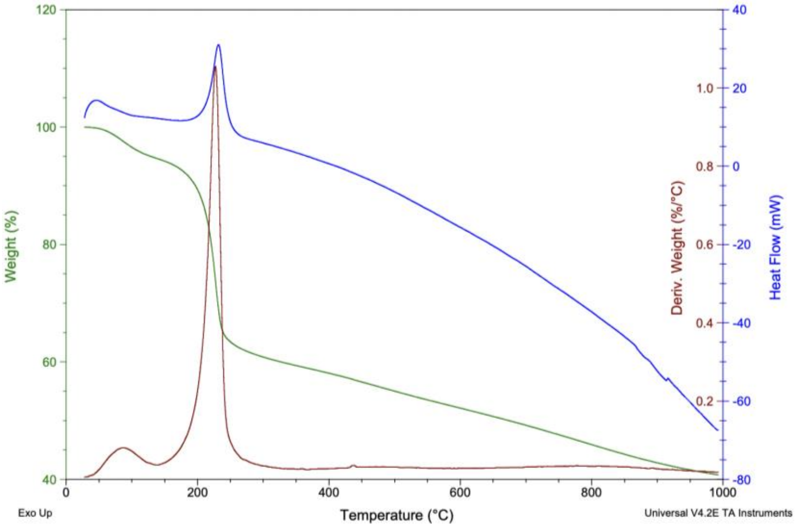
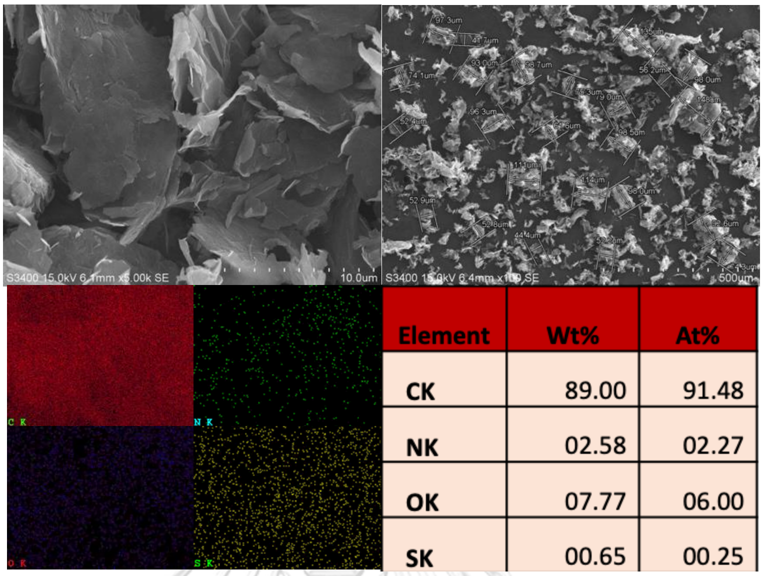


Figure 10 TGA images of Graphene Oxide filler

4.1.5 Scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX), Thermogravimetric analysis (TGA) of <u>Graphene filler.</u>



Element	Wt%	At%
CK	89.00	91.48
NK	02.58	02.27
OK	07.77	06.00
SK	00.65	00.25

Figure 11 SEM-EDX images of Graphene filler

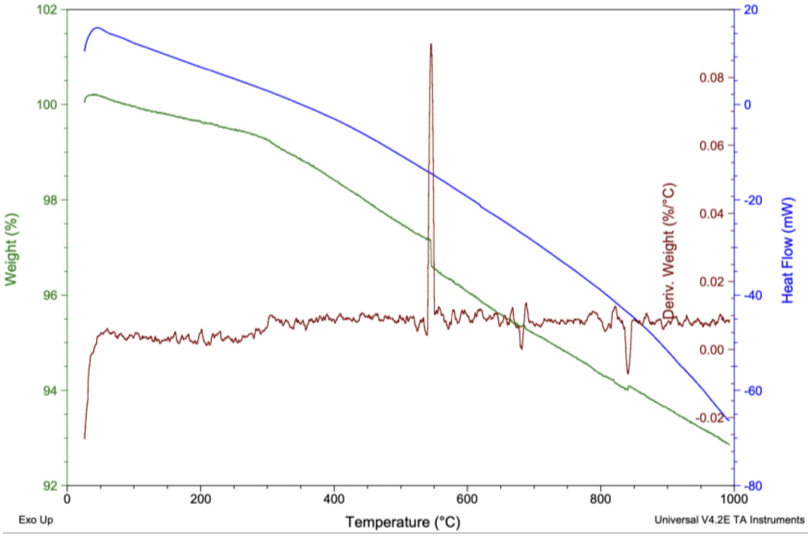
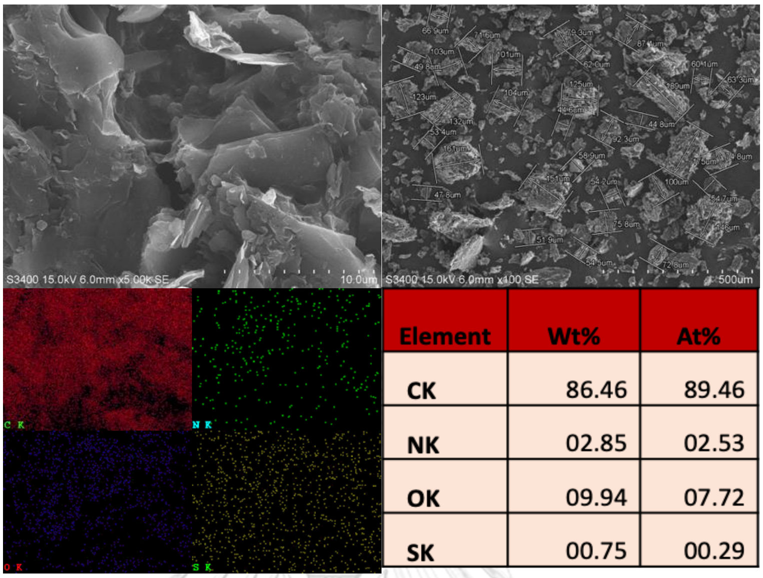


Figure 12 TGA images of Graphene filler

4.1.6 Scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX), Thermogravimetric analysis (TGA) of <u>Graphene Rod filler.</u>



Element	Wt%	At%
CK	86.46	89.46
NK	02.85	02.53
OK	09.94	07.72
SK	00.75	00.29

Figure 13 SEM-EDX images of Graphene Rod filler

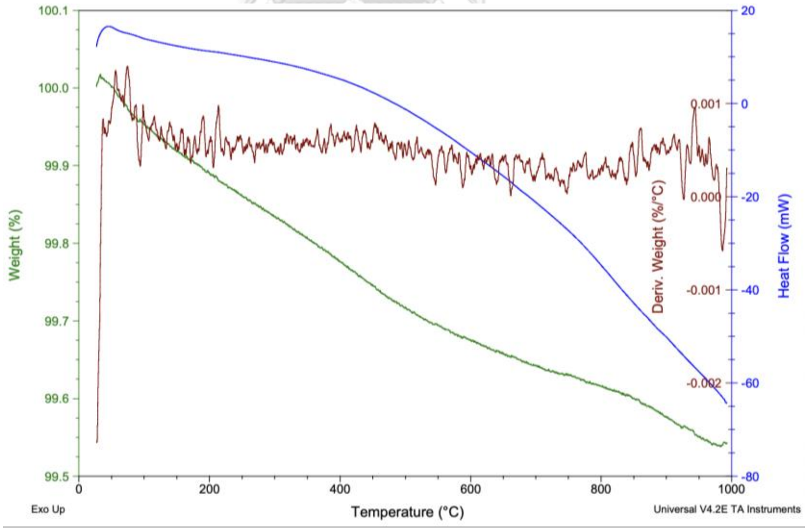
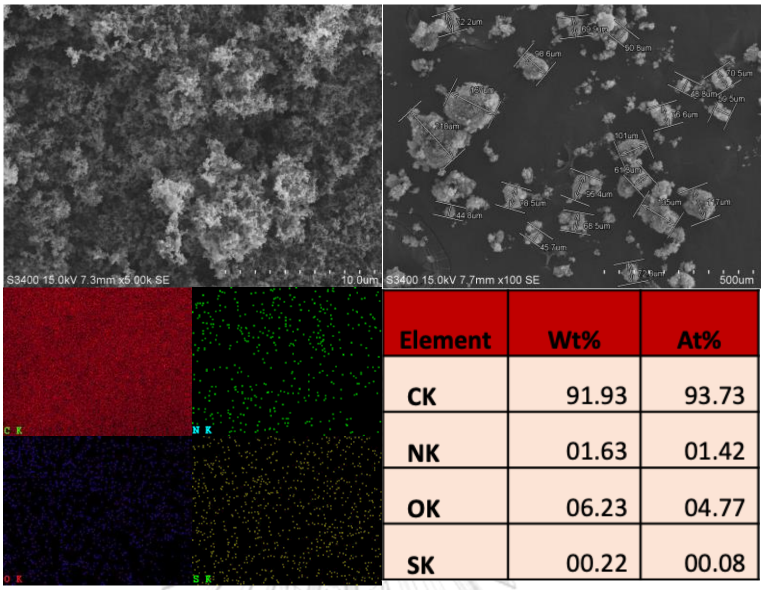


Figure 14 TGA images of Graphene Rod filler

4.1.7 Scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX), Thermogravimetric analysis (TGA) of Carbon Black filler.



Element	Wt%	At%
CK	91.93	93.73
NK	01.63	01.42
OK	06.23	04.77
SK	00.22	00.08

Figure 15 SEM-EDX images of Carbon Black filler

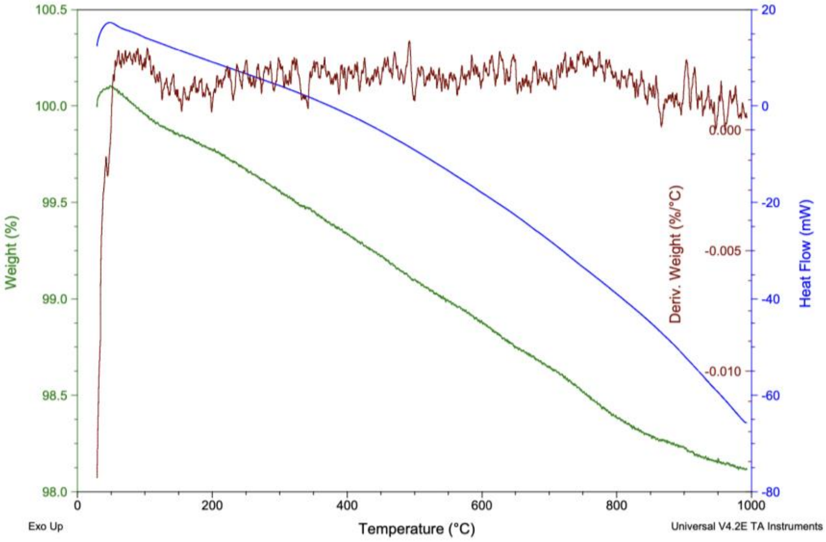
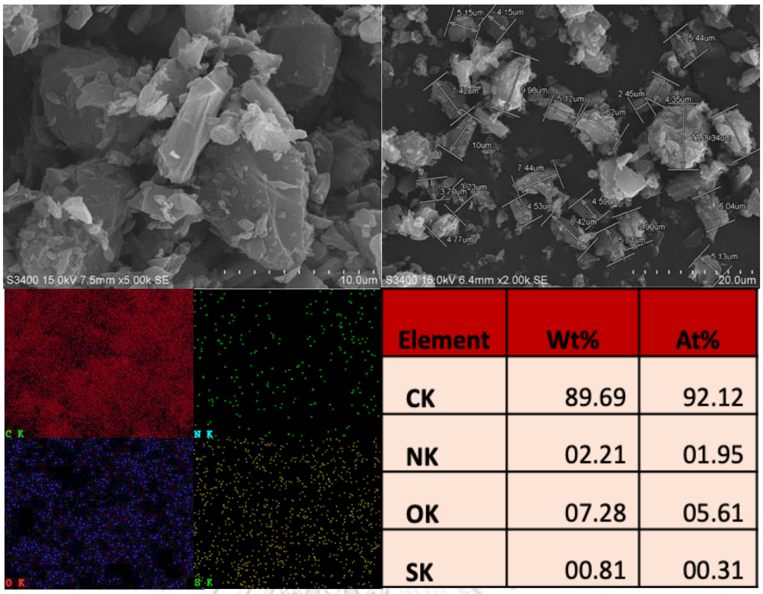


Figure 16 TGA images of Carbon Black filler

4.1.8 Scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX), Thermogravimetric analysis (TGA) of Activated Carbon filler.



Element	Wt%	At%
CK	89.69	92.12
NK	02.21	01.95
OK	07.28	05.61
SK	00.81	00.31

Figure 17 SEM-EDX images of Activated Carbon filler

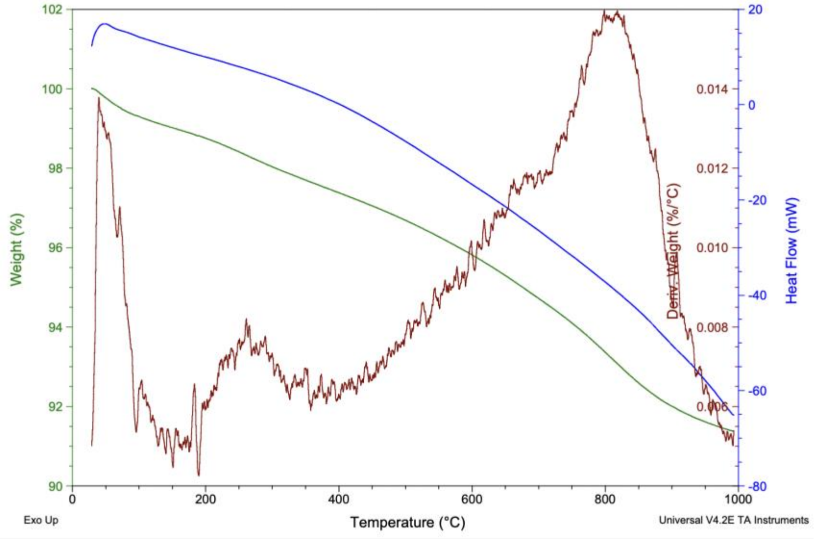


Figure 18 TGA images of Activated Carbon filler

4.1.9 Fourier transform Infrared Spectroscopy (FTIR)

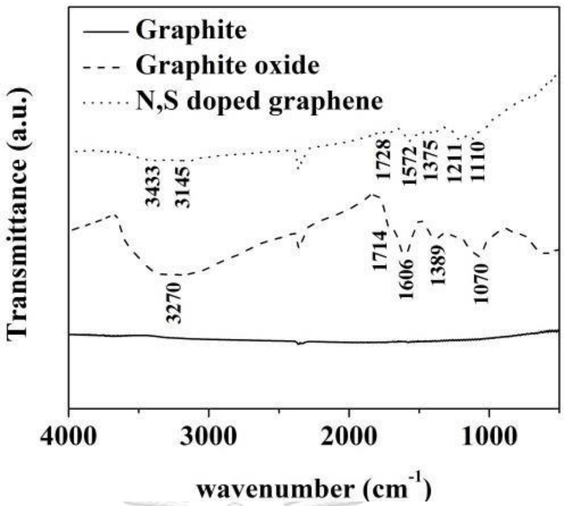


Figure 19 FT-IR spectra of N, S doped graphene, graphite oxide and graphite.

The FT-IR spectra of N, S-G reveals the peak at 3145 cm^{-1} and 3433 cm^{-1} attributing to N-H and O-H stretching vibrations, respectively. These considerable amino and hydroxyl groups can enable hydrophilicity. The peak at around 1728 cm^{-1} corresponds to the stretch vibration of C=O carboxylic groups and the peak at 1375 cm^{-1} can be assigned to the vibration of C-N. Furthermore, the existence of C-O and S=O bonds on N, S-G is confirmed by the peak of 1211 and 1110 cm^{-1}, respectively.

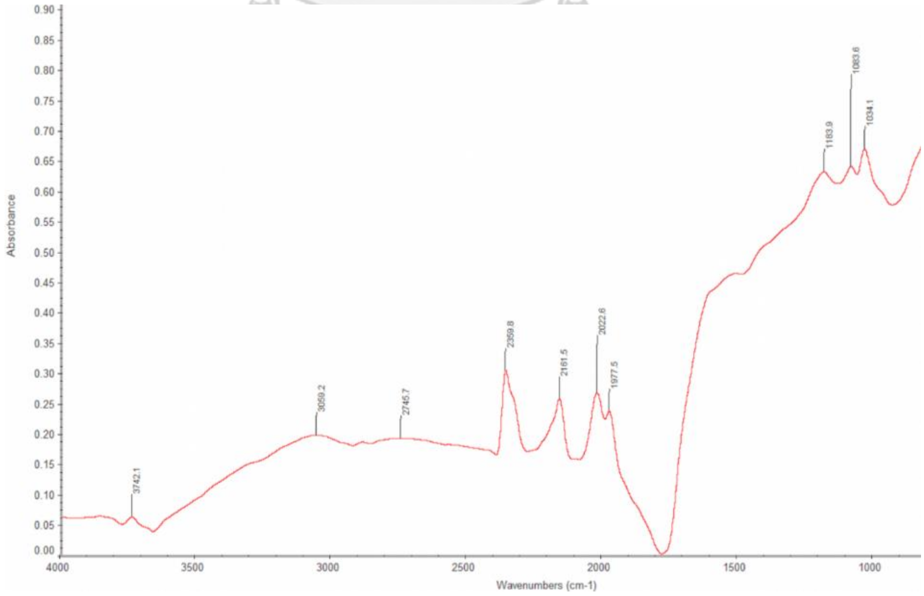


Figure 20 FT-IR images of Carbon syntactic group (CL-1 filler).

Graphite oxide exhibits representative peaks at 3270, 1714, 1606, 1389 and 1070 cm^{-1} corresponding to O-H stretch, C=O stretch, aromatic C=C, C-O stretch, respectively.

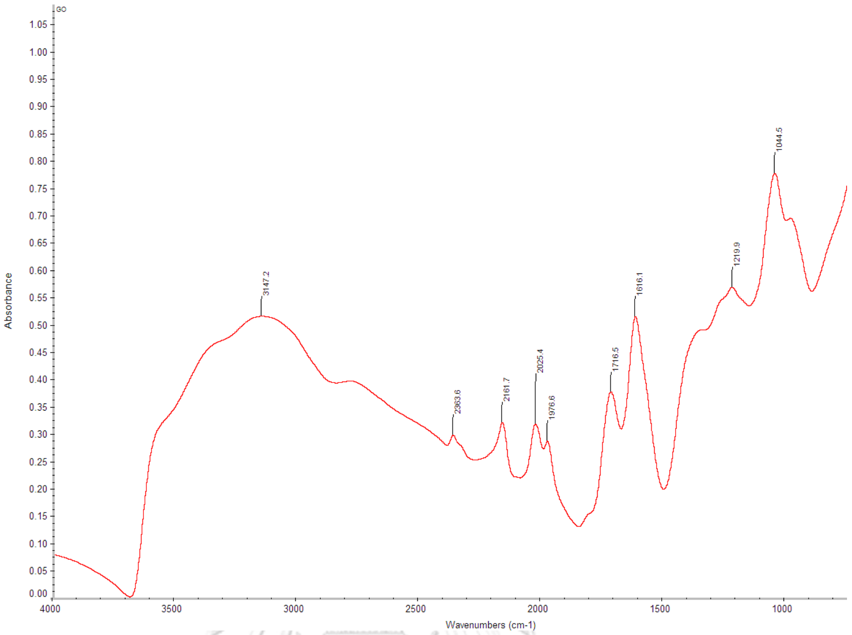


Figure 21 FT-IR images of Carbon Oxide group (Graphene Oxide).

It is clear that no distinct peak can be found from the graphite spectra.

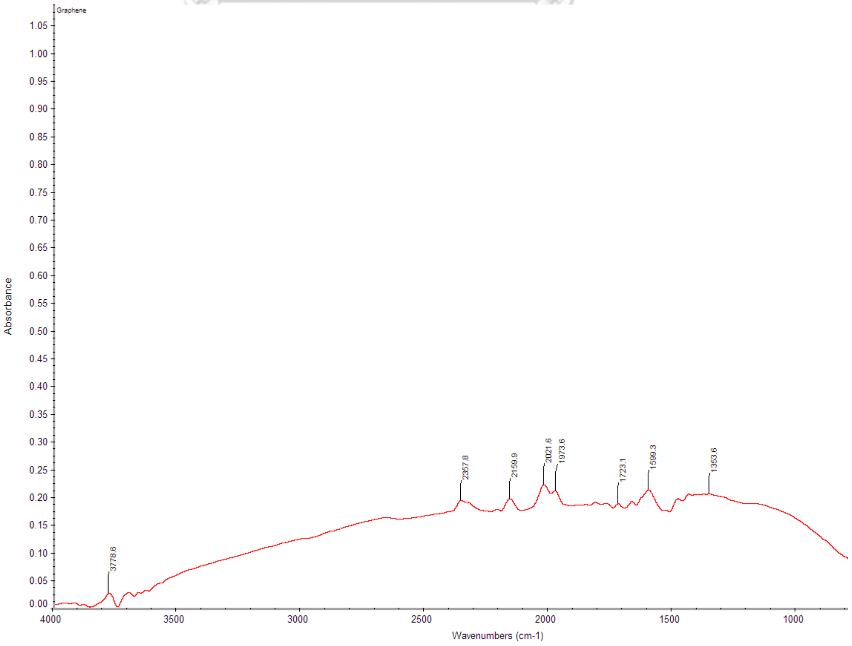


Figure 22 FT-IR images of Pure carbon group (Graphene).

Table 4 Characteristics of the filler.

NO.	**Filler**	**Particle size (um) from SEM**	**Crystal Structure**	**Element from EDX**		**Filler powder remaining at 600 °C* from TGA (Wt%)**
				CK (Wt%)	**OK (Wt%)**	
1	CL-1	71-122	crystalline	40.05	22.69	74.00
2	CL-2	24-117	crystalline	43.00	17.55	67.50
3	CL-3	56-135	crystalline	42.92	13.04	97.00
4	Graphene Oxide	15-69	amorphous	59.72	35.66	52.00
5	Graphene	41-148	crystalline	89.00	7.77	96.00
6	Graphene Rod	41-189	crystalline	86.46	9.94	99.67
7	Carbon Black	44-167	amorphous	91.93	6.23	98.89
8	Activated Carbon	3-10	amorphous	89.69	7.28	95.81

*Note: 925 sterling casting the flask casting temperatures are typically 450-600°C [12] [13]

From SEM images showing the particle size, was found that the average size of carbon material Group 1 Carbon Synthetic (CL-1, CL-2 and CL-3) approximately 50-125 um, Group 2 Carbon Oxide (Graphene Oxide) approximately 15-69 um, Group 3 Pure Carbon (Graphene, Graphene Rod, Carbon Black and Activated Carbon) approximately 89-129 um as shown in the Table 4.

From EDX images showing the element, was found Group 1 The average carbon content of approximately 42 Wt%, oxygen 15 Wt%, nitrogen 17 Wt%, and sulfer 26 Wt% Group 2 The average carbon content of approximately 60 Wt% and oxygen 36 Wt%, Since there are very little nitrogen and sulfur contents, it can be assumed that group 2 contains mainly carbon and oxygen. Group 3 The average carbon content of approximately 90 Wt%, Since there are very little oxygen, nitrogen and sulfur contents, it can be assumed that group 3 contains mainly carbon.

From TGA images showing the weight loss, To confirm that If carbon is used for real use on casting, The carbon we added will remain after heating usually 925 sterling casting the flask casting temperatures are typically 450-600°C [12, 13]. From TGA in Table 4. at temperature 600°C was found Group 1 The average carbon content remain of approximately 79.5 Wt%, Group 2 The average carbon content remain of approximately 52 Wt%, and Group 3 The average carbon content remain of approximately 97.6 Wt%. However, the study of fillers might only yield initial findings. Due to the actual use, the filler and alloy are combined first. As a result, there will be fewer missing.

From FT-IR results, confirm that Carbon syntactic group has a structure like N, S doped graphene, Carbon Oxide group has a structure is graphene oxide and Pure carbon group has a structure like Graphene

4.2 The effect of the amount of carbon material added per default colour of silver.

Illuminance is measured by the L* value. For a variety of causes, the L* number may be higher than 100. for instance, Because the sample contains materials that can reflect light (glitter), the L value is greater than 100.[14]. In this study, The permissible illuminance value for this investigation is L*≥ 100. The dE* value is taken into consideration if L*<100.

The standard method for evaluating color accuracy is dE*. When comparing two colors side by side, experts perceive no change when the value of dE* < 1.00 is present. If dE* < 3.00. significant variations for the typical person.[15] In this study, The permissible illuminance value for this investigation is dE* < 3.00.

4.2.1 Test of CL-1 filler was set to 0%, 0.5%, 0.7% and 1% to study default colors of silver by colorimeter.

The effect of the amount of CL-1 filler added per default color of silver from Figure 19 All samples had L*>100 and at concentrations of 0.7%CL-1, 1%CL-1 were brighter 100%silver, so the addition of CL-1 may contribute to adding luster to the part.

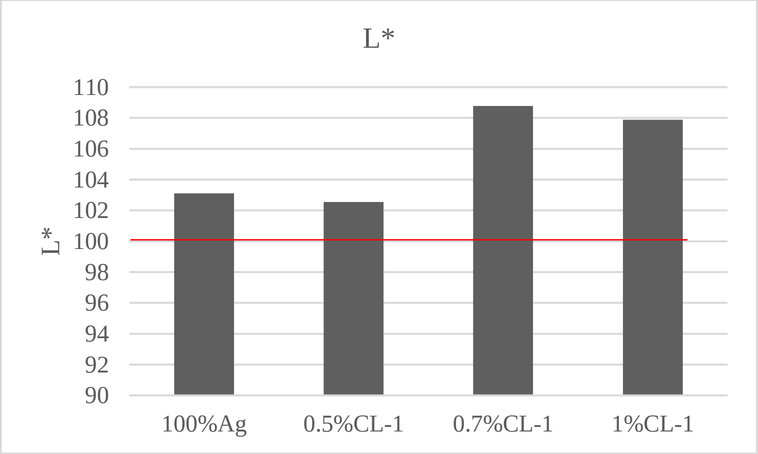


Figure 23 Represents lightness (L) of silver reinforced with CL-1 filler was set to 0%, 0.5%, 0.7% and 1%*

4.2.2 Test of CL-2 filler was set to 0%, 0.5%, 0.7% and 1% to study default colors of silver by colorimeter.

The effect of the amount of CL-2 filler added per default color of silver from Figure 20 All samples had L*>100 and at all concentrations were brighter 100%silver, so the addition of CL-2 may contribute to adding luster to the part.

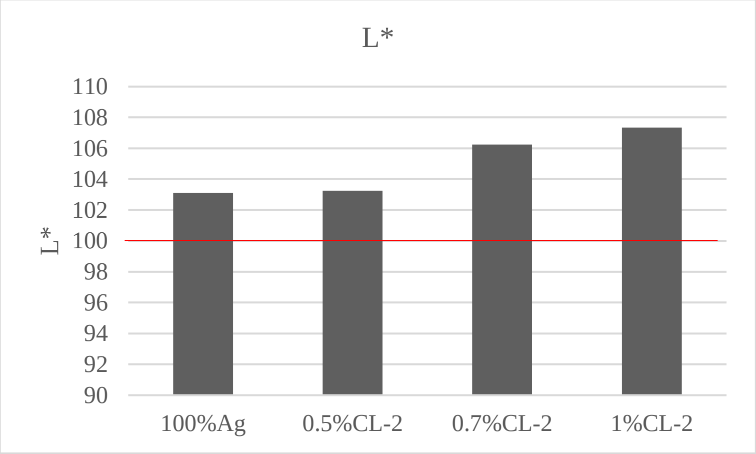


Figure 24 Represents lightness (L) of silver reinforced with CL-2 filler was set to 0%, 0.5%, 0.7% and 1%*

4.2.3 Test of CL-3 filler was set to 0%, 0.5%, 0.7% and 1% to study default colors of silver by colorimeter.

The effect of the amount of CL-3 filler added per default color of silver from Figure 21 All samples had L*>100.

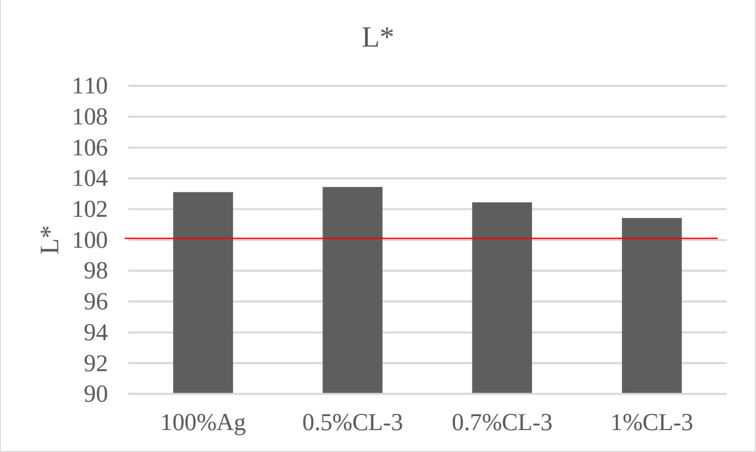


Figure 25 Represents lightness (L) of silver reinforced with CL-3 filler was set to 0%, 0.5%, 0.7% and 1%*

4.2.4 Test of Graphene Oxide filler was set to 0%, 0.5%, 0.7% and 1% to study default colors of silver by colorimeter.

The effect of the amount of Graphene Oxide filler added per default color of silver from Figure 22 All samples had L*>100 and at all concentrations were brighter 100%silver, so the addition of Graphene Oxide may contribute to adding luster to the part.

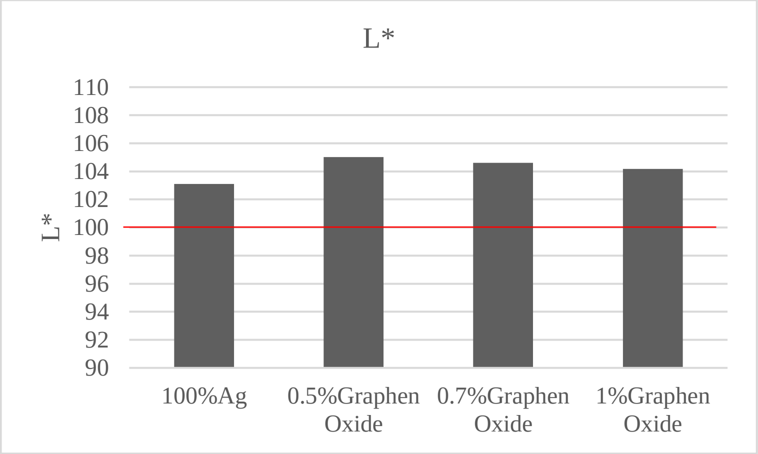
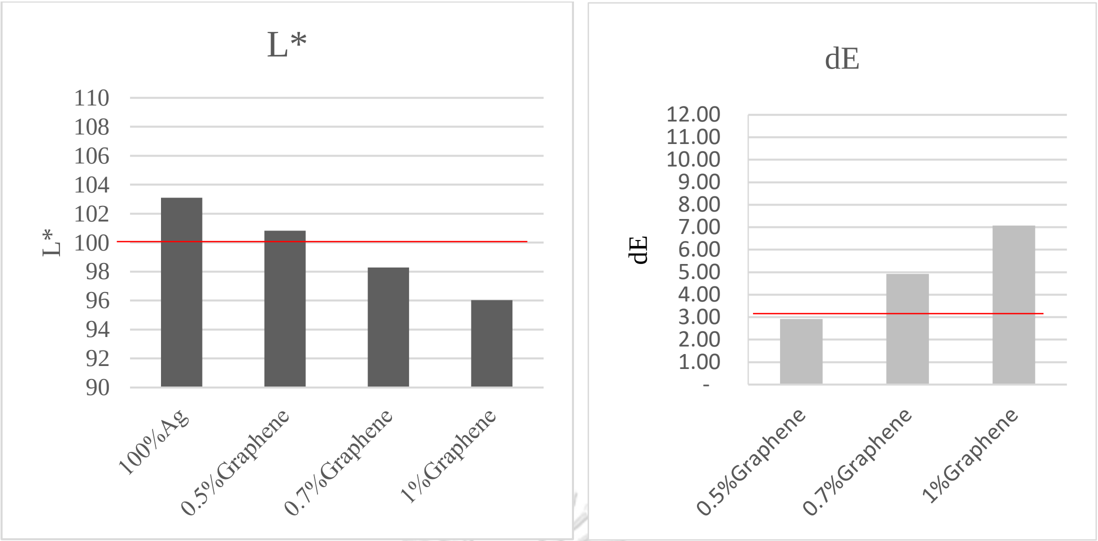


Figure 26 Represents lightness (L) of silver reinforced with Graphene Oxide filler was set to 0%, 0.5%, 0.7% and 1%*

4.2.5 Test of Graphene filler was set to 0%, 0.5%, 0.7% and 1% to study default colors of silver by colorimeter.

The effect of the amount of Graphene filler added per default color of silver from Figure 23 The samples at concentrations of 0.5%Graphene had L*>100 and at concentrations of 0.7%Graphene and 1%Graphene had L* < 100 , Considering the values of dE*, it was found that at concentrations of 0.7%Graphene and 1%Graphene had dE* > 3, which the not accept illuminance value for 0.7%Graphene and 1%Graphene.



(a) (b)

Figure 27 The silver reinforced with Graphene filler was set to 0%, 0.5%, 0.7% and 1% (a) Represents lightness: L, (b) Total color difference: dE*.*

4.2.6 Test of <u>Graphene Rod filler</u> was set to 0%, 0.5%, 0.7% and 1% to study default colors of silver by colorimeter.

The effect of the amount of Graphene Rod filler added per default color of silver from Figure 24 All samples had L*>100, Only 0.5% Graphene Rod brighter than 100% Silver.

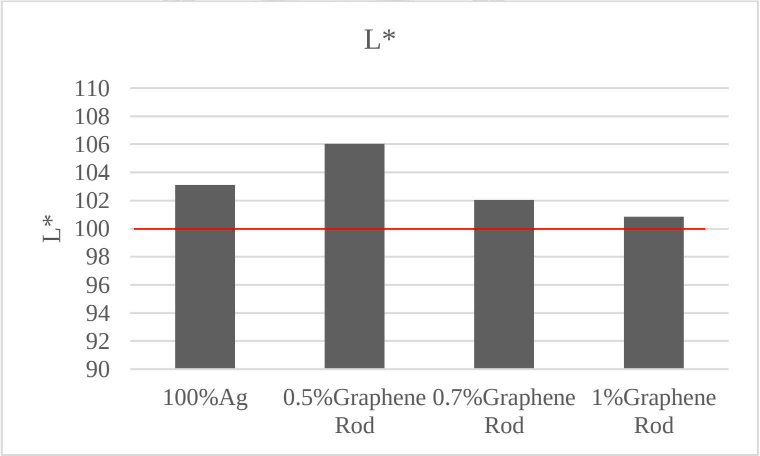
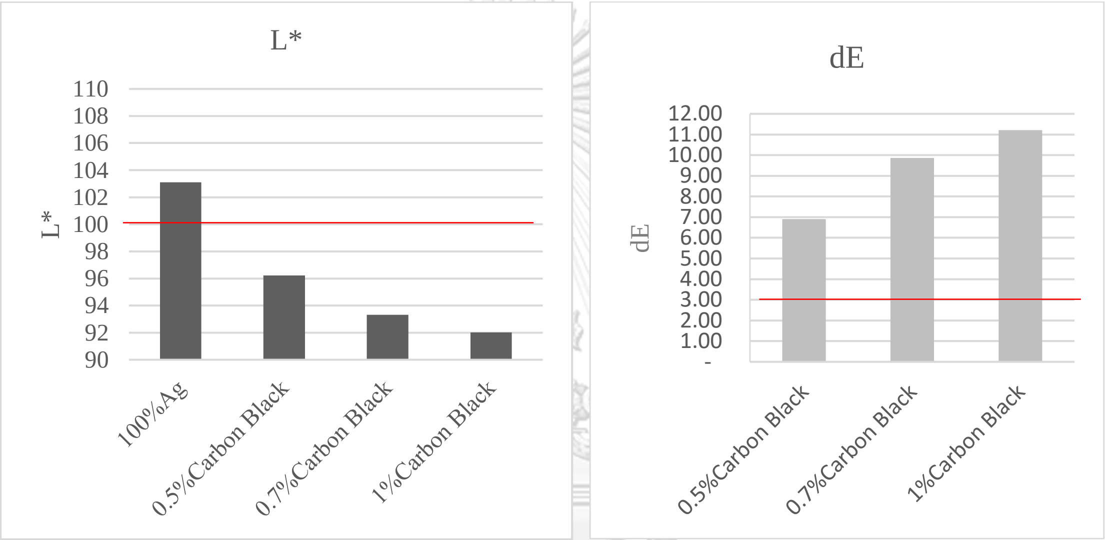


Figure 28 Represents lightness (L) of silver reinforced with Graphene Rod filler was set to 0%, 0.5%, 0.7% and 1%*

4.2.7 Test of Carbon Black filler was set to 0%, 0.5%, 0.7% and 1% to study default colors of silver by colorimeter.

The effect of the amount of Carbon Black filler added per default color of silver from Figure 25 The samples at all concentrations had L*< 100, Considering the values of dE*, it was found that at all concentrations had dE* > 3, which the not accept illuminance value for 0.5% Carbon Black, 0.7% Carbon Black and 1% Carbon Black.

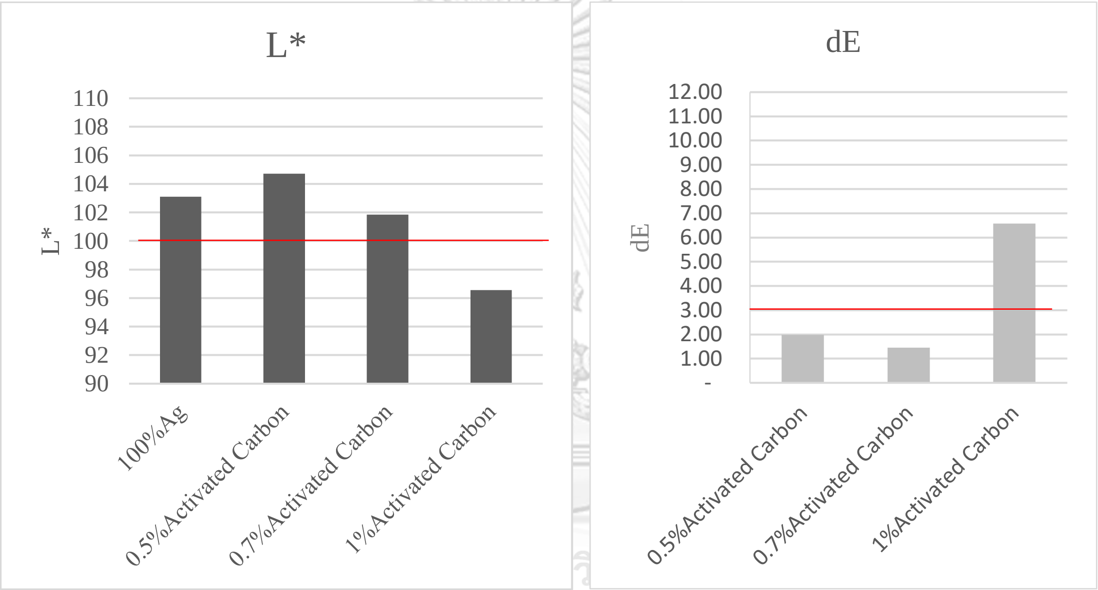


(a) (b)

Figure 29 The silver reinforced with Carbon Black filler was set to 0%, 0.5%, 0.7% and 1% (a) Represents lightness: L, (b) Total color difference: dE*.*

4.2.8 Test of Activated Carbon filler was set to 0%, 0.5%, 0.7% and 1% to study default colours of silver by colorimeter.

The effect of the amount of Activated Carbon filler added per default colour of silver from Figure 26 The samples at concentrations of 0.5% Activated Carbon and 0.7% Activated Carbon had L*>100 and at concentrations of 1% Activated Carbon had L* < 100 , Considering the values of dE*, it was found that at concentrations of 1%Activated Carbon had dE* > 3, which the not accept illuminance value for 1% Activated Carbon.



(a) (b)

Figure 30 The silver reinforced with Activated Carbon filler was set to 0%, 0.5%, 0.7% and 1% (a) Represents lightness: L, (b) Total color difference: dE*.*

Table 5 The table shows ✓is the sample still has a bright and shiny colour value when carbon is added. ✗ when carbon is introduced, the sample's colour value is not bright.

NO.	**Filler**	**%Loading**		
		0.5%	**0.7%**	**1%**
1	CL-1	✓	✓	✓
2	CL-2	✓	✓	✓
3	CL-3	✓	✓	✓
4	Graphene Oxide	✓	✓	✓
5	Graphene	✓	✗	✗
6	Graphene Rod	✓	✓	✓
7	Carbon Black	✗	✗	✗
8	Activated Carbon	✓	✓	✗

Note: ✗ not be applied to the next part's study.

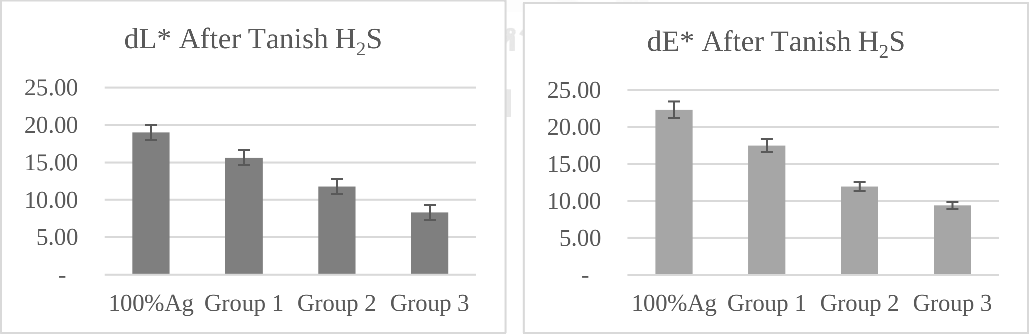
Part II. To compare the colour difference of the sample before and after tarnish and characteristic by colorimeter and SEM-EDX to be used to assess the quality of the sample passed H_2S tarnish method.

4.3 Test of colour resistance to hydrogen sulfide (H_2S) tarnish

To study tarnish resistance, the colour difference was analysed by interpreting the study results into 3 groups: Group 1 is the addition of carbon synthetic, Group 2 is the addition of carbon oxide, and Group 3 is the addition of pure carbon as in Table 2.

4.3.1 Test of hydrogen sulfide tarnish of 0.5% filler to compare the tarnish resistance of the three groups of carbon material by colorimeter.

The dL* value indicates the difference between black and white. between the sample and the standard sample, the results of the measured colour values after testing the colour resistance to hydrogen sulfide tarnish showed that Group 3 (C=90 Wt%) showed the lowest dL* value, indicating the best resistance to tarnishing. followed by group 2 (C=60 Wt%), group 1 (C=42 Wt%) and 100%silver, respectively, the value of dE* and dL* are trending in the same direction, as shown in Figure 27. So, adding carbon material to help reduce tarnishing a lot. According to the hypothesis, more carbon will help react with sulfur more. thus, reducing the formation of silver sulfide more[16, 17].

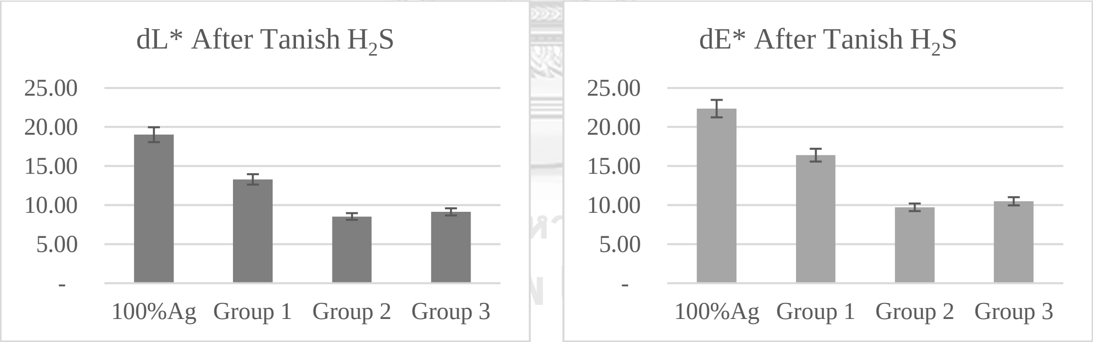


(a) (b)

Figure 31 Silver reinforced with 0.5% filler to compare the hydrogen sulfide tarnish resistance of the three groups of carbon material. (a) Represents lightness difference: dL. (b) Total colour difference: dE*.*

4.3.2 Test of hydrogen sulfide tarnish of 0.7% filler to compare the tarnish resistance of the three groups of carbon material by colorimeter.

The dL* value indicates the difference between black and white. between the sample and the standard sample, the results of the measured colour values after testing the colour resistance to hydrogen sulfide tarnish showed that Group 2 (C=60 Wt%) the best resistance to tarnishing. However, the results from groups 2 and 3 (C=90 Wt%) were very similar results. Therefore, it can be assuming groups 2 and 3 have the greatest resistance to tarnishing. followed by group 1 (C=42 Wt%) and 100%silver, respectively, the value of dE* and dL* are trending in the same direction, as shown in Figure 28. So, Group 2 (which has less carbon than Group 3) When increasing the concentration, the amount of carbon will increase, which will help to resist tarnishing better. Group 3 has no anti-tarnish value different from Group 2 because there is already a lot of carbon (90%Wt). Increasing the intensity of carbon does not help to resist tarnishing better, so carbon group 3 is added to 0.5% is enough.

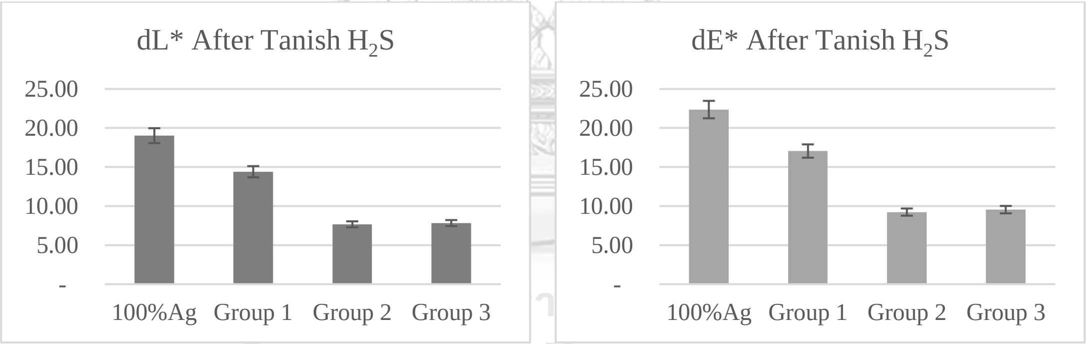


(a) (b)

Figure 32 Silver reinforced with 0.7% filler to compare the hydrogen sulfide tarnish resistance of the three groups of carbon material. (a) Represents lightness difference: dL. (b) Total colour difference: dE*.*

4.3.3 Test of hydrogen sulfide tarnish of 1% filler to compare the tarnish resistance of the three groups of carbon material by colorimeter.

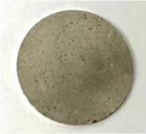
The dL* value indicates the difference between black and white. between the sample and the standard sample, the results of the measured colour values after testing the colour resistance to hydrogen sulfide tarnish showed that Group 2 (C=60 Wt%) the best resistance to tarnishing. However, the results from groups 2 and 3 (C=90 Wt%) were very similar results. Therefore, it can be assuming groups 2 and 3 have the greatest resistance to tarnishing. followed by group 1 (C=42 Wt%) and 100%silver, respectively, the value of dE* and dL* are trending in the same direction, as shown in Figure 29. So, Group 2 (which has less carbon than Group 3) When increasing the concentration, the amount of carbon will increase, which will help to resist tarnishing better. Group 3 has no anti-tarnish value different from Group 2 because there is already a lot of carbon (90%Wt). Increasing the intensity of carbon does not help to resist tarnishing better, so carbon group 3 is added to 0.5% is enough.



(a) (b)

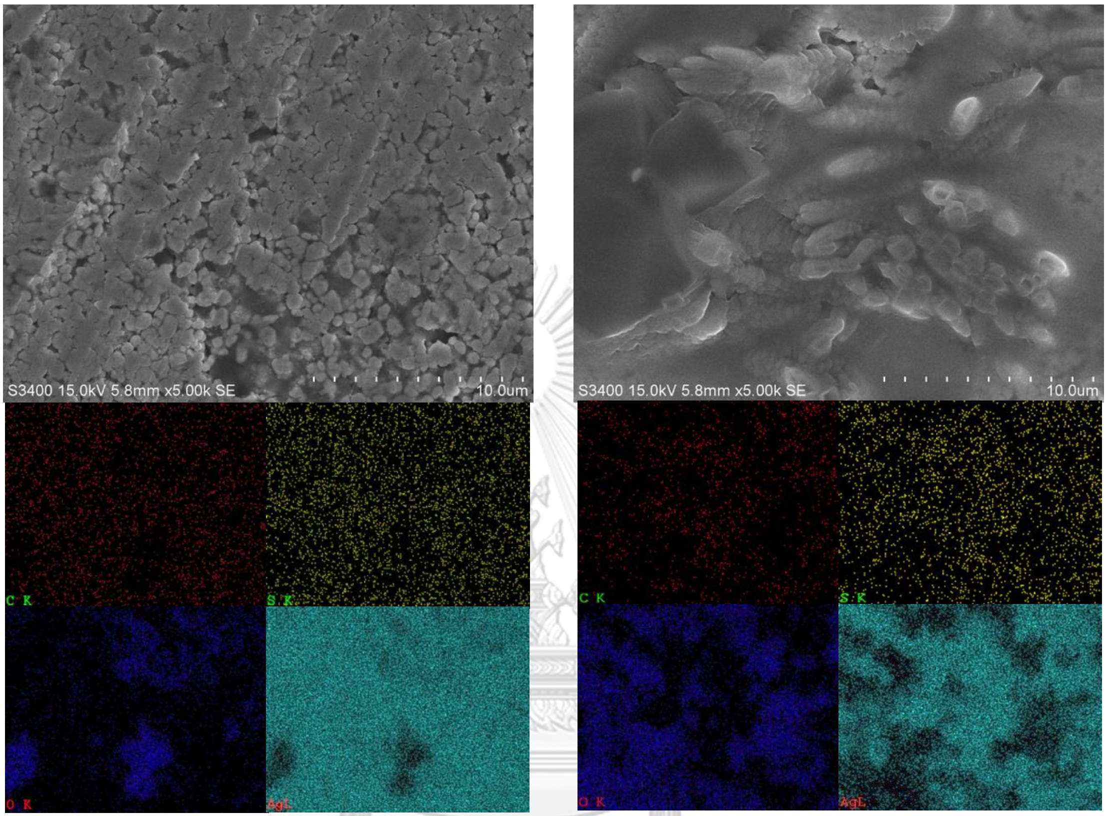
Figure 33 Silver reinforced with 1% filler to compare the hydrogen sulfide tarnish resistance of the three groups of carbon material. (a) Represents lightness difference: dL. (b) Total colour difference: dE*.*

Table 6 Images of the silver reinforced with carbon material, after hydrogen sulfide tarnish test.

NO.	**Filler**	**Sample after H_2S tarnish**
1	100%Ag	
2	Ag + 1%CL-1	
3	Ag + 1%CL-2	
4	Ag + 1%CL-3	
5	Ag + 1%Graphene Oxide	
6	Ag + 1%Graphene	
7	Ag + 1%Graphene Rod	
8	Ag + 1%Carbon Black	
9	Ag + 1%Activated Carbon	

4.4 Characterization of the sample before and after hydrogen sulfide (H_2S) tarnish.

4.4.1 Characterization of the sample before and after hydrogen sulfide (H_2S) tarnish: 100% Silver (100%Ag).



Element	Wt% avg	At% avg
CK	1.38	7.76
NK	0.71	3.38
OK	7.58	31.36
SK	0.24	0.50
ClK	0.25	0.49
AgL	89.85	56.50

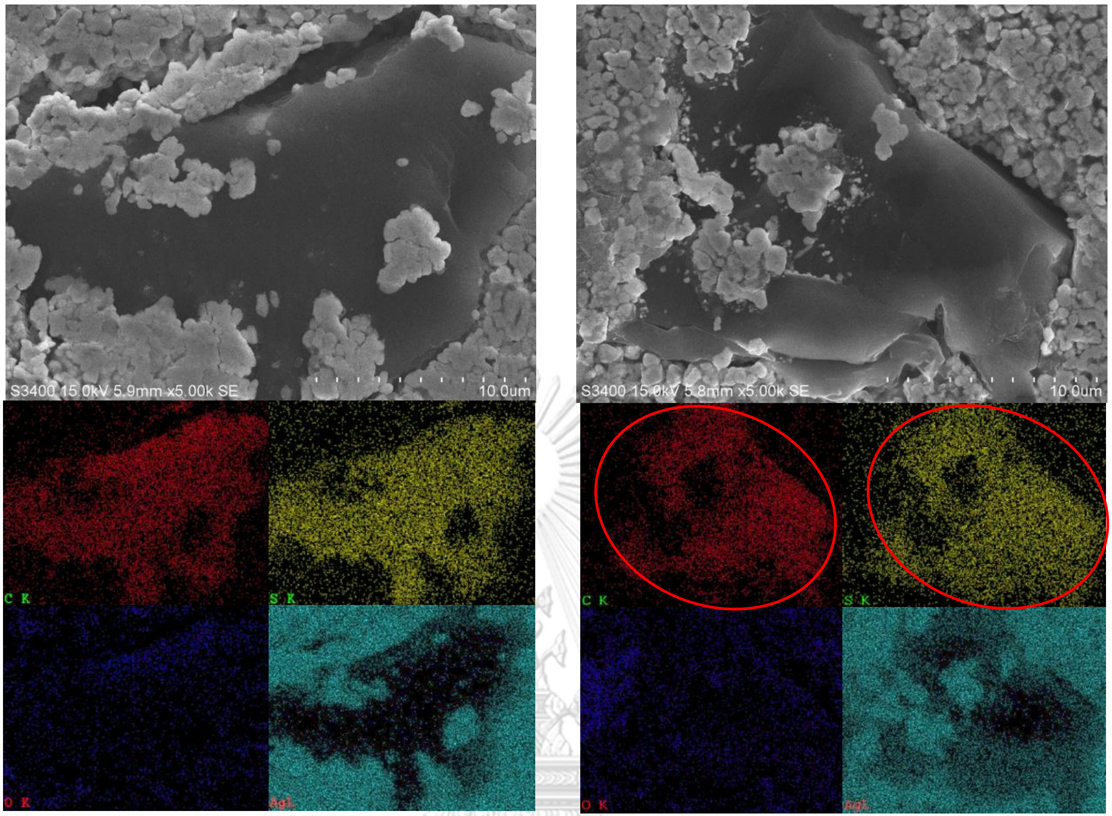
(a)

Element	Wt% avg	At% avg
CK	1.01	3.58
NK	2.26	5.15
OK	33.43	63.53
SK	0.37	0.48
ClK	0.15	0.20
AgL	62.79	27.06

(b)

Figure 34 SEM-EDX images of 100% Silver by hydrogen sulfide tarnish test (a) Before tarnish (b) After tarnish

4.4.2 Characterization of the sample before and after hydrogen sulfide (H_2S) tarnish: Group 1 the addition of carbon synthetic (CL-1).



Element	Wt% avg	At% avg
CK	4.50	17.83
NK	1.50	5.39
OK	7.12	26.20
SK	1.92	2.65
ClK	0.21	0.36
AgL	84.75	47.57

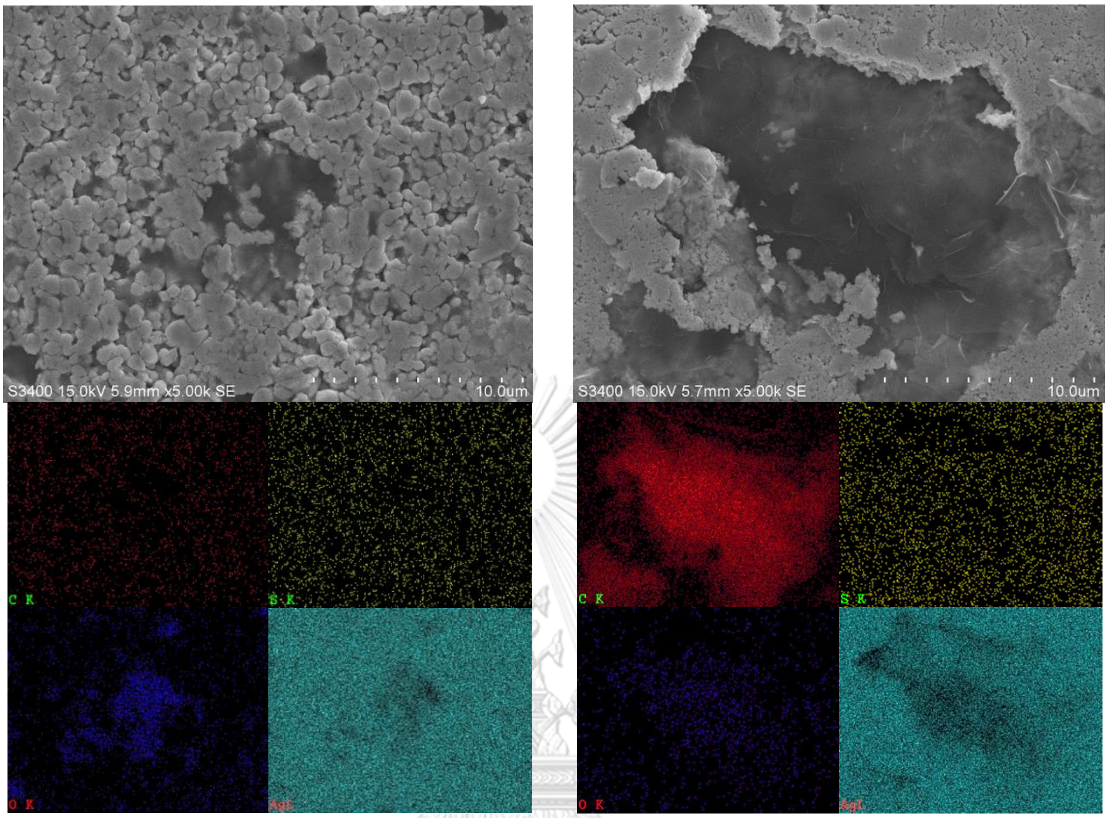
Element	Wt% avg	At% avg
CK	3.93	15.00
NK	1.45	4.99
OK	9.71	32.95
SK	1.76	2.39
ClK	0.25	0.38
AgL	82.89	44.30

(b)

(b)

Figure 35 SEM-EDX images of silver reinforced with CL-1 by hydrogen sulfide tarnish test (a) Before tarnish (b) After tarnish

4.4.3 Characterization of the sample before and after hydrogen sulfide (H_2S) tarnish: Group 1 the addition of carbon synthetic (CL-2).



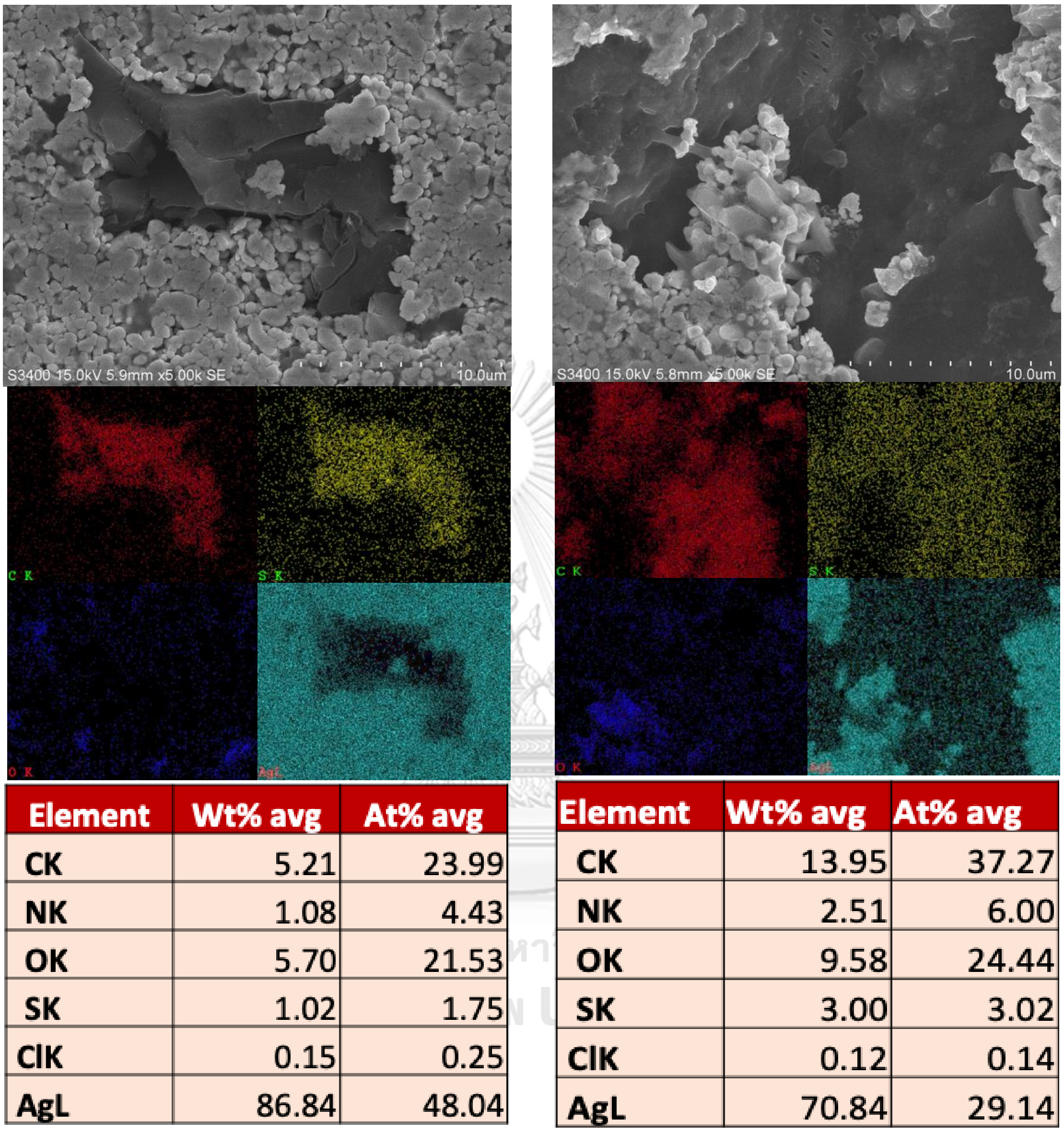
Element	Wt% avg	At% avg
CK	1.40	8.05
NK	0.66	3.27
OK	6.90	29.73
SK	0.26	0.56
ClK	0.24	0.47
AgL	90.54	57.92

Element	Wt% avg	At% avg
CK	14.75	58.04
NK	00.57	01.93
OK	00.97	02.86
SK	00.35	00.51
ClK	00.14	00.19
AgL	83.23	36.47

(a) (b)

Figure 36 SEM-EDX images of silver reinforced with CL-2 by hydrogen sulfide tarnish test (a) Before tarnish (b) After tarnish

4.4.4 Characterization of the sample before and after hydrogen sulfide (H_2S) tarnish: Group 1 the addition of carbon synthetic (CL-3).



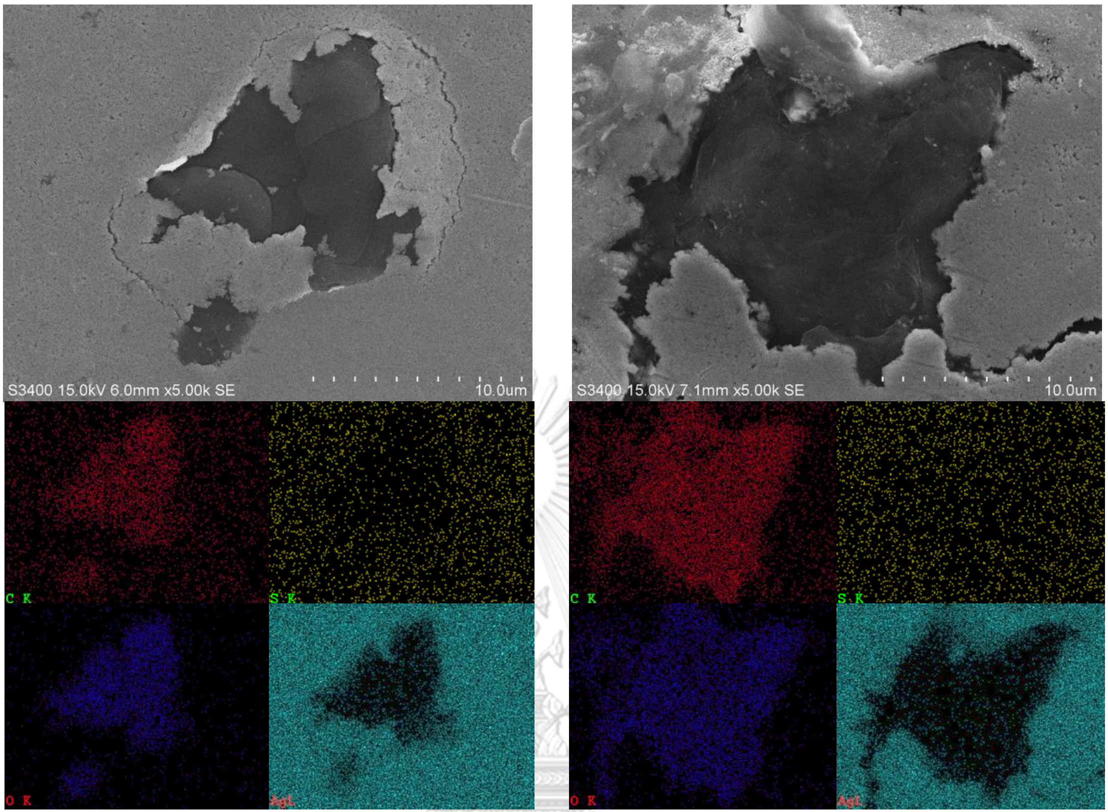
Element	Wt% avg	At% avg
CK	5.21	23.99
NK	1.08	4.43
OK	5.70	21.53
SK	1.02	1.75
ClK	0.15	0.25
AgL	86.84	48.04

Element	Wt% avg	At% avg
CK	13.95	37.27
NK	2.51	6.00
OK	9.58	24.44
SK	3.00	3.02
ClK	0.12	0.14
AgL	70.84	29.14

(a) (b)

Figure 37 SEM-EDX images of silver reinforced with CL-3 by hydrogen sulfide tarnish test (a) Before tarnish (b) After tarnish

4.4.5 Characterization of the sample before and after hydrogen sulfide (H_2S) tarnish: Group 2 the addition of carbon oxide (Graphene Oxide).



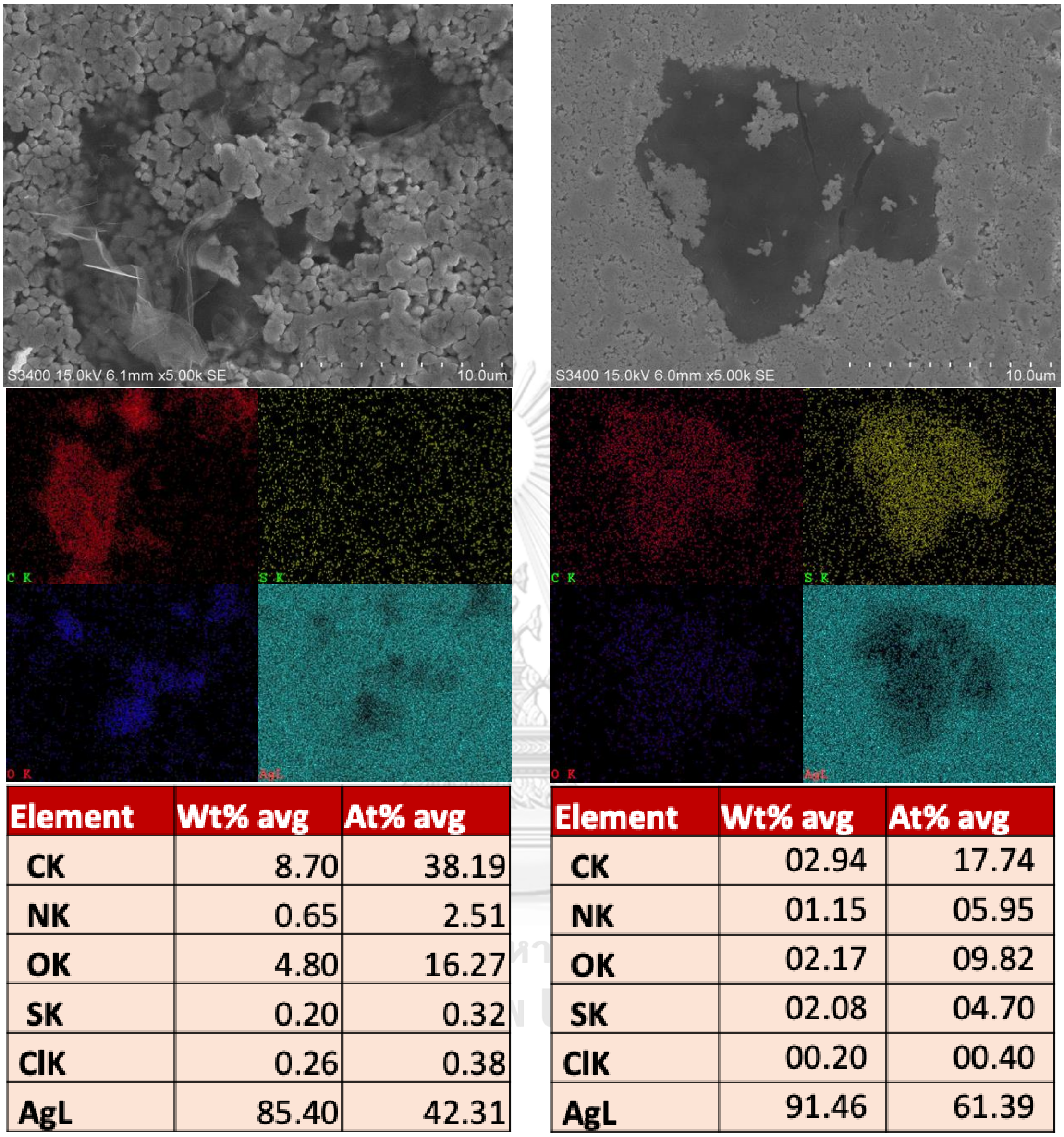
Element	Wt% avg	At% avg
CK	02.39	12.83
NK	00.49	02.28
OK	07.65	30.87
SK	00.18	00.37
ClK	00.18	00.33
AgL	89.10	53.32

Element	Wt% avg	At% avg
CK	07.65	26.97
NK	00.79	02.38
OK	14.69	38.90
SK	00.47	00.62
ClK	01.39	01.67
AgL	75.01	29.46

(a) (b)

Figure 38 SEM-EDX images of silver reinforced with Graphene Oxide by hydrogen sulfide tarnish test (a) Before tarnish (b) After tarnish

4.4.6 Characterization of the sample before and after hydrogen sulfide (H_2S) tarnish: Group 3 the addition of pure carbon (Graphene).



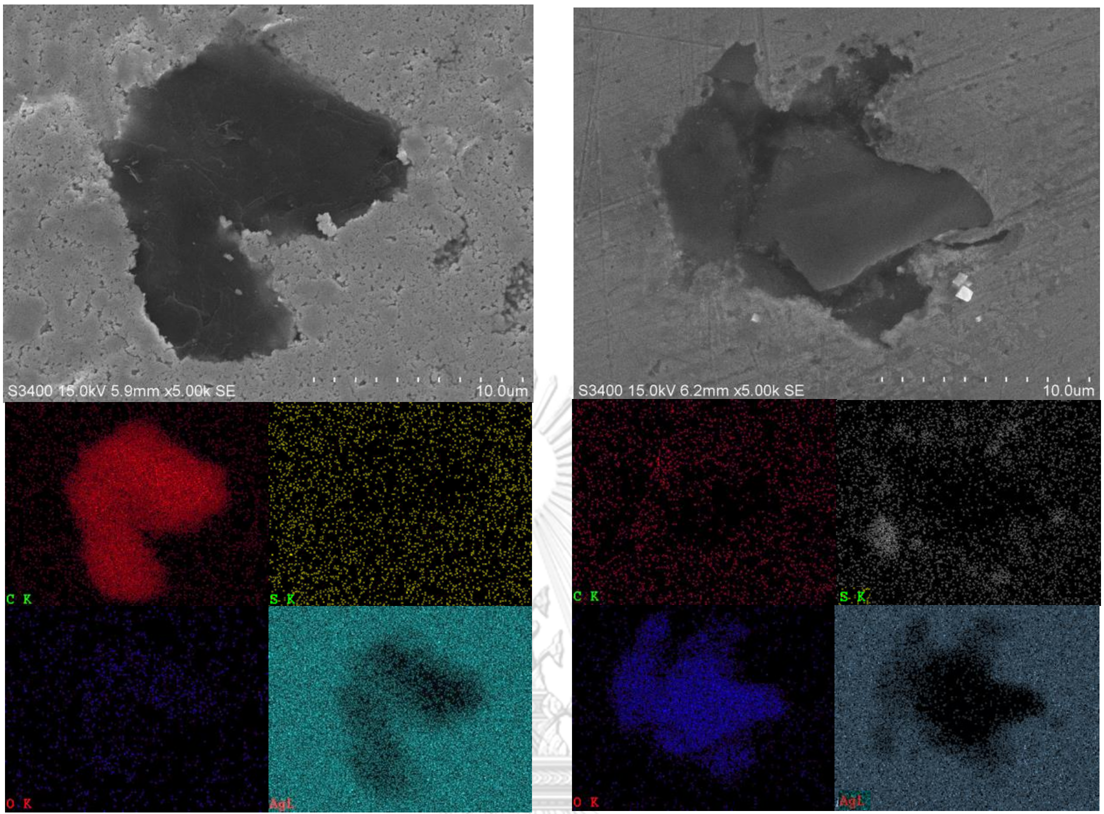
Element	Wt% avg	At% avg
CK	8.70	38.19
NK	0.65	2.51
OK	4.80	16.27
SK	0.20	0.32
ClK	0.26	0.38
AgL	85.40	42.31

Element	Wt% avg	At% avg
CK	02.94	17.74
NK	01.15	05.95
OK	02.17	09.82
SK	02.08	04.70
ClK	00.20	00.40
AgL	91.46	61.39

(a) (b)

Figure 39 SEM-EDX images of silver reinforced with Graphene by hydrogen sulfide tarnish test (a) Before tarnish (b) After tarnish

4.4.7 Characterization of the sample before and after hydrogen sulfide (H_2S) tarnish: Group 3 the addition of pure carbon (Graphene Rod).



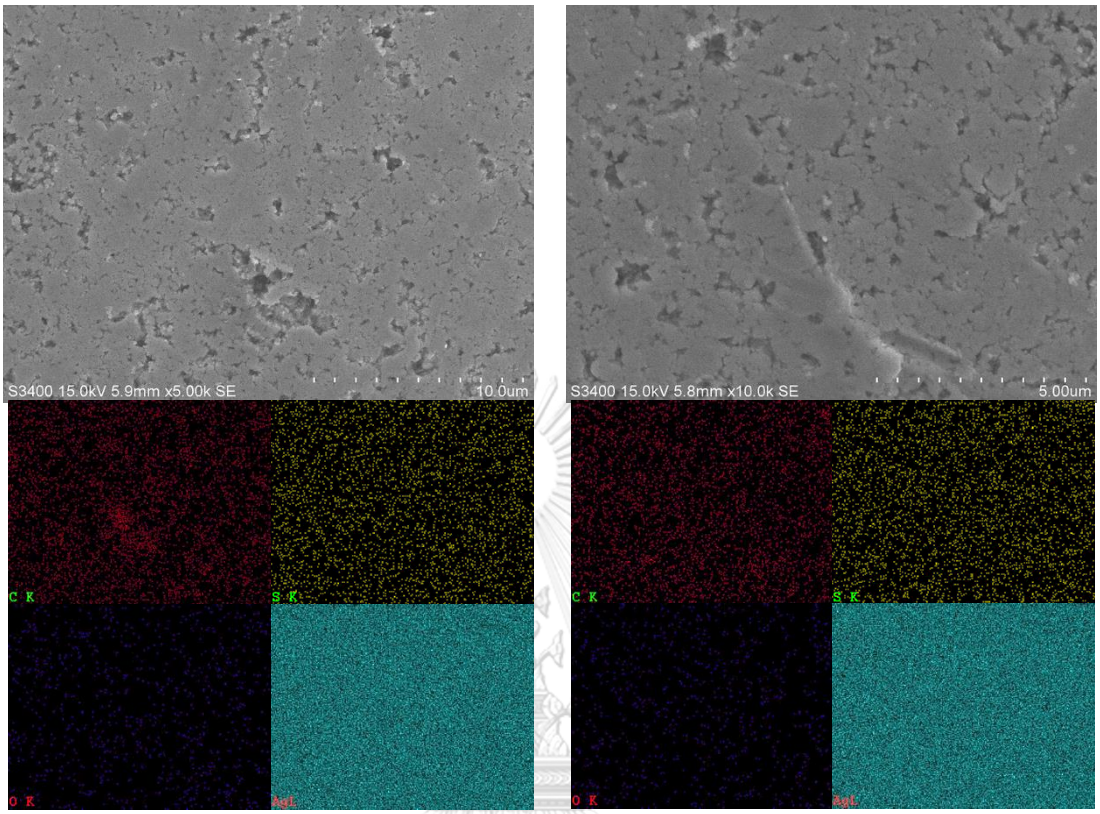
Element	Wt% avg	At% avg
CK	12.25	53.77
NK	00.52	01.97
OK	00.48	01.59
SK	00.12	00.20
ClK	00.13	00.19
AgL	86.49	42.27

Element	Wt% avg	At% avg
CK	02.31	16.38
NK	00.51	03.09
OK	00.67	03.56
SK	00.22	00.59
ClK	00.26	00.63
AgL	96.03	75.75

(a) (b)

Figure 40 SEM-EDX images of silver reinforced with Graphene Rod by hydrogen sulfide tarnish test (a) Before tarnish (b) After tarnish

4.4.8 Characterization of the sample before and after hydrogen sulfide (H_2S) tarnish: Group 3 the addition of pure carbon (Carbon Black).



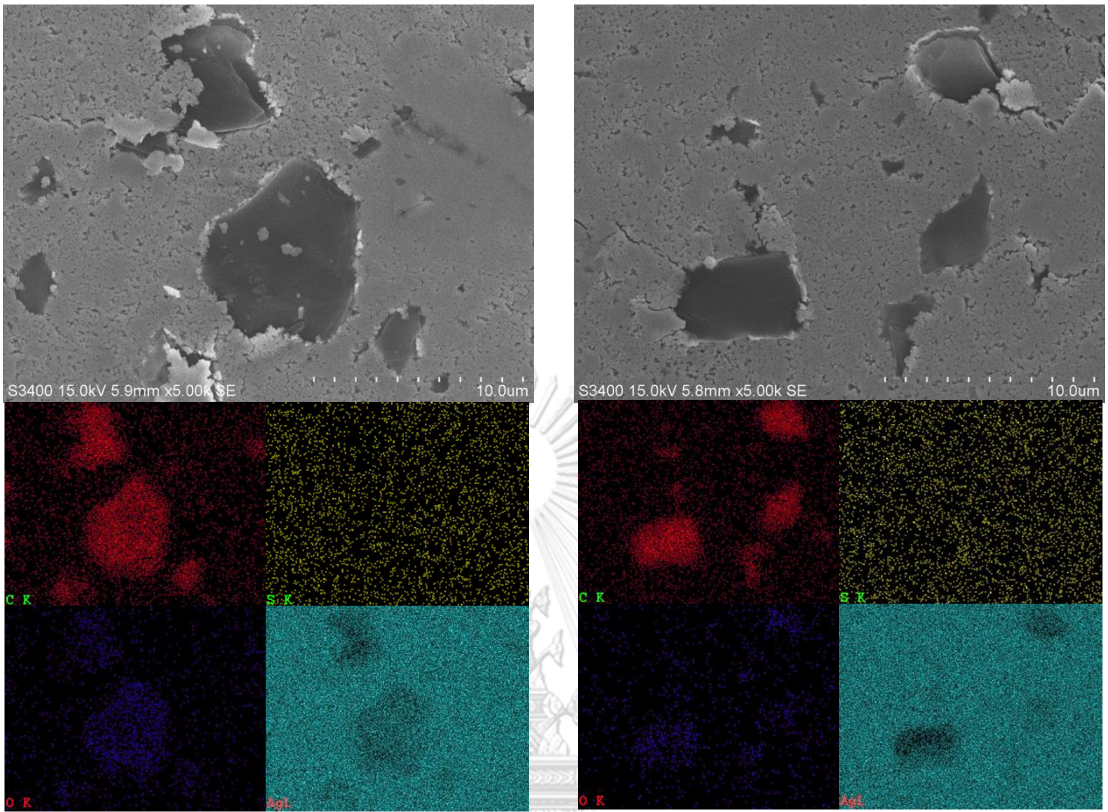
Element	Wt% avg	At% avg
CK	02.06	14.77
NK	00.60	03.71
OK	00.62	03.35
SK	00.23	00.62
ClK	00.22	00.54
AgL	96.27	77.01

Element	Wt% avg	At% avg
CK	01.59	12.03
NK	00.48	03.14
OK	00.32	01.80
SK	00.23	00.66
ClK	00.18	00.46
AgL	97.20	81.91

(a) (b)

Figure 41 SEM-EDX images of silver reinforced with Carbon Black by hydrogen sulfide tarnish test (a) Before tarnish (b) After tarnish

4.4.9 Characterization of the sample before and after hydrogen sulfide (H_2S) tarnish: Group 3 the addition of pure carbon (Activated Carbon).



Element	Wt% avg	At% avg
CK	03.63	22.55
NK	00.47	02.50
OK	02.00	09.30
SK	00.21	00.49
ClK	00.30	00.64
AgL	93.39	64.52

Element	Wt% avg	At% avg
CK	03.14	20.75
NK	00.52	02.96
OK	01.02	05.05
SK	00.43	01.06
ClK	00.17	00.39
AgL	94.72	69.79

(a) (b)

Figure 42 SEM-EDX images of silver reinforced with Activated Carbon by hydrogen sulfide tarnish test (a) Before tarnish (b) After tarnish.

Results of SEM-EDX study. When hydrogen sulfide gas was used to test the samples that had been added with carbon material, will notice that silver (Ag) are not found where carbon (C), and where carbon (C) is present found sulfur (S) according to Figure 30-38, Therefore, it can be concluded that carbon (C) reacts with sulfur (S) with a new substance, carbon sulfide (CS_2), which is a colorless substance. Which prevents sulfur from reacting with silver (Ag), So which prevents the formation of silver sulfide (Ag_2S) that is the cause of tarnishing[18].

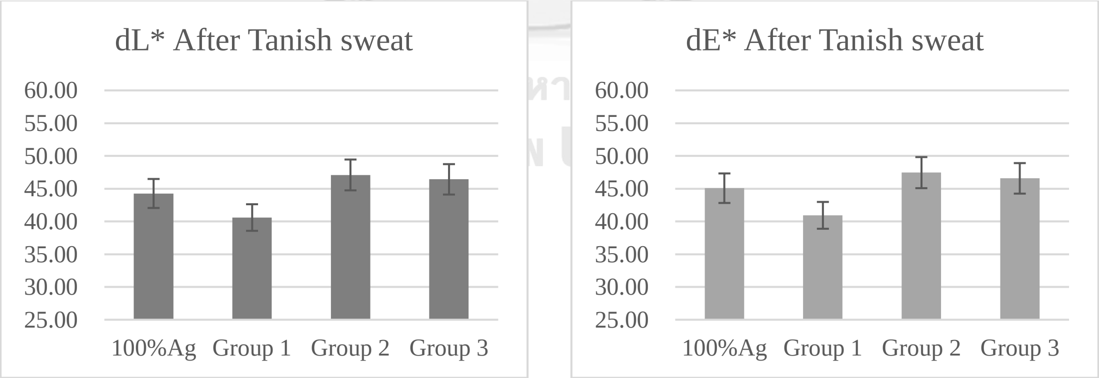
Part III. To compare the colour difference of the sample before and after tarnish and characteristic by colorimeter and SEM-EDX to be used to assess the quality of the sample passed sweat tarnish method.

4.5 Test of colour resistance to sweat tarnish

To study tarnish resistance, the colour difference was analysed by interpreting the study results into 3 groups: Group 1 is the addition of carbon synthetic, Group 2 is the addition of carbon oxide, and Group 3 is the addition of pure carbon as in Table 2

4.5.1 Test of sweat tarnish of 0.5% filler to compare the tarnish resistance of the three groups of carbon material by colorimeter.

The dL* value indicates the difference between black and white. between the sample and the standard sample, the results of the measured colour values after testing the colour resistance to sweat tarnish showed that Group 1 the best resistance to tarnishing followed by 100%silver Group 3, and Group 2 respectively, the value of dE* and dL* are trending in the same direction, as shown in Figure 39. However, the results from groups 2 and 3 were very similar results. Therefore, it can be assuming groups 2 and 3 have the same effect resistance to tarnishing.

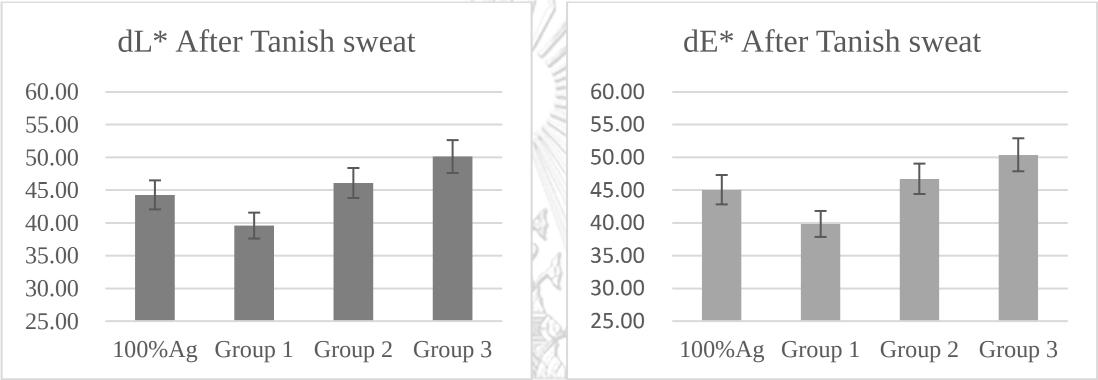


(a) (b)

Figure 43 Silver reinforced with 0.5% filler to compare the sweat tarnish resistance of the three groups of carbon material. (a) Represents lightness difference: dL. (b) Total color difference: dE*.*

4.5.2 Test of sweat tarnish of 0.7% filler to compare the tarnish resistance of the three groups of carbon material by colorimeter.

The dL* value indicates the difference between black and white. between the sample and the standard sample, the results of the measured color values after testing the color resistance to sweat tarnish showed that Group 1 the best resistance to tarnishing followed by 100%silver Group 2, and Group 3 respectively, the value of dE* and dL* are trending in the same direction, as shown in Figure 40.

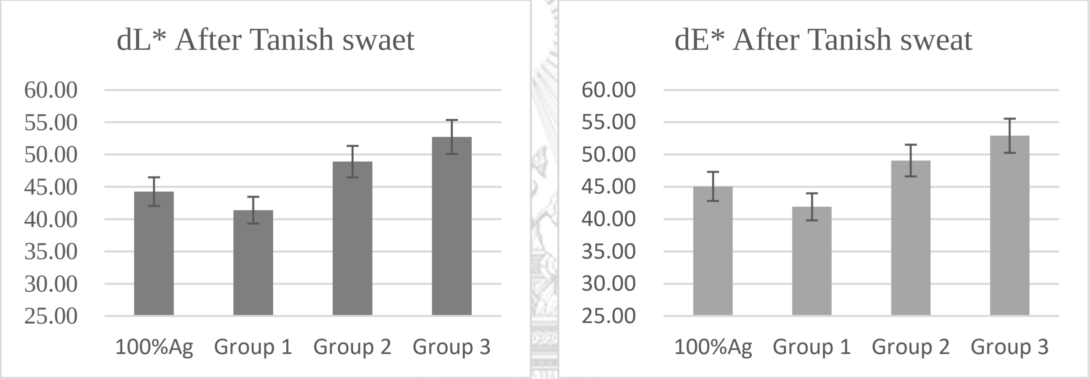


(a) (b)

Figure 44 Silver reinforced with 0.7% filler to compare the sweat tarnish resistance of the three groups of carbon material. (a) Represents lightness difference: dL. (b) Total color difference: dE*.*

4.5.3 Test of sweat tarnish of 1% filler to compare the tarnish resistance of the three groups of carbon material by colorimeter.

The dL* value indicates the difference between black and white. between the sample and the standard sample, the results of the measured color values after testing the color resistance to sweat tarnish showed that Group 1 the best resistance to tarnishing followed by 100%silver Group 2, and Group 3 respectively, the value of dE* and dL* are trending in the same direction, as shown in Figure 42.



(a) (b)

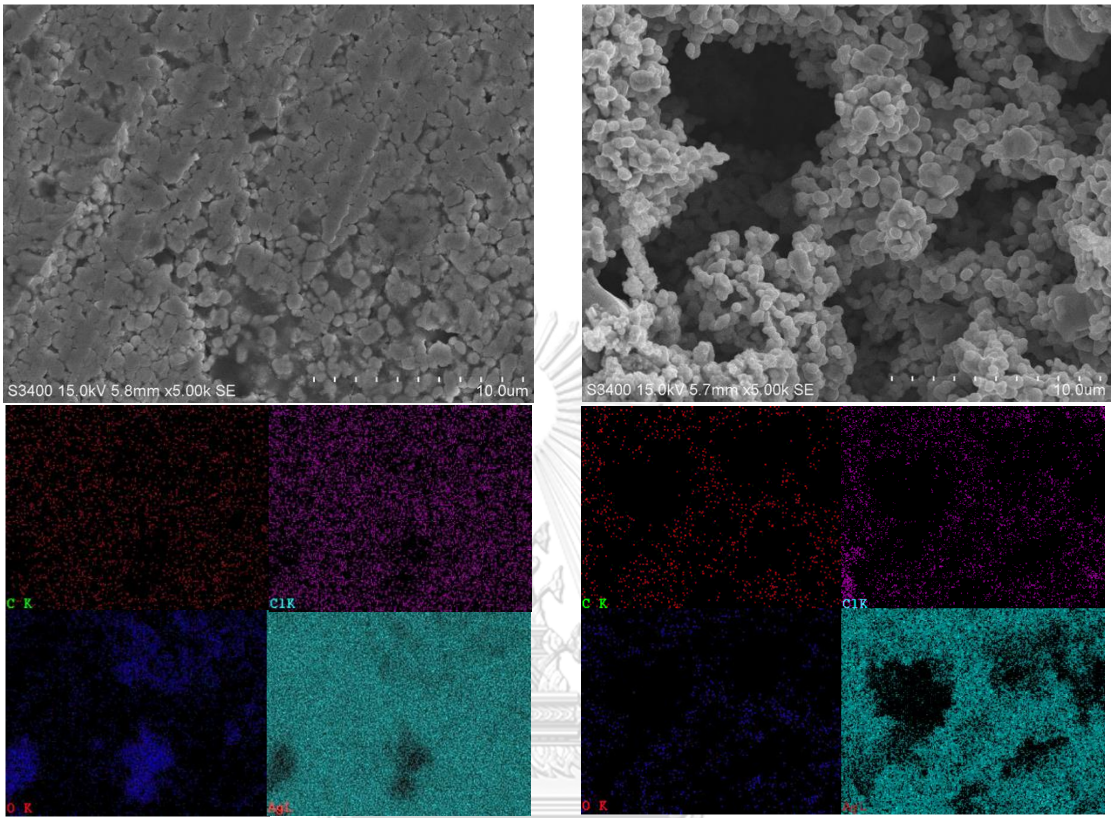
Figure 45 Silver reinforced with 1% filler to compare the sweat tarnish resistance of the three groups of carbon material. (a) Represents lightness difference: dL. (b) Total color difference: dE*.*

Table 7 Images of the silver reinforced with carbon material, after sweat tarnish test.

NO.	**Filler**	**Sample after sweat tarnish**
1	100%Ag	
2	Ag + CL-1	
3	Ag + CL-2	
4	Ag + CL-3	
5	Ag +Graphene Oxide	
6	Ag + Graphene	
7	Ag + Graphene Rod	
8	Ag + Carbon Black	
9	Ag + Activated Carbon	

4.6 Characterization of the sample before and after sweat tarnish.

4.6.1 Characterization of the sample before and after sweat tarnish: 100% Silver (100%Ag).



Element	Wt% avg	At% avg
CK	1.38	7.76
NK	0.71	3.38
OK	7.58	31.36
SK	0.24	0.50
ClK	0.25	0.49
AgL	89.85	56.50

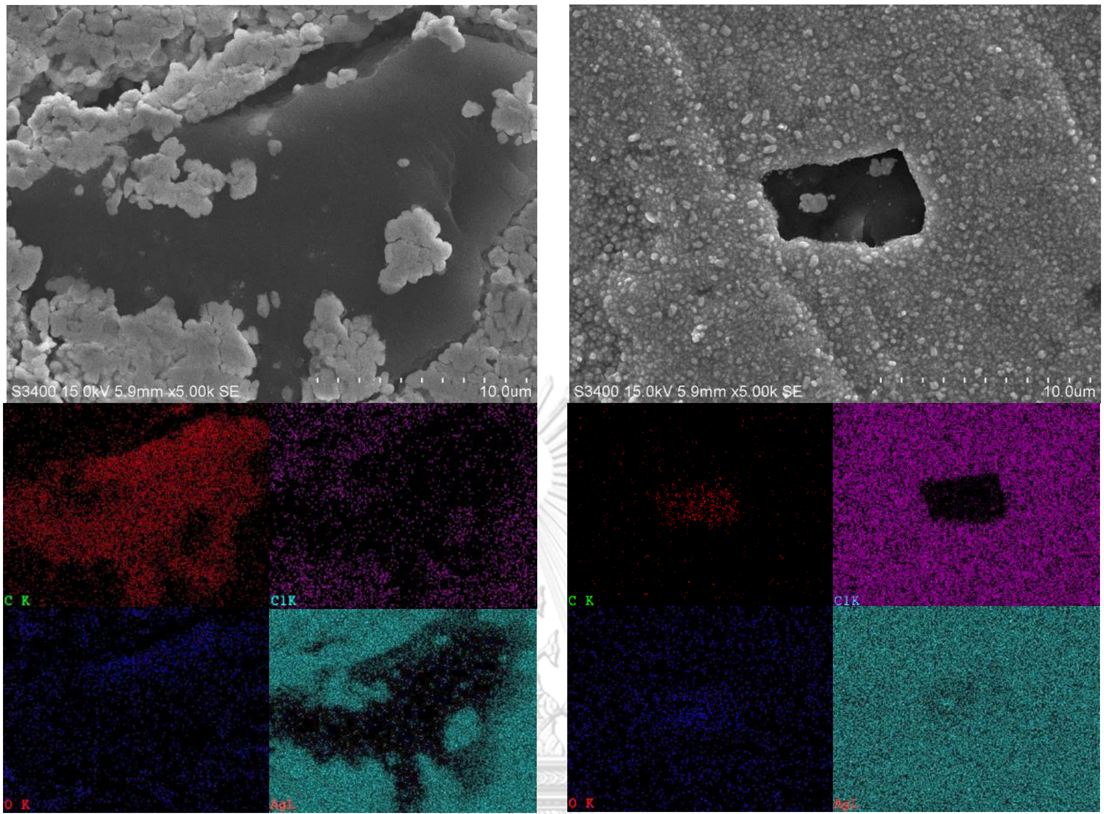
(a)

Element	Wt% avg	At% avg
CK	1.34	6.97
NK	0.64	2.79
OK	5.39	20.31
SK	0.31	0.62
ClK	13.04	20.65
AgL	79.28	48.66

(b)

Figure 46 SEM-EDX images of 100% Silver by sweat tarnish test (a) Before tarnish (b) After tarnish

4.6.2 Characterization of the sample before and after sweat tarnish: Group 1 the addition of carbon synthetic (CL-1).



Element	Wt% avg	At% avg
CK	4.50	17.83
NK	1.50	5.39
OK	7.12	26.20
SK	1.92	2.65
ClK	0.21	0.36
AgL	84.75	47.57

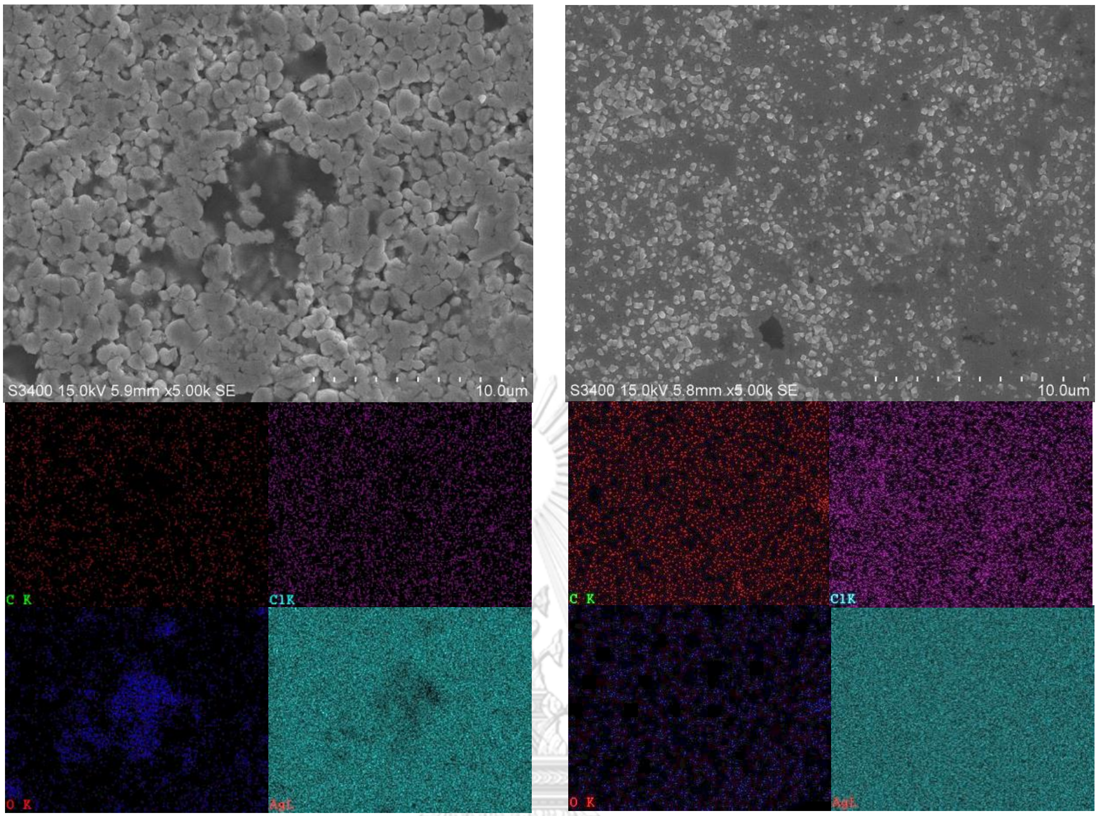
(a)

Element	Wt% avg	At% avg
CK	1.76	8.34
NK	0.57	2.32
OK	4.50	16.10
SK	0.28	0.51
ClK	21.60	34.88
AgL	71.29	37.84

(b)

Figure 47 SEM-EDX images of silver reinforced with CL-1 by sweat tarnish test (a) Before tarnish (b) After tarnish

4.6.3 Characterization of the sample before and after sweat tarnish: Group 1 the addition of carbon synthetic (CL-2).



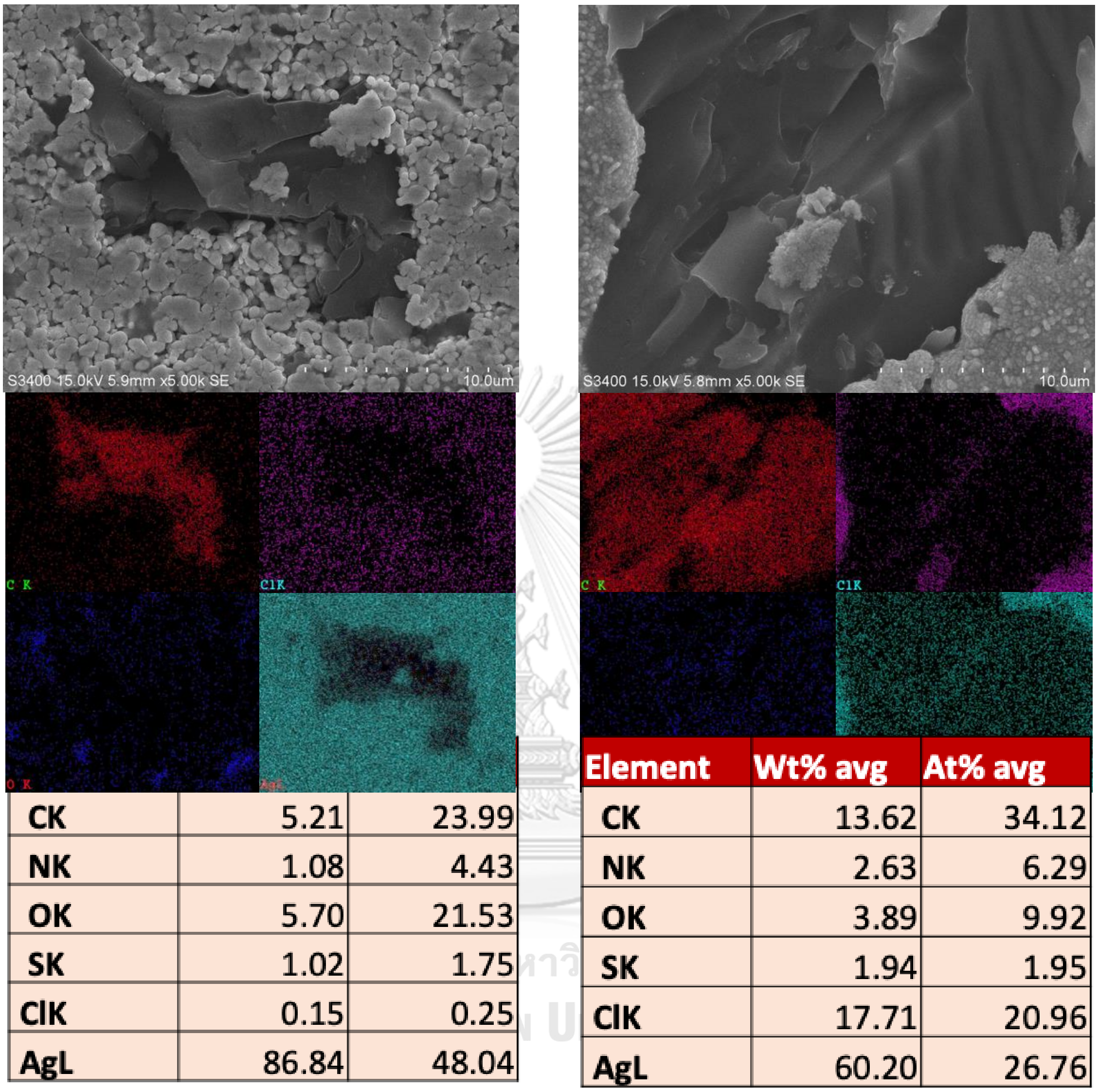
Element	Wt% avg	At% avg
CK	1.40	8.05
NK	0.66	3.27
OK	6.90	29.73
SK	0.26	0.56
ClK	0.24	0.47
AgL	90.54	57.92

Element	Wt% avg	At% avg
CK	13.62	34.12
NK	2.63	6.29
OK	3.89	9.92
SK	1.94	1.95
ClK	17.71	20.96
AgL	60.20	26.76

(a) (b)

Figure 48 SEM-EDX images of silver reinforced with CL-2 by sweat tarnish test (a) Before tarnish (b) After tarnish

4.6.4 Characterization of the sample before and after sweat tarnish: Group 1 the addition of carbon synthetic (CL-3).



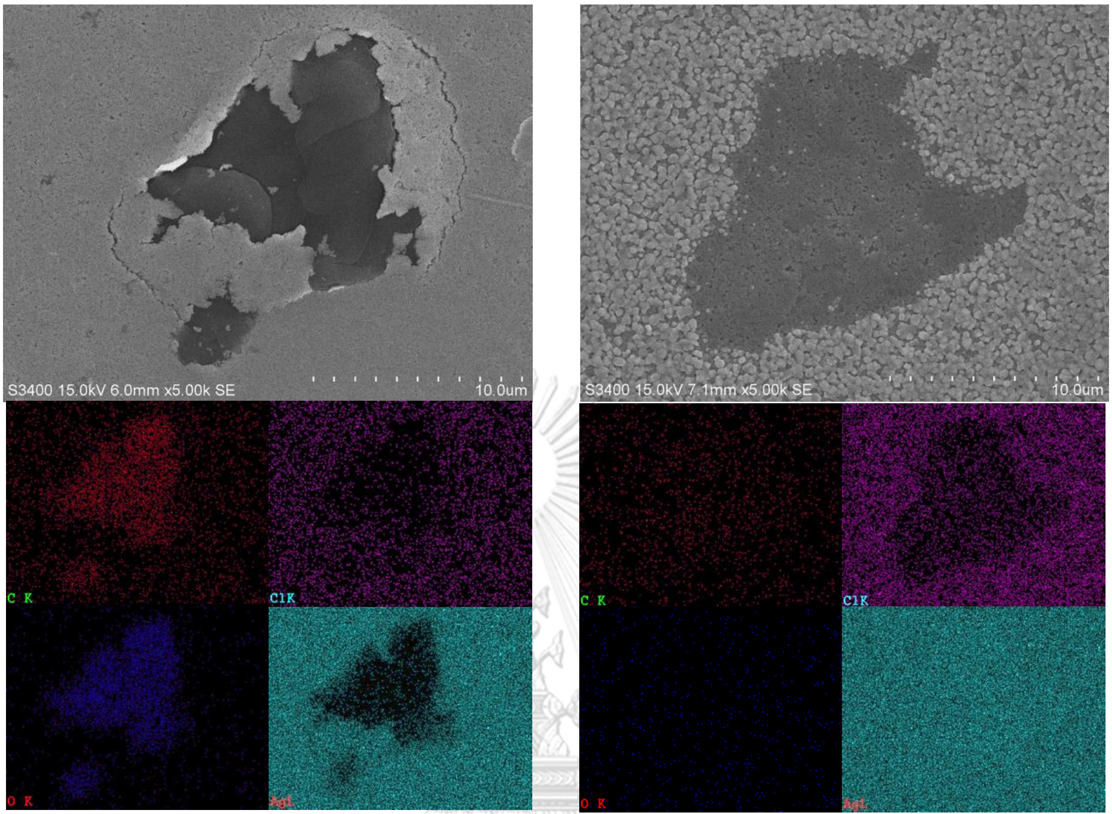
CK	5.21	23.99
NK	1.08	4.43
OK	5.70	21.53
SK	1.02	1.75
ClK	0.15	0.25
AgL	86.84	48.04

Element	Wt% avg	At% avg
CK	13.62	34.12
NK	2.63	6.29
OK	3.89	9.92
SK	1.94	1.95
ClK	17.71	20.96
AgL	60.20	26.76

(a) (b)

Figure 49 SEM-EDX images of silver reinforced with CL-3 by sweat tarnish test (a) Before tarnish (b) After tarnish

4.6.5 Characterization of the sample before and after sweat tarnish: Group 2 the addition of carbon oxide (Graphene Oxide).



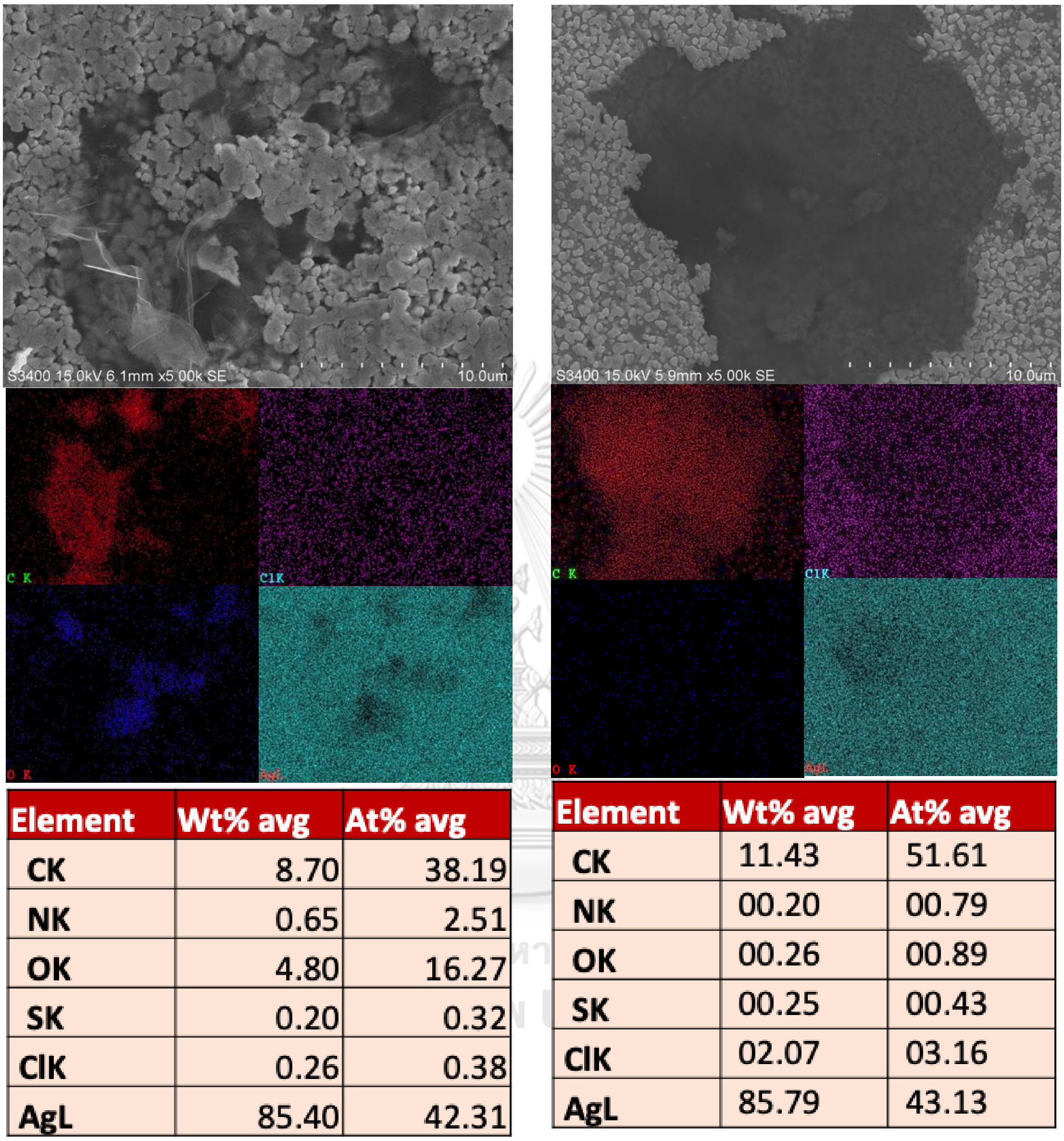
Element	Wt% avg	At% avg
CK	02.39	12.83
NK	00.49	02.28
OK	07.65	30.87
SK	00.18	00.37
ClK	00.18	00.33
AgL	89.10	53.32

Element	Wt% avg	At% avg
CK	00.96	06.85
NK	00.54	03.30
OK	00.55	02.95
SK	00.30	00.80
ClK	04.99	12.11
AgL	92.67	73.98

(a) (b)

Figure 50 SEM-EDX images of silver reinforced with Graphene Oxide by sweat tarnish test (a) Before tarnish (b) After tarnish

4.6.6 Characterization of the sample before and after sweat tarnish: Group 3 the addition of pure carbon (Graphene).



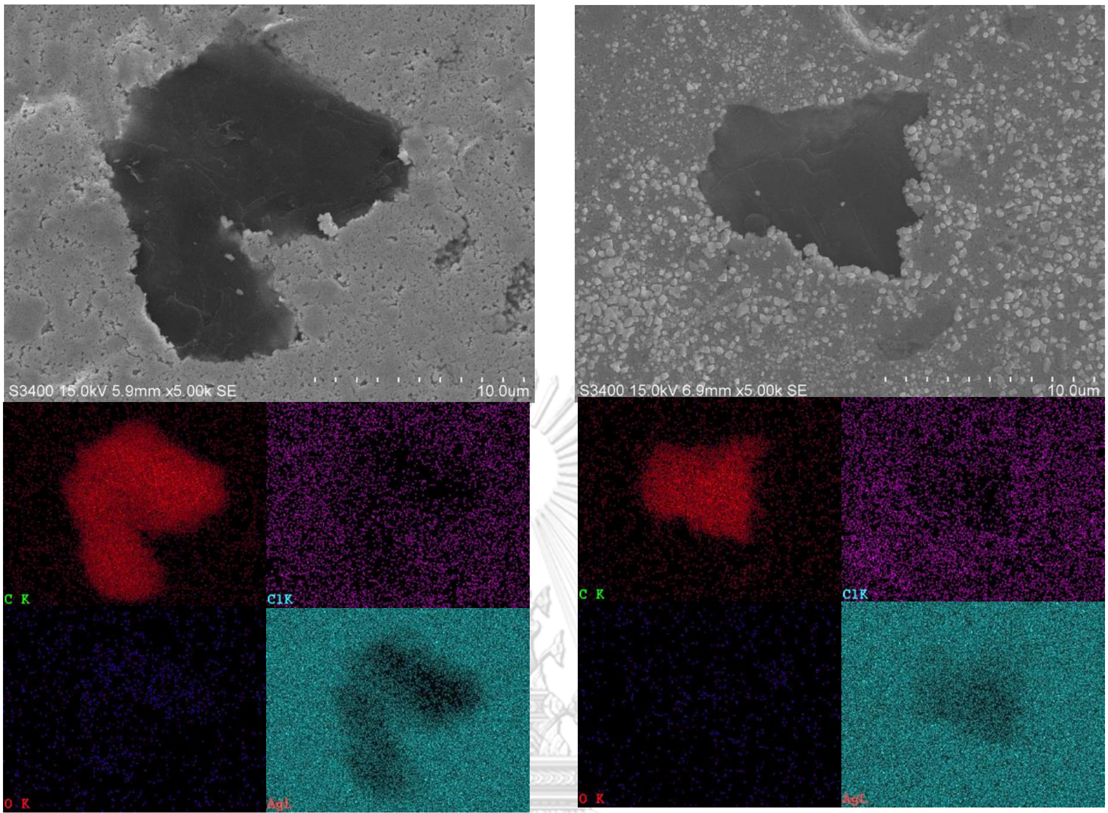
Element	Wt% avg	At% avg
CK	8.70	38.19
NK	0.65	2.51
OK	4.80	16.27
SK	0.20	0.32
ClK	0.26	0.38
AgL	85.40	42.31

Element	Wt% avg	At% avg
CK	11.43	51.61
NK	00.20	00.79
OK	00.26	00.89
SK	00.25	00.43
ClK	02.07	03.16
AgL	85.79	43.13

(a) (b)

Figure 51 SEM-EDX images of silver reinforced with Graphene by sweat tarnish test (a) Before tarnish (b) After tarnish

4.6.7 Characterization of the sample before and after sweat tarnish: Group 3 the addition of pure carbon (Graphene Rod).



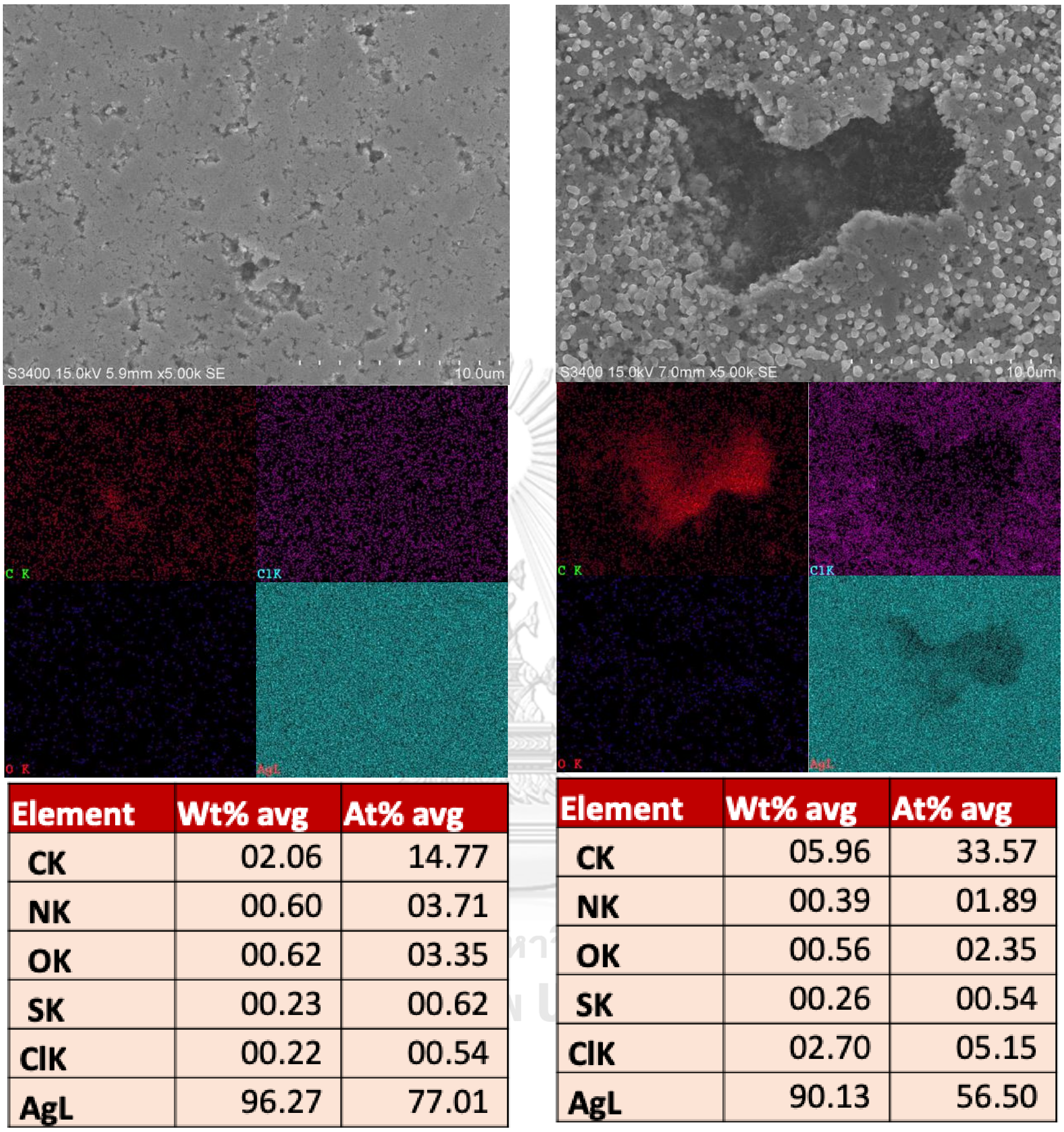
Element	Wt% avg	At% avg
CK	12.25	53.77
NK	00.52	01.97
OK	00.48	01.59
SK	00.12	00.20
ClK	00.13	00.19
AgL	86.49	42.27

Element	Wt% avg	At% avg
CK	06.23	34.96
NK	00.51	02.45
OK	00.54	02.27
SK	00.28	00.58
ClK	01.52	02.89
AgL	90.93	56.84

(a) (b)

Figure 52 SEM-EDX images of silver reinforced with Graphene Rod by sweat tarnish test (a) Before tarnish (b) After tarnish

4.6.8 Characterization of the sample before and after sweat tarnish: Group 3 the addition of pure carbon (Carbon Black).



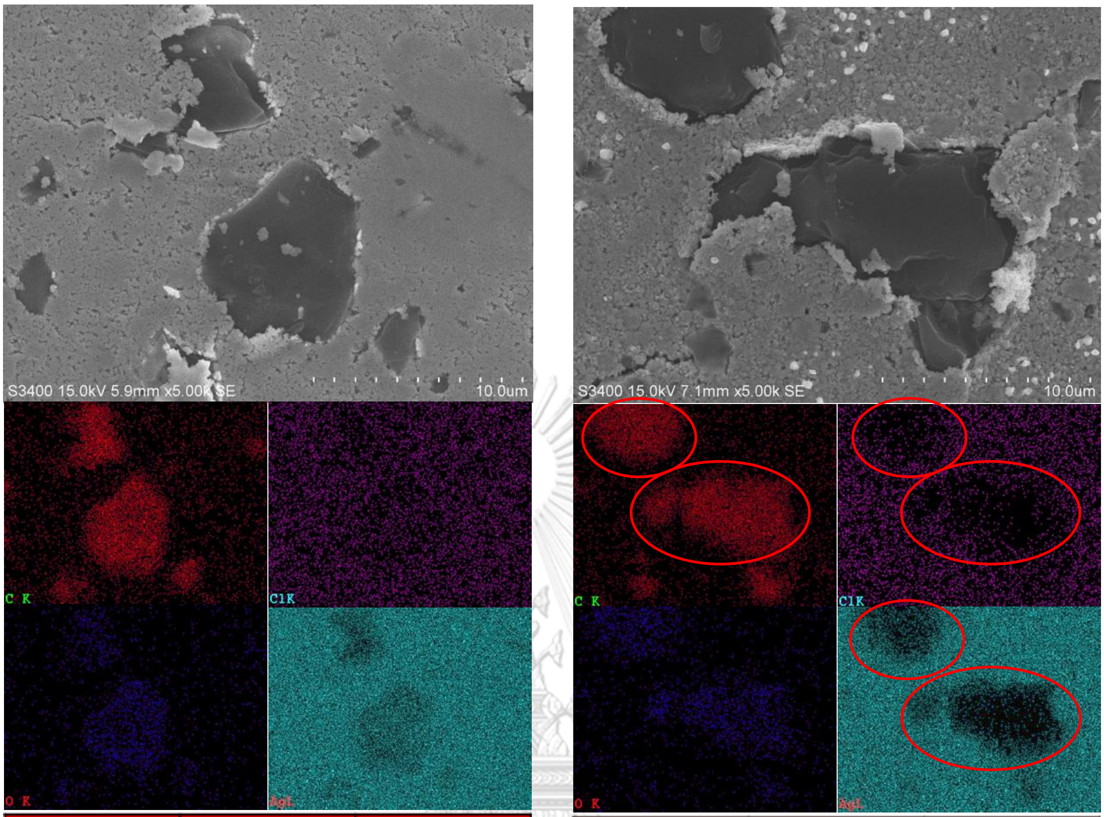
Element	Wt% avg	At% avg
CK	02.06	14.77
NK	00.60	03.71
OK	00.62	03.35
SK	00.23	00.62
ClK	00.22	00.54
AgL	96.27	77.01

Element	Wt% avg	At% avg
CK	05.96	33.57
NK	00.39	01.89
OK	00.56	02.35
SK	00.26	00.54
ClK	02.70	05.15
AgL	90.13	56.50

(a) (b)

Figure 53 SEM-EDX images of silver reinforced with Carbon Black by sweat tarnish test (a) Before tarnish (b) After tarnish

4.6.9 Characterization of the sample before and after sweat tarnish: Group 3 the addition of pure carbon (Activated Carbon)



Element	Wt% avg	At% avg
CK	03.63	22.55
NK	00.47	02.50
OK	02.00	09.30
SK	00.21	00.49
ClK	00.30	00.64
AgL	93.39	64.52

Element	Wt% avg	At% avg
CK	06.24	31.26
NK	00.45	01.93
OK	04.35	16.37
SK	00.25	00.46
ClK	00.40	00.68
AgL	88.32	49.30

(a) (b)

Figure 54 SEM-EDX images of silver reinforced with Activated Carbon by sweat tarnish test (a) Before tarnish (b) After tarnish

Results of SEM-EDX study, after sweat tarnishing test If the position where C is found, Cl is not found in that place. It can be inferred that C does not like to bond Cl according to Figure 44-50, and CCl4 is colourless substance, but when C is dispersed in Ag, Causing the area of Ag to have a less to reduce silver chloride which is the cause of tarnishing from dipping sweat, and then silver less dull.

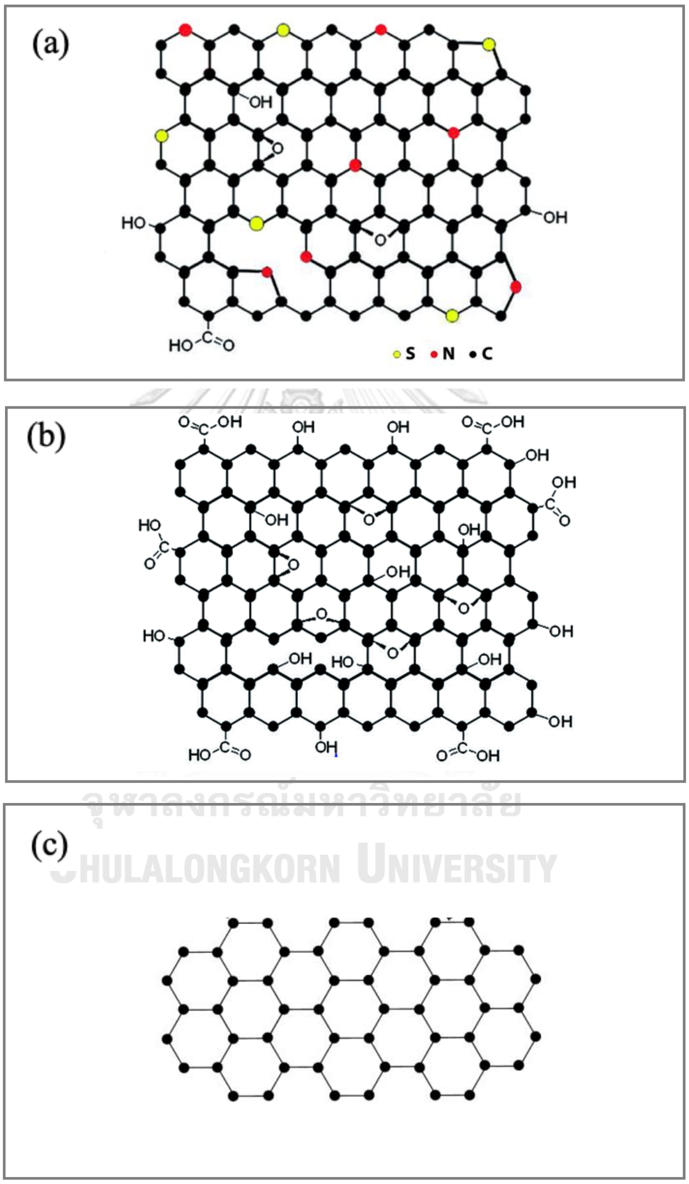


Figure 55 Schematic of the structure of (a) a nitrogen and sulfur co-doped graphene (b) graphene oxide (c) graphene.[19]

From the results group 1 of samples, which are synthetic carbon, consists of elements carbon, oxygen, nitrogen and sulfur. structured as s nitrogen and sulfur co-doped graphene as in Figure. 51 (a), Group 2 is a carbon oxide composed of carbon, oxygen, structured as graphene oxide as in Figure. 51(b), and Group 3 is pure carbon. It has a graphene structure as shown in Figure. 51(c) due to the addition of carbon as a fragmentation instead of silver. It can be seen that Group 1 gives the best results. Because it has many functional groups, It helps in fragmentation well. Followed by the Group 2, and finally, it is the Group 3 which has the least number of function groups. Therefore, the Group 1 (carbon synthetic) is the best resistance to tarnishing from sweat.

CHAPTER V
CONCLUSION

5.1 Conclusion

- Carbon intensification can be determined from the L* and aE* value, the lightness should be L* > 100. The dE* value must be considered if L*<100, assuming that the dE* value < 3.00.
- Results of tarnish resistance of silver reinforced with carbon material to hydrogen sulfideweat study, the carbon (C) reacts with sulfur (S) with a new substance, carbon disulfide (CS_2), which is a colorless substance. Which prevents sulfur (S) from reacting with silver (Ag), So which prevents the formation of silver sulfide (Ag_2S) that is the cause of tarnishing. The dL* value indicates the difference between black and white. between the sample and the standard sample, the results of the measured color values after testing the colour resistance to hydrogen sulfide tarnish showed that Group 2 the best resistance to tarnishing. However, the results from groups 2 and 3 were very similar results. Therefore, it can be assuming groups 2 and 3 have the greatest resistance to tarnishing. followed by group 1 and 100%silver, respectively, the value of dE* and dL* are trending in the same direction So, Group 2 (which has less carbon than Group 3) When increasing the concentration, the amount of carbon will increase, which will help to resist tarnishing better. Group 3 has no anti-tarnish value different from Group 2 because there is already a lot of carbon (90%Wt). Increasing the intensity of carbon does not help to resist tarnishing better, so carbon group 3 is added to 0.5% is enough. It shows that each carbon can only increase its concentration to a certain extent. If added more than that, it will not increase the ability to resist tarnishing from hydrogen sulfide.

- Results of tarnish resistance of silver reinforced with carbon material to artificial sweat study, after sweat tarnishing test, CCl_4 is colourless substance, C does not like to bond Cl, but when C is dispersed in Ag, Causing the area of Ag to have a less to reduce silver chloride which is the cause of tarnishing from dipping sweat, and then silver less dull. Adding of carbon as a fragmentation instead of silver. The distribution of carbon is influenced by the number of functional groups. It can be seen that Group 1 gives the best results. Because it has many functional groups, it helps in fragmentation well. Followed by the Group 2, and finally, it is the Group 3 which has the least number of function groups. Therefore, the Group 1 (carbon synthetic) is the best resistance to tarnishing from sweat.

5.2 Recommendation

The mixing ratio may change more or less from the specified value because the mixing ratio of the metals used is directly related to the quality control of the paint. The concentration of adding carbon material based on weight only may not be possible because the density is not the same, the dispersion and the colour of the initial Ag may different. In further studies, it may be possible to study at additional carbon material densities.

Further study in the field of silverware production must take into account other elements as well. Introducing other alloying elements that act as secondary alloys that affect mechanical properties. The microstructure and color of silver alloys have not been studied. Therefore, it is very important that the influence of various secondary alloys should be studied. That can be found in sterling silver in addition to carbon.

However, the results of this research show that the effect between carbon and silver, Carbon can really help reduce the tarnishing of silver. Just need to find the right amount for actual use in order to get the best yield.

APPENDIX

1 Calculation method of dL and dE before tarnish

L* is represents Lightness

a* is represents the Redness/Greenness axis

b* is represents the yellowness/blueness axis

ΔE is used to express Delta Error, the total color difference computed using a color difference equation.

The color difference between the sample and the standard sample can be found as the equation.

$$\Delta L^* = L^*\text{of } 100\%\text{Ag} - L^*\text{of the sample with filler}$$

$$\Delta a^* = a^*\text{of } 100\%\text{Ag} - a^*\text{ of the sample with filler}$$

$$\Delta b^* = b^*\text{ of } 100\%\text{Ag} - b^*\text{ of the sample with filler}$$

Illuminance is measured by the L* value. For a variety of causes, the L* number may be higher than 100. for instance, Because the sample contains materials that can reflect light (glitter), the L value is greater than 100. In this study, The permissible illuminance value for this investigation is $L^* \geq 100$. The dE* value is taken into consideration if $L^* < 100$.

The standard method for evaluating color accuracy is dE*. When comparing two colors side by side, experts perceive no change when the value of $dE^* < 1.00$ is present. If $dE^* < 3.00$. significant variations for the typical person. In this study, The permissible illuminance value for this investigation is $dE^* < 3.00$.

In addition to telling the difference by ΔL*, Δa*, Δb*, it can tell the total color difference between the sample and the standard sample (total color difference) ΔE when

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

2 Calculation method of dL and dE after tarnish

The color difference between the sample and the standard sample can be found as the equation.

$$\Delta L^* = L^* \text{of before tarnish} - L^* \text{of after tarnish}$$

$$\Delta a^* = a^* \text{of before tarnish} - a^* \text{ of after tarnish}$$

$$\Delta b^* = b^* \text{ of before tarnish} - b^* \text{ of after tarnish}$$

For Group 1 = $[(\Delta L^*_{\text{CL-1}}) + (\Delta L^*_{\text{CL-2}}) + (\Delta L^*_{\text{CL-3}})]/3$

For Group 2 = $[(\Delta L^*_{\text{Graphene Oxide}})]/1$

For Group 3 =$[(\Delta L^*_{\text{Graphene}}) + (\Delta L^*_{\text{Graphene Rod}}) + (\Delta L^*_{\text{Carbon black}}) + (\Delta L^*_{\text{Activaed}} \text{ carbon})]/4$

In addition to telling the difference by ΔL*, Δa*, Δb*, it can tell the total color difference between the sample and the standard sample (total color difference) ΔE when

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

For the Group 1 = $[(\Delta E^*_{\text{CL-1}}) + (\Delta E^*_{\text{CL-2}}) + (\Delta E^*_{\text{CL-3}})]/3$

For the Group 2 = $[(\Delta E^*_{\text{Graphene Oxide}})]/1$

For the Group 3 =$[(\Delta E^*_{\text{Graphene}}) + (\Delta E^*_{\text{Graphene Rod}}) + (\Delta E^*_{\text{Carbon black}}) + (\Delta E^*_{\text{Activated carbon}})]/4$

3 Experimental data

3.1 The sample Ag with 0.5% filler

Sample	Before Tarnish		After Tarnish H_2S		After Tarnish Sweat	
	L*	**dE**	**dL***	**dE**	**dL***	**dE**
100%Ag	103.11		19.02	22.36	44.27	45.07
0.5%CL-1	102.55	0.80	5.91	8.42	45.08	45.38
0.5%CL-2	103.26	1.06	29.22	29.34	39.91	40.31
0.5%CL-3	103.44	1.60	11.80	14.82	36.79	37.11
0.5%Graphene Oxide	105.03	2.60	11.77	11.94	47.10	47.45
0.5%Graphene	100.83	2.92	3.27	3.58	39.37	39.41
0.5%Graphene Rod	106.03	3.17	12.50	14.58	55.64	55.73
0.5%Carbon Black	96.22	(10.53)				
0.5%Activated Carbon	104.71	1.98	9.14	10.00	44.27	44.58

Note: 0.5%Carbon Black not be applied to the next part's study.

Average				
Sample	After Tanish H_2S		After Tanish Sweat	
	dL*	**dE**	**dL***	**dE**
100%Ag	19.02	22.36	44.27	45.07
Group 1	15.64	17.53	40.60	40.93
Group 2	11.77	11.94	47.10	47.45
Group 3	8.30	9.39	46.43	46.58

3.2 The sample Ag with 0.7% filler

Sample	Before Tarnish		After Tarnish H_2S		After Tarnish sweat	
	L*	**dE**	**dL***	**dE**	**dL***	**dE**
100%Ag	103.11		19.02	22.36	44.27	45.07
0.7%CL-1	108.77	5.69	11.90	13.28	43.44	44.69
0.7%CL-2	106.24	3.38	15.25	17.77	41.60	41.93
0.7%CL-3	102.45	1.43	12.74	18.15	33.76	33.96
0.7%Graphene Oxide	104.60	1.83	8.55	9.72	46.11	46.72
0.7%Graphene	98.29	-8.46				
0.7%Graphene Rod	102.04	1.22	7.90	10.08	57.66	57.88
0.7%Carbon Black	93.33	-13.42				
0.7%Activated Carbon	101.84	1.45	10.37	10.90	42.57	42.88

Note: 0.7%Graphene and 0.7%Carbon Black not be applied to the next part's study.

Average				
Sample	After Tarnish H2S		After Tarnish sweat	
	dL*	**dE**	**dL***	**dE**
100%Ag	19.02	22.36	44.27	45.07
Group 1	13.30	16.40	39.60	40.19
Group 2	8.55	9.72	46.11	46.72
Group 3	9.14	10.49	50.12	50.38

3.3 The sample Ag with 1% filler

Overall						
Sample	Before Tarnish		After Tarnish H2S		After Tarnish sweat	
	L*	**dE**	**dL***	**dE**	**dL***	**dE**
100%Ag	103.11		19.02	22.36	44.27	45.07
1%CL-1	107.89	5.83	18.19	20.14	42.71	47.69
1%CL-2	107.34	4.52	16.26	19.89	45.31	45.48
1%CL-3	101.42	1.71	8.75	11.12	37.74	38.24
1%Graphene Oxide	104.18	1.56	7.67	9.23	48.90	49.08
1%Graphene	96.04	(10.71)				
1%Graphene Rod	100.86	2.26	7.82	9.54	52.35	52.68
1%Carbon Black	92.02	(14.73)				
1%Activated Carbon	96.55	(10.20)				

Note: 1%Graphene, 1%Carbon Black and 1%Activated Carbon not be applied to the next part's study.

Average				
Sample	After Tarnish H_2S		After Tarnish sweat	
	dL*	**dE**	**dL***	**dE**
100%Ag	19.02	22.36	44.27	45.07
Group 1	14.40	17.05	41.92	43.81
Group 2	7.67	9.23	48.90	49.08
Group 3	7.82	9.54	52.35	52.68

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VITA

NAME	Kunthida Chanthaban
DATE OF BIRTH	3 April 1996
PLACE OF BIRTH	Nakhon Phanom, Thailand
INSTITUTIONS ATTENDED	B.Eng Chemical Engineering Faculty of Engineering, Thammasat University
HOME ADDRESS	565/52 Ram Inthra Rd, Khwaeng Ram Inthra, Khet Khan Na Yao, Bangkok, Thailand 10230