DEVELOPMENT OF THERMAL INTERFACE MATERIAL

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Mechanical Engineering

> Faculty of Engineering and Science Universiti Tunku Abdul Rahman

> > **JUNE 2015**

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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I certify that this project report entitled "DEVELOPMENT OF THERMAL INTERFACE MATERIAL" was prepared by TAN CHEOW HOONG has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Mechanical Engineering at Universiti Tunku Abdul Rahman.

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Specially dedicated to Richard

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DEVELOPMENT OF THERMAL INTERFACE MATERIAL

ABSTRACT

Since the successful isolation of single layer graphene by Nobel rize winners Novoselov and Geim in 2004, graphene has gained the attention of researchers worldwide. Two dimensional honeycomb structured graphene was discovered to have superlative properties and many research has been conducted to utilise these properties. In this project, graphene was used as a filler material to produce thermal interface material. Firstly, graphene was synthesised using hydrazine reduction of graphene oxide. Raman analysis were conducted and characteristic graphene spectrum was obtained with G peak at 1596 and 1597 cm⁻¹ for HRGO reduction in water and ethanol respectively. HRTEM imaging confirmed successful synthesis of graphene using both formulations with interlayer spacing of 0.31-0.35nm and hexagonal SAED patterns were also obtained. Besides, XPS showed reduction in ethanol was more effective than in water. Dispersion using surfactants IGEPAL CO-890 and SDBS were performed to reduce agglomeration. XPS analysis detected CO-890 functionalization of HRGO with 44.85% C=O bond concentration while SDBS functionalization was indicated by 4.19% atomic concentration of sodium present in filler produced. Optical microscope images qualitatively showed dispersion of filler in epoxy. Lastly, all samples produced were filled into epoxy to make TIM and thermal conductivity experiments were conducted. It was found that dispersion of graphene through functionalization was successful in reducing agglomeration but thermal conductivity was reduced as a result. Highest thermal conductivity (13.42 W/m.K) was obtained from filler that was not functionalised.

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LIST OF SYMBOLS / ABBREVIATIONS

A	Area, m ²
k	thermal conductivity, W/m.K
<i>q</i> "	heat flux, W/m ²
Q	rate of heat transfer, W
Т	temperature, K
x	distance, m
R	mass flow rate ratio
CO-890	polyoxyethylene (40) nonylphenylether
HRGO	hydrazine reduced graphene oxide / graphene
SDBS	sodium dodecyl benzene sulfonate

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CHAPTER 1

INTRODUCTION

1.1 Background

When two surfaces are placed together, it is not possible to achieve 100% surface contact between them. Although both surfaces may look even to the naked eye and have glossy finishes, there are microscopic air spaces between them as illustrated in Figure 1 (left). These air spaces are undesirable because air is a good heat insulator and will affect the heat conduction between the two surfaces. Thermal interface material (TIM) is a compound that is placed between two surfaces to improve their surface contact as shown in Figure 1 (right). It functions as a heat conductor to transfer heat from one surface to another. Commercially available thermal greases and thermal pads are examples of TIM which are used in the industry. TIM is important in transporting heat away from a source to prevent overheating of components. Examples of applications include microprocessors and solar cells.



Figure 1.1: Microscopic air spaces (left) and air spaces filled with TIM (right)

Graphene is an allotrope of carbon. Single layer graphene is two dimensional with carbon atoms arranged in a honeycomb lattice structure as shown in Figure 1.2. In 2008, Lee et al. (2008) measured the mechanical properties of monolayer graphene and determined its Young Modulus to be 1000 GPa. The Royal Swedish Academy of Science (2010) compiled a properties summary for graphene and stated the electrical conductivity of graphene is $0.96 \times 106 \ \Omega^{-1} \text{cm}^{-1}$ while its thermal conductivity is measured approximately 5000 Wm⁻¹K⁻¹. This makes graphene more electrically and thermally conductive than copper. With such interesting potential, this project hopes to explore the use of graphene as a component of TIM.



Figure 1.2: 2D structure of graphene

1.2 Aims and Objectives

Development of TIM using graphene as filler material and epoxy as binder to form a graphene-epoxy matrix is the aim of this project. In order to accomplish this, three main objectives were established.

First objective is the synthesis of graphene. Graphene synthesis is done chemically. Graphene oxide (GO) will have to be produced followed by hydrazine reduction to yield graphene or more accurately, hydrazine reduced graphene oxide (HRGO). Both GO and HRGO produced will be characterized to check their quality.

Second objective is the dispersion of HRGO. HRGO has a tendency to agglomerate when it is dried. Dispersion of HRGO is important to ensure even distribution of filler material in epoxy. To do this, two types of surfactants will be used and compared.

Third objective is to study the thermal conductivity of HRGO-epoxy TIM produced. HRGO combined with surfactants will be stirred in epoxy at fixed weight percentage then cured into TIM samples. These samples will be inserted into polystyrene which acts as an insulator and tested using the SOLTEQ thermal conductivity machine.

1.3 Overview

The next chapter is Literature Review. Journals pertaining to this project will be examined and discussed. Chapter 3 contains Methodology. Gantt chart depicting the activities that need to be executed and their duration will be shown. Detailed experimental procedures will also be included in that chapter. After Chapter 3, results will be compiled and discussed in Chapter 4. The final chapter which is Chapter 5 will conclude this project.

CHAPTER 2

LITERATURE REVIEW

2.1 Graphene Synthesis

As understanding towards graphene deepens, fabrication methods became more varied. Das et al. (2013) summarised the various graphene preparation methods. Among them are mechanical exfoliation using scotch tape, chemical exfoliation with alkaline metals, chemical synthesis, thermal chemical vapour deposition (CVD) and graphene transfer. In order to produce large yield graphene at low cost for lab use, chemical synthesis is the most suitable method. However, this method produces graphene which are damaged and inferior in quality compared to CVD method.

Chemical synthesis of graphene via hydrazine reduction has been performed by Stankovich et al. and Marcano et al. Before hydrazine reduction can be done, GO has to be acquired. Huang et al. (2011) managed to produce large yield of GO through chemical oxidation of graphite at room temperature. Once there is a source of GO, HRGO can be prepared. Stankovich et al. (2007) reduced GO in hydrazine for 24 hours while Marcano et al (2010) only performed hydrazine reduction for an hour using the same amount of GO to hydrazine to water ratio (0.1g:1ml: 100ml) as Stankovich.

Since Huang et al. managed to produce high yield GO, that method was selected for use. However, due to time constraint and possibility of over-oxidation of

graphite by Huang, experimental procedures shall be modified. Furthermore, in hydrazine reduction of GO, Marcano et al. has shown that the reduction process does not require 24 hours as conducted by Stankovich et al. This revelation shortens synthesis duration significantly.

2.2 Graphene Dispersion

Agglomeration of graphene is one of the main issues which reduces its potential when used in composites. Achieving even dispersion of graphene exposes its surfaces to the epoxy matrix and is important in order to utilise its thermal properties effectively. Wallace et al. (2008) managed to produce colloids of graphene nanosheets through hydrazine reduction of GO with addition of ammonia. Yu et al. (2011) discovered notable improvement in thermal conductivity of nanofluids which contains graphene dispersed using sodium dodecylbenzene sulfonate (SDBS). In the following year, Pu et al. (2012) dispersed graphene in aqueous solution using three types of surfactants. It was found that polyoxyethylene (40) nonylphenylether (IGEPAL CO-890) performed the best in terms of graphene dispersion. Moriche et al. (2014) studied the morphological changes in graphene nanoplatelets dispersed in epoxy by different techniques and found that dispersion method can induce stress and create defects into graphene.

Those papers indicate the different methods of dispersing graphene. Wallace's reduction method has a very important prerequisite which is difficult to achieve. GO used for reduction has to be very clean and thus was subjected to dialysis. Using surfactants to aid dispersion would be a more feasible method. Surfactants could be added with hydrazine during reduction of GO or sonicated with reduced GO. Since comparison between SDBS and IGEPAL CO-890 was not conducted, it will be an interesting path to explore in this project. Furthermore, hydrazine reduction is usually carried out in water but Yu used ethanol instead without elaborating on the effect of changing the medium of reduction. Hence, hydrazine reduction of GO in ethanol will be studied in this project.

Understanding the stabilisation mechanism of surfactants used is also important. Smith et al. (2010) described the stabilisation mechanism of ionic and nonionic surfactants. For ionic surfactants such as SDBS, the tail group can adsorb onto non-polar graphene by Van der Waals forces. Head group will dissociate from the tail group thus creating a electrostatic charge on the molecules to repel each other. Nonionic surfactants such as IGEPAL CO-890 has a hydrophobic tail and long hydrophilic head. Hydrophobic tail will adsorb onto graphene while hydrophilic head will extend out and cause stearic repulsion when two hydrophilic heads approach each other. However, instead of using HRGO in colloid solutions, HRGO produced with addition of surfactants will be dried so that they can be filled into epoxy. Dispersion level of fillers in epoxy will indicate how well dispersed these fillers are.

2.3 Thermal Interface Materials (TIM)

Before incorporation of graphene into TIM, thermal conductivity studies on graphene was conducted. Cai et al. (2010) grew single layer graphene using CVD and suspended it over a hole. Their research determined the thermal conductivity of their suspended single layer graphene to be 320W/m.K at room temperature.

Graphene based filler TIM has been subjected to extensive research. In 2012, Shalil et al. prepared multi-layered graphene cured in epoxy and studies its thermal properties. They discovered the thermal conductivity of their TIM can increase up to a factor of 23 when it was loaded with 10% volume fraction of multi-layered graphene. Garimella (2014) has conducted research on TIM using graphene which are vertically grown onto silicon or copper. Thermal resistance of his TIM was very low. Moving forward to this year, Johnson (2015) wrote an article in IEEE Spectrum regarding the use of graphene based coatings on light emitting diodes (LED). Graphene- based coating will remove heat from the bulb and extend its lifespan. It is no doubt that graphene filled TIM can effectively conduct heat.

For graphene-epoxy composites, thermal conductivity research has been performed by some researchers as well. Tang et al. (2013) managed to establish a linear relationship between graphene filler loading in epoxy and thermal conductivity in their TIM. Using 10.10 wt% graphene sheets filled epoxy thermal adhesive produced by Fu et al. (2014) has thermal conductivity which is 22 times better than blank epoxy.

There are several key ideas obtained from these readings. Firstly, thermal conductivity of graphene based TIM is lower than that of pure graphene. That is to be expected as binder materials have different conductivity than graphene. Secondly, increasing volume percent of graphene filled into the TIM improves thermal conductivity but too at the expense of the TIM's viscosity and hence ease of spreading decreases. Excessive graphene filler may cause clumping and fail in its purpose to improve thermal contact between two conducting surfaces. Thirdly, thermal conductivity increases with increasing filler content and characterisations are done using laser flash apparatus.

CHAPTER 3

METHODOLOGY

3.1 Project Planning

A project plan is important as the activities that needs to be done will be identified and their respective duration will also be estimated. Figure 3.1 shows the Gantt chart for the first semester of this project (FYP 1) while Figure 3.2 shows the Gantt chart for the second semester of this project (FYP 2). Gantt chart displays the task name, duration start date and end date. It also shows the sequence of tasks. For example, referring to Figure 3.1, Task 1 shows Project Title Selection has a duration of 6 days excluding weekends. This task starts at 16th January and ends on 23rd January. Task 2 Literature Reviews starts after task 1 has been completed.



Figure 3.1: FYP 1 Gantt Chart



Figure 3.2: FYP 2 Gantt Chart

3.2 Flow Chart

Figure 3.3 shows the flow chart depicting the expected processes that needs to be completed in order to complete this project. This project started off with literature review because more information and deeper understanding of the topic were required. After better understanding was obtained, aims and objectives were established as goals that this project should accomplish. Next, planning of project was performed. Activities that needed to be executed were identifies as detailed as possible followed by planning of experimental procedures to achieve the objectives established previously. Once that was done, the planned experiments were be carried out. Results obtained from experiments and testing were complied and interpreted. Lastly, the whole project was presented in the form of a final year report and presentation.



Figure 3.3: Project Flow Chart

3.3 Materials

Following are the list of materials used followed by brand at the end. Graphite Grade: Nano25, Cummings-Moore Sulphuric acid, Systerm Phosphoric acid, Systerm Potassium permanganate, Systerm Hydrogen peroxide, Systerm Hydrochloric acid, Systerm Ethanol absolute, HmbG Chemicals Hydrazine hydrate, Sigma-Aldrich Sodium dodecylbenzene sulfonate, Sigma-Aldrich IGEPAL CO-890, Sigma-Aldrich Bisphenol A diglycidyl ether, Sigma-Aldrich Diethylene triamine, Sigma-Aldrich

3.4 Experimental Procedures

Following sub-sections contains the experimental procedures for this project. Precautions and illustrations as guides were also included.

3.4.1 Synthesis of GO

The chemical synthesis of GO followed Huang's method but with some modifications. First, 2.0g of graphite was weighed in a large beaker (A). Next, 8g of potassium permanganate (KMnO₄) was weighed in a small beaker. A magnetic plate was placed in a fume hood and a stir bar was inserted into the beaker containing graphite. 20ml of phosphoric acid (H₃PO₄) was then measured and poured gently into the beaker. After that, 180 ml of sulphuric acid (H₂SO₄) was measured and added into the beaker as well. Beaker containing graphite, H₃PO₄ and H₂SO₄ was then placed onto the center of a magnetic plate. The plate was switched on and its stirring speed was increased gradually. Care must be taken to ensure the stir bar does not knock against the sides of the beaker. If any knocking was heard, the stirring was reduced to zero and beaker's position was adjusted till no further knocking was heard when the stir bar is stirring to prevent splashing. Stirring speed was increased gradually until a vortex can be seen in beaker A's solution.

Next, an infrared thermometer was used to check the initial temperature of the contents in the beaker. Using a spatula, small amounts of KMnO₄ was added slowly. The temperature of the solution was monitored closely and kept below 55°C. If the temperature becomes close to 55°C, addition of KMnO₄ was stopped and the solution is left to cool a little. Once all KMnO₄ was dissolved into the solution, reaction was left to continue for 48 hours as shown in. After 48 hours, the reaction was stopped by addition of hydrogen peroxide (H₂O₂) until it stopped fizzing. The resulting solution was diluted with equal amounts of distilled water and centrifuged at 4000rpm. Washing process was repeated by adding 1M hydrochloric acid (HCl) and centrifuged again. Distilled water was then added to the residues and left to sit overnight. On the following day, the distilled water was poured away and all sediments were transferred

into a beaker and placed into a drying oven to dehydrate the GO. The appearance of contents during synthesis of GO are depicted in Figure 3.4.



Figure 3.4: Appearance of mixture as synthesis progressed

3.4.2 Synthesis of HRGO

For chemical synthesis of graphene, hydrazine reduction method was employed to produce HRGO. In this project, Marcano's method was chosen. However, due to the small yield of Marcano's procedure, attempts were made to scale up that process. To start, 1g of dried GO was weighed in a beaker. Then, 200ml of distilled water was added into the flask and its contents were sonicated until all GO has dissolved. Dissolved GO was then transferred into a round bottom flask held by a retort stand and another 300ml of distilled water was added to increase the final volume of liquid to 500ml.

Meanwhile, a large pot of glycerine bath was placed onto a hot plate at medium heat setting to warm. Next, 10ml of hydrazine was added into the round bottom flask containing dissolved GO. Using another retort stand, a reflux tube was positioned above the round bottom flask. One end of reflux tube was secured to mouth of flask with tape. Flask with reflux tube attached was lowered into the glycerine bath and secured in place as shown in Figure 3.5. Water supply was turned on for reflux tube. An infrared thermometer was used to check the temperature of glycerine bath. Hydrazine reduction was carried out at boiling temperature for 3 hours.



Figure 3.5: Final experimental setup

After 3 hours, the flask was removed from glycerine and left to cool. Resulting compound was filtered out and washed with 20ml of ethanol then 100ml of distilled water as shown in Figure 3.6, followed by drying in an oven to obtain HRGO. This filler material was labelled as MW. Another batch was made but ethanol was used to replace distilled water as medium of reaction. Synthesis steps were unchanged and filler produced by hydrazine reduction of GO in ethanol was named ME.



Figure 3.6: Washing of HRGO using filter method

3.4.3 Dispersion of HRGO

Dispersion of HRGO utilised SDBS and IGEPAL CO-890. Method of preparation followed that of hydrazine reduction of HRGO in ethanol in previous section with some modifications to incorporate the surfactants. First, 10g of SDBS was weighed in a beaker. Next, 50 ml of dissolved GO was poured into the beaker containing SDBS. Mixture was sonicated for 5 minutes and poured back into the round bottom flask containing remaining GO. 10ml of hydrazine was then added and reduction was carried out under reflux as described in Section 3.4.2.

After reduction, mixture was cleaned with ethanol four times using centrifuge machine because HRGO produced can no longer be filtered by filter paper. Ethanol caused the mixture to separate into 2 distinct layer (Figure 3.7). After cleaning, sediment was transferred into a beaker and dried in drying oven. This batch of filler will be referred to as S1 in future discussion. Another batch of filler called S0.1 was made but with only 1g SDBS for 1g dried GO.



Figure 3.7: HRGO mixture separated after centrifuge with ethanol

IGEPAL CO-890 is a wax like substance that was very difficult to scoop out. Therefore, the whole bottle was placed overnight in the oven at 35°C to melt its contents. Filler C1 was made using 10g of IGEPAL CO-890 to 1g of dried GO. Procedures remained unchanged as the steps described above. Final batch was made with 1g of IGEPAL CO-890 to 1g of dried GO and labelled C0.1.

To avoid confusion, filler names and their respective formulations were compiled into Table 3.1.

Filler Name	Reduction	Type of	Amount of	Amount of
	Medium	Surfactant	Surfactant (g)	Dried GO (g)
MW	Water	None	0	1
ME	Ethanol	None	0	1
C1	Ethanol	CO-890	10	1
C0.1	Ethanol	CO-890	1	1
S1	Ethanol	SDBS	10	1
S0.1	Ethanol	SDBS	1	1

Table 3.1: HRGO filler information

3.4.4 Preparation of TIM Samples

TIM requires even dispersion of filler material. First, 0.5wt% of filler was added to 5ml of warm epoxy and stirred evenly with a glass rod for 20 minutes. Then, 9wt% of diethylene triamine (DETA) curing agent was added into the epoxy-filler compound and vigorously stirred for another 15 minutes. Compound was poured into a syringe and left overnight to pre-cure. Hardened compound was placed into a vacuum oven at 120°C for 1.5 hour. TIM was taken out of vacuum oven and left to cool. Lastly, it was removed from its syringe and sand into dimension to fit into a SOLTEQ machine for thermal conductivity test. Figure 3.8 shows TIM sample making process.



Figure 3.8: TIM sample preparation process

3.5 Equipment

These equipment were used for characterisation of samples prepared throughout this project. A brief introduction of their working principles and the samples that were tested using the respective equipment are as elaborated below.

3.5.1 Cary 100 Ultraviolet-Visible Spectrophotometer (UV/VIS)

UV/VIS utilises light in the ultraviolet and visible light region of the electromagnetic spectrum to radiate a sample. When light is adsorbed by molecules, energy is transferred thus increasing the energy content of the molecules. Transitions from low to high energy level by molecules will product the absorbance spectra (Owen, 2000).

UV/VIS was used to characterize GO produced. Figure 3.9 (a) shows 2 quartz cuvette. One contained the solvent which was distilled water and the other contained GO diluted in distilled water. These 2 cuvettes were inserted into the UV/VIS spectrophotometer in Figure 3.9 (b) to obtain the absorbance spectrum of GO.



Figure 3.9: (a) Quartz cuvette containing distilled water (left) and diluted GO (right) (b) UV/VIS spectrophotometer

3.5.2 Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-Ray (EDX)

In FESEM, an electron gun shoots electrons onto the surface of a sample. Secondary electrons are produced as a result and the intensity of these secondary electrons are dependent on their surface topology. By measuring the intensity of the secondary electrons with respect to the position of the primary electrons from the electron gun, an image of the sample can be produced (Leung, 2015). Compared to conventional optical microscope, electron microscope can provide very high magnification, up to 30 000 times, unlimited depth of focus and good resolutions. FESEM can produce sharper and clearer images compared to SEM.

EDX which comes with FESEM uses back scattering of electrons to provide chemical information of the sample. Emitted X-rays are characteristic of different elements (Leung 2015).

In order to use FESEM, all samples has to be completely dried. The presence of moisture in the samples will cause charging and images produced would be blurred. Sample preparation for FESEM required a small amount of material to be placed onto a carbon tape stuck onto the sample holder. Then, the sample holder with materials on top was placed into the sputter machine in Figure 3.10 (a). Sputter machine coated every sample with a thin film of platinum. After sputtering, the samples were placed into FESEM in Figure 3.10 (b). FESEM images were obtained for GO and HRGO produced while EDX was conducted on GO only.





Figure 3.10: (a) JFC-1600 Auto Fine Coater (b) FESEM

3.5.3 High Resolution Transmission Electron Microscope (HRTEM)

Transmission electron microscope in Figure 3.11 (a) is an imaging tool which uses an electron beam to obtain high magnification images of nanomaterials. An electron gun produces a stream of electrons which is then focused into a monochromatic beam. Electron beam is then directed onto the specimen but a portion of the beam will get transmitted through. Transmitted beam is then focused by the objective lens onto an image which is enlarged by intermediate and projector lenses. Phosphor screen in Figure 3.11 (b) enables image to be produced and viewed by the user.

Fillers MW and ME was tested using HRTEM. First, both fillers were sonicated in ethanol as shown in Figure 3.11 (c). After sonication, a lacy copper grid was used to trap sheets of suspended fillers.









(c)

Figure 3.11: (a) F20 X-Twin HRTEM at MIMOS (b) Phosphor screen (c) Sample preparation (left: sonicated MW and ME, right: MW and ME on copper grid)

3.5.4 Phi Quantera II X-ray Photoelectron Spectroscope (XPS)

XPS (Figure 3.12) is used to analyse the surface chemistry of a sample. The term surface is used because XPS only analyses the top 1-10nm layers. A beam of X-ray is focused onto the surface of the sample causing photoelectrons to be ejected. Different atoms emit different characteristic energy which will be detected as peaks in the XPS spectra. This equipment can be used to measure composition of elements, empirical formula, chemical and electronic state of the elements of the sample (ThermoScientific n.d). XPS analysis was used on MW, ME, C1 and S1.



Figure 3.12: Phi Quantera II XPS at MIMOS

3.5.5 Raman Spectroscope

Raman spectroscopy, similar to is a vibrational spectroscopy. A sample is placed into the microscope and a monochromatic laser beam will be directed onto it. Renishaw inVia Raman equipment depicted in Figure 3.13 uses a 514nm monochromatic laser. This laser beam will cause inelastic scattering of photons in the sample. Difference in energy produces discrete lines which make up the Raman spectrum. Raman analysis was performed on all HRGO samples produced.



Figure 3.13: Raman spectroscope

3.5.6 Olympus Optical Microscope

When a specimen is placed after the focal point but less than two times the focal length of the objective lens, a magnified image of the specimen is produced. A second lens called the eyepiece is used to detect this image which formed at its focal length (Ruhl, 2012). The optical microscope shown in Figure 3.14 has a camera behind the eyepiece to enable pictures of the magnified images to be taken. This optical microscope can perform a 5X, 10X and 20X magnification on a specimen. Fillers produced in this experiment was mixed into epoxy at 1 wt% loading and viewed under the microscope.



Figure 3.14: Optical microscope
3.5.7 SOLTEQ Thermal Conductivity Bench

When heat is supplied to one end of a rod, molecules at the hot end will gain energy and vibrate. These vibrations are transmitted along the rod and heat is conducted. Heat conduction requires a temperature gradient to occur. SOLTEQ thermal conductivity bench in Figure 3.15 enables the determination of a material's thermal conductivity by having one side heated by a constant power supply while the other is cooled with flowing tap water. A constant temperature gradient will be established at steady state and temperature at different points of the material can be obtained using thermocouples. TIM produced with fillers synthesised were tested with this machine.



Figure 3.15: SOLTEQ thermal conductivity bench

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Synthesis of HRGO

Synthesis of HRGO from graphite was a two stage process. First, tightly stacked graphite was subjected to oxidation to produce GO with large interlayer spacing. GO produced was then reduced into HRGO which is graphene.

4.1.1 Synthesis of GO

Since GO was the precursor for making HRGO, it was produced as part of this project. GO produced was characterized using FESEM, EDX and UV/VIS. Problems faced during synthesis were also discussed below.

4.1.1.1 Characterisation

In order to confirm whether the material produced using the procedures outlined in Section 3.4.1 was indeed GO, FESEM imaging was performed. Figure 4.1 shows the

FESEM image of the material produced at 5500X magnification. From the image obtained, this material has layers after layers closely stacked onto each other.



Figure 4.1: FESEM image of GO

EDX analysis was also performed on GO and the results obtained are as shown in Figure 4.2. Carbon content of GO produced was 11.22 wt% compared to oxygen which was 47.75 wt%. High oxygen content relative to carbon indicated oxidation in the material. Another significant peak was sulphur which made up 28.28 wt%. Sulphate salts which was the by-product of GO synthesis and its presence in the EDX results was to be expected. However, such high intensity of the sulphur peak showed that GO produced was dirty. This will be further discussed in Section 4.1.1.2.



Element	Wt%	At%	
CK	11.22	17.92	
OK	47.75	57.25	
SiK	04.65	03.18	
PK	05.59	03.46	
SK	28.28	16.92	
ClK	00.62	00.34	
KK	01.89	00.93	
Matrix	Correction	MThin	

Figure 4.2: EDX report of GO produced

Next, UV/VIS analysis was conducted. This is a crucial characterisation method for GO which was introduced by Huang et al. (2011). GO produced for this project was tested and compared against GO bought from Sigma-Aldrich as shown in Figure 4.3. GO produced exhibited a peak at 231nm wavelength while Sigma's GO had a peak at 227nm. Slight difference in wavelength was expected as the formulation of Sigma's GO was unknown. However, both GOs displayed the same shape of absorption curve which was also obtained by Huang et al. (2011) as shown in Figure 4.4. Their GO had peaks at wavelengths of 229nm, 232nm and 233nm depending on the level of oxidation. Vertical differences in UV/VIS spectra was due to difference in concentrations which was not accurately controlled during testing as it was not pertinent to the characterisation. Hence, it was confirmed that the material produced is actually GO.



Figure 4.3: UV/VIS spectra of GO produced compared with commercial GO



Figure 4.4: UV/VIS spectra of GO by Huang et al. (2011)

4.1.1.2 Problems Encountered

Total time taken for the synthesis of one batch of GO, from oxidation to cleaning and drying took 1 week. Oxidation of GO was carried out over a period of 2 days which was also one of the duration Huang et al. (2011) performed. However, cleaning the residual salts from GO was very time consuming and a lot of wastage occurred. This was due to the breakdown of the 14 000rpm high speed centrifuge machine. With the high speed centrifuge, cleaning can be done within 3 hours. Unfortunately, it was not working. Hence, a low speed 4 000rpm centrifuge machine was used. Cleaning called for washing with HCl three times followed by repeated washing with water as described by Huang. Figure 4.5 (a) shows what happened when the GO was centrifuged with distilled water. Supernatant layer was not clear as it contained some dissolved GO in it. GO in supernatant could not be extracted anymore and had to be poured away. This was very wasteful and yield of GO reduced because of repeated washing with distilled water.

After some trial and error, it was observed that GO will settle completely when centrifuged with only 1M HCl as shown in Figure 4.5 (b). The clear supernatant was poured away and distilled water was added slowly in order to avoid disturbing the



Figure 4.5: Centrifuged with (a) distilled water (b) HCl

GO sediment in centrifuge tube turned from light brown to dark brown after sitting in distilled water overnight. When the layer of GO sediment was too thick, as shown in Figure 4.6 (a), it would not turn dark brown overnight. It would require 2 nights to completely darken (Figure 4.6 (b)). Wastage also occurred as diffusion progressed because GO is water soluble. However, wastage has been reduced by performing cleaning with distilled water only once.



Figure 4.6: (a) Thick GO sediment after overnight diffusion (b) GO gel after complete diffusion

Furthermore, cleaning using the low speed centrifuge machine also caused the GO produced for this project to be dirtier compared to GO that was cleaned using a high speed centrifuge as shown in Figure 4.7. Liew (2015) managed to synthesise GO with 15.40 wt% sulphur content. This is 12.88 wt% sulphur less than what was present in GO produced in this project. Therefore, it has been proven that yield and cleanliness of GO produced was lower and synthesis was more time consuming when low centrifuge machine was used.



Figure 4.7: GO cleaned using high speed centrifuge by Liew (2015)

4.1.2 Synthesis of HRGO

With the confirmation that precursor GO was successfully produced, experiment proceeded to the synthesis of HRGO which was the first objective. Two formulations were tried. One was hydrazine reduction in water (MW) while the other was reduction in ethanol (ME). HRGOs produced (Figure 4.8) were characterised using FESEM, Raman spectroscopy, HRTEM and XPS. Problems encountered during the execution of experimental procedures will also be shared below.

At%

36.66

54.72

00.98

07.64

MThin



Figure 4.8: HRGO produced

4.1.2.1 Characterisation

FESEM images of MW at different magnifications are shown in Figure 4.9 (a) and (b). MW has thin, crumpled sheets which are randomly oriented. At 40 000X magnification, a randomly selected fold has a thickness of approximately 22.99nm.



Figure 4.9: FESEM images of MW (a) 40 000X magnification (b) 80 000X magnification

ME was also analysed with FESEM to obtain Figure 4.10 (a) and (b). ME displayed similar appearance as MW. Fold thickness of 16.1nm was measured in Figure 4.10 (b).



Figure 4.10: FESEM images of ME (a) 40 000X magnification (b) 70 000X magnification

Both MW and ME FESEM images were similar to SEM images obtained by Stankovich et al. (2007) adapted in Figure 4.11 but clearer.



Figure 4.11: SEM images by Stankovich et al. (2007)

Raman spectroscopy was the next characterisation conduced. Figure 4.12 (a) shows the Raman spectrum for MW and ME. Both spectrum obtained are characteristic of graphene with presence of disorder (D) peak, graphitic (G) peak, 2D peak and D+G peak. For comparison, Raman spectrum of graphene sheets obtained by



Fu et al. (2014) was attached as Figure 4.12 (b). Graphene sheets produced by Fu displayed D, G, 2D and D+G peaks as well.

Figure 4.12: Raman spectra (a) MW and ME (b) Fu et al (2014)

For MW, locations of D, G, 2D and D+G peaks were 1356cm⁻¹, 1596cm⁻¹, 2651cm⁻¹ and 3016cm⁻¹ respectively. G band is caused by C-C bond stretching (Yan et al. 2010). This band is very intense in sp² carbon structures such as graphite and graphene. G band of MW was very intense. Hence, it has a sp² carbon structure. Next,

D band occurs due to the defects present in the sp² carbon structure. The intensity of D band in MW was very high. In perfect graphene, the D band is not present. 2D band is an overtone of D band but not necessarily present because of defects (Hodkiewicz et al. 2010). Presence of D+G peak is due to the disorder present in graphene as well. ME Raman spectrum exhibited D, G, 2D and D+G bands at 1355cm⁻¹, 1597cm⁻¹, 2723cm⁻¹ and 2912cm⁻¹ respectively. From the appearance of Raman spectrum and locations of D, G 2D bands it can be concluded that MW and ME were likely to be graphene because Raman spectrum are fingerprints of a material. Table 4.1 is the summary of Raman spectra of MW and ME.

G-peak 2D-peak D+G peak Sample **D**-peak ID/IG MW 1356 1596 2651 3016 1.202 2723 ME 1355 1597 2912 1.301

Table 4.1: Summary of Raman Spectra of MW and ME

Defect ratio, I_D/I_G of MW is 1.202 while ME is 1.301. Higher defect ratio of ME could be due to over sonication of GO because GO was not very soluble in ethanol. Although dried GO was first sonicated in a small amount water, sonication was not performed till it dissolved completely in water. Ethanol was added and sonication was continued but because GO did not dissolve very well, the duration was extended. Long exposure to sonication damaged GO thus when more damaged GO was reduced, it produced more defective HRGO.

HRTEM was the third characterisation for MW and ME. Figure 4.13 (a) depicts the overall view of MW while Figure 4.13 (b) shows the overall view of ME. Spider web like structure at the back was the lacy copper grid which captured the sonicated material. From both images it can be observed that there were sheets of different shades of darkness. Thicker sheets appeared darker in HRTEM image. Figure 4.13 illustrates agglomeration present in MW and ME samples. Van der Waals forces of attraction between surfaces of nanomaterial is the cause of agglomeration.



Figure 4.13: Overall HRTEM image (a) MW (b) ME

Under high magnification MW (Figure 4.14(a)) and ME (Figure 4.14 (b)) both have similar translucent crumpled plastic bag appearance characteristic of graphene.



(a)



Figure 4.14: Crumpled plastic appearance (a) MW (b) ME

Graphene has interlayer distance of 0.34nm (Novoselov, 2007). Figure 4.15 shows the interlayer spacing and edge thickness of MW and ME measured by HRTEM. Sample MW has interlayer distance of 0.31nm and 0.35nm while ME has an interlayer distance of 0.33nm. These values were very close to the interlayer distance of graphene. Figure 4.15 (b) was the edge thickness obtained at a fold. It is 8.74nm wide. Taking average interlayer spacing of MW to be 0.33nm, that edge of MW consists of around 13 layers of graphene. On the other hand, 4.98nm edge of ME in Figure 4.15 (c) has around 14 layers.



Figure 4.15: (a) Interlayer spacing of MW (b) Fold thickness of MW (c) Interlayer spacing and edge thickness of ME

Lastly, MW and ME were both subjected to Selected Area Electron Diffraction (SAED) by the HRTEM and diffraction patterns in Figure 4.16 (a) and (b) were obtained. Bright and focused diffraction points indicated the crystal structure of the material, In Figure 4.16, both Mw and ME has five points and one more obscured by the beam stopper indicated a hexagonal structure. After performing HRTEM characterisation, it can be concluded without a doubt that MW and ME are both graphene.





(a) (b) Figure 4.16: SAED pattern (a) MW (b) ME

XPS analysis was performed to study the surface chemistry of MW and ME. Figure 4.17 (a) and (b) are Survey spectrum of MW and ME respectively with atomic concentration table attached inset. MW consisted of 80.48% carbon, 4.92% nitrogen and 14.60% oxygen. On the other hand, ME comprised of 87.27% carbon, 4.96% nitrogen and 7.77% oxygen. High carbon to oxygen ratio on both samples showed that GO was reduced into HRGO. Presence of nitrogen in both samples was from hydrazine. Higher oxygen content of MW compared ME indicated that MW was slightly under reduced compared to ME. Compositions of MW and ME were close to what Marcano reported for her HRGO. Atomic compositions were 89% carbon, 3% nitrogen and 8% oxygen (Marcano et al. 2011).



Figure 4.17: Survey spectrum (a) MW (b) ME

In order to obtain a better picture of the chemical states of the atoms identified in survey scan, high resolution scan normalised to C=C bond was conducted. Figure 4.18 (a) is the resulting XPS spectrum for MW while Figure 4.18 (b) is that of ME. Each figures has inset containing corresponding atomic concentration table. Sample MW has 65.78% concentration of C-C/C=C bonds at binding energy of 284eV. C-C/C=C bonds are sp² bonds present in graphitic carbon ring. Hydroxyls (C-O), carbonyls(C=O) and carboxylates (O-C=O) are bonds present in oxidised carbon (Marcano et al. 2010). In MW, C-O, C=O and O-C=O bonds with 16.95%, 9.58% and 6.84% concentrations respectively. Total percentage of oxidised carbon present was 33.37%. Stankovich et al. (2007) suggested C-N bonds present was due to nitrogen functionalization of carbon atoms. For MW, C-N bonds concentration was 0.85%.





Figure 4.18: XPS spectrum (a) MW (b) ME

XPS spectrum of ME exhibited 66.74% of C-C/C=C bonds and 3.45% of π - π bonds, both belonging to carbon sp² bonding. C-O, C=O and O-C=O bonds were present at 12.66%, 9.63% and 5.82% concentration respectively, yielding a total of 28.11% concentration of oxygen functionalized carbon present in ME. Compared to MW, ME has 5.26% less oxidised carbon bonds and is thus better reduced. C-N bonds concentration in ME was higher than MW. At 1.72% concentration, ME had almost twice the amount of nitrogen functionalization. However, presence of C-N bonds in MW and ME were relatively low.

4.1.2.2 Problems Encountered

Hydrazine reduction of GO to produce MW and ME produced very low yield. From 0.1g of dried GO, only about 0.05g or less HRGO could be obtained. Initial plan was to keep ratio of GO: water: hydrazine at 0.1g: 100ml: 1ml and just scale up accordingly to produce larger batches. However, that was not feasible because the apparatus

required became too large and could not fit into a beaker of oil bath. In order to fit a 500ml round bottom flask properly into the oil bath, a pot was used instead. Unfortunately, following Marcano's ratio, only 0.5g of GO would be reduced in 500ml of water thus yielding a measly 0.25g of MW. For thermal conductivity testing, TIM samples require 0.5g of filler. Marcano's formulation would have been too slow. Therefore, the amount of GO and hydrazine were doubled to increase productivity. Reduction duration was increased from 1 hour to 3 hours to accommodate the increase in amount of GO that has to be hydrazine reduced. To reduce experimental noise, HRGO produced prior to the final formulation was not used.

Marcano's open beaker setup was also not practical with the equipment available in the lab. Hot plates available do not have programmable temperature setting. On many occasions the mixture in the beaker was boiling because it was difficult to control temperature of the hot plate. Flash point of hydrazine hydrate is 96°C and when mixture boiled, hydrazine could have vaporised. Since hydrazine is the reducing agent, vaporisation would have caused HRGO produced to be under reduced. To solve this issue, reduction was carried out under reflux as conducted by Stankovich. Any hydrazine which turned into vapour would have been condensed in the reflux tube and flow back into the flask below.

HRTEM imaging of both samples also proved to be a challenge. Samples MW and ME could not withstand the high energy electron beam. Figure 4.19 shows the altered edge of ME after being exposed to electron beam. Therefore, the operator had to quickly snap an image and move away from a spot to avoid further damaging the edge.



Figure 4.19: Altered edge of ME

4.2 HRGO Dispersion

Addition of surfactants SDBS and IGEPAL CO-890 was intended to reduce agglomeration as seen in MW and ME fillers in Figure 4.8. HRGO fillers C1, C0.1, S1 and S0.1 synthesised were depicted in Figure 4.20 below. Judging from the appearance of the fillers, ranking of filler size from smallest to largest would be C1 followed by S1, C0.1 and lastly S0.1. During handling, it was noted that fillers reduced with surfactants adopted its surfactant's characteristics. IGEPAL CO-890 is like a slab hardened candle while SDBS is a detergent-like powder. For C1 and C0.1 both fillers felt wax-like when pressed with a glass rod while S1 and S0.1 had washing detergent texture. These fillers are no longer brittle and grainy like MW and ME.



Figure 4.20: Fillers C1, C0.1, S1 and S0.1 synthesised

4.2.1 Characterisation

Raman spectroscopy characterisation of fillers were conducted and results are as shown in Figure 4.21. Spectrum obtain resemble that of graphene and were similar to fillers MW and ME. For C0.1 D, G, 2D and D+G peaks were at 1349cm⁻¹, 1592cm⁻¹, 2698cm⁻¹ and 2936cm⁻¹ respectively while I_D/I_G ratio was 1.193. Filler S1 exhibited D,

G, 2D and D+G peaks at 1346cm⁻¹, 1598cm⁻¹, 2689cm⁻¹ and 2915cm⁻¹ respectively with I_D/I_G ratio of 1.303. Lastly, filler S0.1 has D, G, 2D and D+G peaks at 1346 cm⁻¹, 1597cm⁻¹, 2691cm⁻¹ and 2962cm⁻¹ respectively. I_D/I_G ratio of S0.1 was 1.194. Unfortunately, there was insufficient filler C1 left for Raman testing thus, Raman spectrum of C1 is unavailable. Table 4.2 is the summary of Raman analysis of S1, S0.1 and C0.1.



Figure 4.21: Raman spectrum of fillers synthesised with surfactants

Sample	D peak	G peak	2Dpeak	D+G peak	ID/IG
C0.1	1349	1592	2698	2936	1.193
S1	1346	1598	2689	2915	1.303
S0.1	1346	1597	2691	2962	1.194

Table 4.2: Summary of Raman analysis for C1, S1, S0.1

XPS was performed on fillers C1 and S1. Figure 4.22 (a) is the survey scan while Figure 4.22 (b) is the high resolution scan of C1 normalised to C=C. Respective atomic concentration tables were attached inset both figures. Under survey scan, atomic concentrations of carbon, nitrogen, oxygen and sulphur were detected to be 74.85%, 2.82%, 21.34% and 0.98%. All of these elements were also present in ME except sulphur. Trace amount of sulphur could be residual sulphates from precursor GO.





Figure 4.22: (a) Survey spectrum (b) XPS spectrum of C1

In Figure 4.22 (b), sample C1 displayed significantly higher concentration of C-O bonds compared to ME. 44.85% concentration of C-O bonds was due to bond formation between IGEPAL CO-890 molecule and HRGO. Figure 4.23 is the structure of IGEPAL CO-890. One molecule of IGEPAL CO-890 contains long chain of C-O bonds which explains the high concentration found in XPS spectra of C1. High C-O bond concentration thus indicated that C1 has been functionalised by IGEPAL CO-890.



Figure 4.23: Chemical structure of IGEPAL CO-890 by Sigma-Aldrich

Next will be the XPS analysis of S1. Figure 4.24 (a) shows the spectrum obtained from initial survey scan and Figure 4.23 (b) shows spectrum from high resolution scan normalised to C=C. Initial survey scan detected 4.19% concentration

of sodium present in S1. Presence of sodium was from SDBS as shown in Figure 4.25. Significantly higher presence of sulphur was also due to SDBS thus further confirming functionalization of filler by SDBS. High resolution scan of carbon in Figure 4.23 (b) shows higher C-C/C=C bond concentration in S1 compared to ME and this could be due to the aromatic ring in SDBS.



Figure 4.24: (a) Survey spectrum (b) XPS Spectrum of S1



Figure 4.25: Chemical structure of SDBS

Final goal of adding surfactants was to better disperse HRGO filler in epoxy. Hence, dispersion behaviour of fillers in epoxy was characterised. In order to do that, 1 wt% of filler was stirred into epoxy and cured in a small centrifuge tube cap. Cured samples were broken into smaller pieces as shown in Figure 4.26 and the cracked surfaces were viewed under an optical microscope. These samples were specially prepared at low filler loading in order to better view fillers inside under the optical microscope. Before putting each broken samples under the microscope some initial observations should be pointed out. At 1 wt% filler loading MW and ME settled to the bottom of the centrifuge cap. Sample MW and ME in Figure 4.18 were turned bottom up. C1, C0.1 and S1 pieces were completely black while there is a large piece of S0.1 filler in the broken sample.



Figure 4.26: Broken samples

Figure 4.27 shows the optical microscope images of the samples produced. MW and ME will be used as a reference to compare the ones with surfactants akin to a before and after illustration. Length of the ruler in all images is 200µm. Measuring from the location of the ruler, MW was 527µm across while ME was 496µm. Pieces of C1, C0.1 and S1 were all pitch black and no individual grains were observable. A light source had to be shined from the side to give the images below. Bright zones in the images were due to reflection of light on the cracked surface. Optical image of S0.1 showed a huge filler that could already be seen in Figure 4.26 previously.



MW



ME



C1













Figure 4.27: Optical microscope images

Images in Figure 4.27 has shown clearly that dispersion was successful to a certain extent but not quantifiable. Filers C1, C0.1 and S1 were all smaller than MW and ME. So much smaller and well dispersed in epoxy that individual particles could not be observed under the optical microscope even at 1 wt% loading. S0.1 was not effectively dispersed.

4.3 Thermal Conductivity Study of TIM

Law of heat conduction more commonly known as Fourier's Law of thermal conductivity states that the heat flux q" is rate of heat transfer, in x direction over a unit of area perpendicular to direction of heat flow is proportional to the temperature gradient, dT/dx (Incropera, 2011).

$$q''_x = -k\frac{dT}{dx} \quad (W/m^2) \tag{4.1}$$

For a one-dimensional steady state heat conduction, equation 4.1 becomes

$$Q = -kA\frac{dT}{dx} \tag{4.2}$$

where Q=rate of heat transfer, W

k=thermal conductivity, W/m.K

A=cross sectional area, m^2

dT=temperature difference between hot and cold end, m

dx=distance between hot and cold end, m

4.3.1 Characterisation

Thermal conductivity test using SOLTEQ bench applies equation 4.2. Thermal conductivity of a material can be determined using equation 4.3. Rate of heat transfer, Q is known from the power input. A represents the cross sectional area of the TIM sample while dT/dx would be the temperature gradient established along the sample at steady state. Using the aforementioned information, the only unknown, k can be determined. Equation 4.3 is a rearrangement of equation 4.2.

$$k = -\frac{Qdx}{AdT} \tag{4.3}$$

TIM samples prepared using all 6 different fillers synthesised in previous sections were depicted in Figure 4.28. During testing each samples was placed at the removable center part of the SOLTEQ bench. Figure 4.29 (a) shows how a sample sits in the bench while Figure 4.29 (b) shows the polystyrene insulating block with a sample inside that was obscured by view.



Figure 4.28: TIM samples prepared





(b)

Figure 4.29: Final SOLTEQ test setup (a) TIM without insulation (b) TIM with insulation

Table 4.3 shows the experimental results for SOLTEQ thermal conductivity experiment. Temperature readings at other points along the brass in SOLTEQ bench can be found in Appendix A. Thermal conductivity, *k* of MW, ME C1, C0.1, S1 and S0.1 were 12.92 W/m.K, 13.42 W/m.K, 10.95 W/m.K, 10.75 W/m.K 10.59 W/m.K and 9.29 W/m.K respectively. Arranging the samples from largest to smallest thermal

conductivity would yield ME > MW > C1 > C0.1 > S1 > S0.1. Values obtained were larger than actual thermal conductivity due to losses which will be further explained in Section 4.3.2.

Sample	D	Α	T4	T6	dx	k
	(mm)	(m ²)	(°C)	(°C)	(m)	(W/m.K)
MW	12.38	0.000120	32.0	27.5	0.01	12.92
ME	12.43	0.000121	31.8	27.5	0.01	13.42
C1	12.39	0.000121	32.9	27.6	0.01	10.95
C0.1	12.39	0.000121	33.4	28.0	0.01	10.75
S1	12.37	0.000120	34.2	28.7	0.01	10.59
S0.1	12.44	0.000122	33.7	27.5	0.01	9.29

Table 4.3: TIM thermal conductivity results

Results obtained indicated although HRGO filler was better dispersed in epoxy, thermal conductivity values dropped when surfactants were used for synthesis. Very low thermal conductivity of S0.1 was the lowest because there were presence of SDBS in the filler and filler also agglomerated badly. Size of the grains were so large that they settled at the bottom of the TIM samples. There was an uneven dispersion of S0.1 filler due to its wide range of sizes.

For samples C1, C0.1 and S1, thermal conductivity values were better than S0.1 but still significantly lower than MW and ME. Pop et al. (2012) explained that any sort of additional disorder including but not limited to residue from fabrication will cause more phonon scattering and reduce the thermal conductivity. Agglomeration itself is a disorder. However, this thermal conductivity experiment demonstrated that even though filler was better dispersed, presence of surfactants in HRGO was more detrimental to the performance of HRGO filler compared to agglomeration.

Comparison can also be made between MW and ME. XPS analysis of both fillers demonstrated that ME was better reduced compared to MW. Better reduction

means less oxygen functionalization present. Hence, less phonon scattering occurred in ME and higher thermal conductivity compared to MW was obtained.

4.3.2 Problems Encountered

Curing of epoxy was problematic. DOW Chemicals provides a method of calculating the exact amount of curing agent required to react with every single epoxy molecule. Detailed calculations can be found in Appendix B. Theoretical amount of DETA curing agent required was 11.86 wt%. Figure 4.30 (a) shows the result of curing epoxy with 11.5% DETA. Curing is an exothermic process and with that amount of curing agent, the tube containing cured epoxy had melted and some epoxy oozed out of the tube. When amount of DETA was reduced to 10 wt%, sample in Figure 4.30 (b) was obtained. Cured epoxy is supposed to be clear but sample in Figure 4.30 (b) was cloudy. This effect is called amine blushing and is caused by humidity, curing rate and temperature. Air conditioned environment in the lab was not conducive for curing due to high humidity and low temperature. As soon as DETA was added, condensation started to form at the inner sides of the beaker. Moreover, cool temperature also caused the rate of curing to decrease and give opportunity for curing agent to react with surrounding air.



Figure 4.30: Epoxy cured with (a) 11.5 wt% DETA (b) 10 wt% DETA

In order to prevent epoxy from blushing, amount of curing was further decreased to make the reaction less exothermic and reduce condensation. Beaker and glass rod that were going to be used for curing were warmed in the drying oven first. Lastly, once DETA was added to epoxy, vigorous stirring was conducted beside an open window. At 9 wt% DETA a clear epoxy was successfully produced following the aforementioned steps.

Next, achieving steady state was difficult when testing TIM produced using SOLTEQ thermal conductivity bench. When power input was too high (5W), temperatures at the hot end will keep rising even after 3 hours. Entire SOLTEQ setup is not completely insulated. After running the equipment for a few hours, the insulating nylon block started to feel warm which shows heat loss. Besides, thermocouple used for measuring temperature are made of metal. Heat loss occurs when heat is travelling from the sample to the thermocouple sensors. All the heat loss will cause the actual heat flowing through sample to be smaller than power set thus thermal conductivity reading obtained would be inflated. Unfortunately, using very low power setting (0.7W) was not optimal. At low power setting, power input was unable to produce significant temperature gradient for accurate results. Hence, final round of testing was conducted at 2.5W and steady state was achieved after 3 to 4 hours.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

First objective which was the synthesis of HRGO was successfully achieved using two different formulations, MW and ME. Similar FESEM images of HRGO with Stankovich et al (2007) and Raman spectrum characteristic of graphene were obtained. HRTEM also confirmed both materials produced were indeed graphene.

Second objective was the dispersion of HRGO. XPS analysis confirmed the presence of functionalization by surfactants used. Dispersion was achieved with 3 out of 4 formulations tested. Those fillers are C1, C0.1 and S1. Although optical microscope images showed good dispersion in the samples, the degree of dispersion remains unquantifiable.

Third objective was the thermal conductivity study for the TIM produced. Thermal conductivity was determined and the values indicate that the presence of surfactants from dispersion reduced thermal conductivity of TIM although agglomeration was significantly reduced. TIM with functionalized filler C1 recorded the highest thermal conductivity, 10.95 W/m.K among four functionalized fillers produced. However it was still lower than TIM containing filler ME which was not functionalised. Filler ME has thermal conductivity of 13.42 W/m.K.

5.2 Recommendations

Agglomeration of HRGO occured when it was dried. Hence, it is recommended to avoid drying and use HRGO in wet form. Wet HRGO cannot be added into epoxy because it causes epoxy to become watery and incapable of curing. Adhesive materials that will not be degraded by water would be a better option. Instead of producing a TIM and adhesive 2-in-1 material, incorporation of wet HRGO into thermal greases is also another option.

As Smith et al. (2010) explained, functionalization of graphene using surfactants aid in dispersion due to electrostatic for SDBS and osmotic repulsion for IGEPAL CO-890 dispersed graphene. Dispersed graphene can be cleaned by methods described by Irin et al (2015) and clean sheets of graphene suspended in water can then be used in thermal sprays or coatings.

Unfortunately, no matter how many applications of HRGO can be tried, they are of no use if no proper characterisation equipment are available. Raman spectroscopy, HRTEM and XPS are tool required to characterise HRGO produced and determine its quality. Furthermore, thermal conductivity testing can be more accurately done with a laser flash equipment. Laser flash method will produce less errors as well. Laser pulse is exposed to one side of the specimen and temperature signal is measured at the other side. No other interfaces to disrupt the heat flow like the SOLTEQ equipment.

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APPENDICES

APPENDIX A: Complete temperature readings for each sample

TIM samples produced were placed in between 2 brass samples belonging to the SOLTEQ machine. Temperatures T1, T2, T3, T7, T8, and T9 were temperature readings on brass specimen while T4 and T6 were from TIM sample. All experiments were conducted at 2.5W power setting.

Table A-1.1: MW

Thermocouple	T1	T2	T3	T4	T6	T7	T8	T9
Temperature (°C)	47.5	47.1	47.5	32.0	27.5	24.4	24.4	24.4

Table A-1.1: ME

Thermocouple	T1	T2	T3	T4	T6	T7	T8	T9
Temperature (°C)	48.2	47.7	48.2	31.8	27.5	24.3	24.3	24.3

Table A-1.1: C1

Thermocouple	T1	T2	T3	T4	T6	T7	T8	Т9
Temperature (°C)	48.0	47.6	48.0	32.9	27.6	24.3	24.3	24.3

Table A-1.1: C0.1

Thermocouple	T1	T2	T3	T4	T6	T7	T8	T9
Temperature (°C)	48.0	47.7	48.0	33.4	28.0	24.4	24.4	24.4

Thermocouple	T1	T2	T3	T4	T6	T7	T8	T9
Temperature (°C)	49.1	48.8	49.1	34.2	28.7	25.2	25.2	25.2

Table A-1.1: S1

Table A-1.1: S0.1

Thermocouple	T1	T2	T3	T4	T6	T7	T8	T9
Temperature (°C)	48.0	47.5	48.0	33.7	27.5	24.2	24.2	24.2

APPENDIX B: Calculation of theoretical amount of DETA required for curing

In order to obtain optimum properties, epoxy resin and curing agent should react at stoichiometric ratio. To determine this ratio calculations were done as follows using DETA (Figure A-1). First, amine H equivalent weight was determined.



Figure A-2.1: Chemical structure of DETA

$$Amine \ H \ equivalent \ weight = \frac{Molecular \ weight \ of \ amine}{No. \ of \ avtive \ hydrogen}$$
(A. 1)

Amine equivalent weight for DETA = $\frac{103.17}{5}$ = 22.634

Concentration of the curing agent has to be adjusted to cure only the portion of the mix that is reactive. Epoxide equivalent weight (EEW) has to be determined and then applying equation (A.1) to determine the amount of curing agent to add to 100 parts of formulation. For bispenol A diglycidyl ether epoxy resin, EEW= 172-176 as provided by Sigma-Aldrich. Average EEW of 174 will be used in future calculations.

Parts by weight per 100 parts resin,

$$phr amine = \frac{Amine \ equivalent \ weight}{EEW} \times 100 \qquad (A.2)$$

phr DETA =
$$\frac{20.634}{174} \times 100$$

= 11.86%