THE FUNCTIONAL PROPERTIES OF SILVER/CARBON NANOTUBE HYBRID COMPOSITES

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DECLARATION

I declare that this project entitled "The Functional Properties of Silver/Carbon Nanotube Hybrid Composites" is the result of my own work except as cited in references.

Signature : ....

Supervisor's Name : ....

Date : ....

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of the degree of Bachelor of Mechanical Engineering (Hons).

Signature : ....

Supervisor's Name : ....

Date : ....

DEDICATION

This report is dedicated to my beloved mother and father.

ABSTRACT

This project investigates the functional properties of silver/carbon nanotube hybrid composites of electrically conductive adhesives (ECA). The multi-walled carbon nanotube are considered and the then filler loadings are varied at 5 wt.%, 6 wt.% and 7 wt.%, and the formulation was established using the Rule of Mixture for composites. For the electrical performance, six strips of the ECA was applied onto a 3-mm thick acrylic with dimensions of 45 mm (wide) and 88.9 mm (length) by using printing technique. The strip is 12.7 mm in lengthand 2 mm wide and were subjected to electrical test using a four-point probe test unit, with reference to ASTM F390-11.Theresult of four-point probe test reveals that the sheet resistance of the ECA decreased with an increase in the MWCNT filler loading due to enhanced formation of percolated linkages between MWCNT particles. Meanwhile, mechanical characterization was done via Lap shear test under tensile mode as per ASTM D1002-10 using a universal testing machine, with ECA nominal thickness of 0.1 mm and aluminum substrate with dimensions of 25.4 mm wide,101.6 mm length and 1.5 mm thick. The mechanical properties of ECA show an increase in shear strength with an increase MWCNT filler loading from 5 wt.% to 6 wt.% and decrease in shear strength with an increase of MWCNT filler loading from 6 wt.% to 7 wt.%. The sudden decrease of shear strength possibly because of the agglomeration that is formed at the conductive filler.

ABSTRAK

Projek ini menyiasat sifat fungsian perak / karbon nanotube hibrid komposit perekat konduktif elektrik (ECA). Nanotube karbon berbilang bertitik dipertimbangkan dan beban pengisi kemudian berubah-ubah pada 5% berat, 6% berat dan 7% berat, dan perumusan dibuat dengan menggunakan Peraturan Campuran untuk komposit. Untuk prestasi elektrik, enam jalur ECA digunakan pada akrilik tebal 3 mm dengan dimensi 45 mm (lebar) dan 88.9 mm (panjang) dengan menggunakan teknik percetakan. Jalur ini panjang 12.7 mm dan lebar 2 mm dan tertakluk kepada ujian elektrik menggunakan unit ujian kuar empat titik, dengan merujuk kepada ASTM F390-11. Hasil ujian probe empat titik menunjukkan bahawa rintangan lembaran ECA menurun dengan peningkatan pengisian MWCNT karena pembentukan ditingkatkanhubungan percolated antara zarah MWCNT. Sementara itu, pencirian mekanikal dilakukan melalui ujian ricih Lap di bawah mod tegangan seperti ASTM D1002-10 menggunakan mesin uji universal, dengan ketebalan nominal ECA ketebalan 0,1 mm dan aluminium dengan dimensi 25,4 mm lebar, panjang 101.6 mm dan tebal 1,5 mm. Sifat mekanik ECA menunjukkan peningkatan dalam kekuatan ricih dengan peningkatan beban pengisi MWCNT dari 5 wt% hingga 6 wt% dan pengurangan kekuatan ricih dengan peningkatan beban pengisi MWCNT dari 6 wt% hingga 7 wt%. Penurunan kekuatan ricih secara tiba-tiba mungkin disebabkan oleh aglomerasi yang terbentuk pada pengisi konduktif.

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LIST OF ABBREVATIONS

3D	Three Dimensional
PCB	Printed Circuit Boards
WEEE	Waste Electrical and Electronic Equipment Directive
RoHS	Restriction of Hazardous Substances Directive
AgNP	Silver Nanoparticles
Ag	Silver
ACA	Anisotropic Conductive Adhesives
CNT	Carbon Nanotube
ECA	Electrically Conductive Adhesives
ICA	Isotropic Conductive Adhesives
MWCNT	Multiwalled Carbon Nanotubes
SWCNT	Single-Walled Carbon Nanotubes
SEM	Scanning Electron Microscope

LIST OF SYMBOLS

°C	=	Degree Celsius
k	=	Kelvin
Ω	=	Ohm
sq	=	Square
g	=	Gram
m	=	Meter
nm	=	nanometer
µm	=	micrometer
L	=	Length
wt.%	=	Weight Percentage
τ	=	Shear
F	=	Force
A	=	Area
V	=	Voltage
I	=	Current
C	=	Lateral Correction Factor
Pa	=	Pascal
Mpa	=	Mega Pascal
Gpa	=	Giga Pascal

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Electrically Conductive Adhesives (ECAs) has been commercially used over the decade to replace lead-based solder material for the interconnection of electronics components on printed circuit boards (PCBs). The European Union Waste Electrical and Electronic Equipment Directive (WEEE) and Restriction of Hazardous Substances Directive (RoHS) has banned the use of lead in electronics in 2006 because of the adverse environmental impacts upon lead containing solder disposal [1]. ECA is classified into two categories which are Anisotropic Conductive Adhesives (ACA) and Isotropic Conductive Adhesives (ICA) which consist of inorganic fillers and organic fillers respectively. Electronic packaging using ECA is beneficial because of environmental friendliness e.g. elimination of lead, flux cleaning, mild processing conditions and fewer processing steps. These ECAs composition can tuned to a myriad of conductivity values with the proper selection of filler, its size, shape and loading concentration into its host polymeric matrix [2].

ECAs mainly consist of polymeric binder and conductive fillers. The main requirement of ECA industries is the high electrical conductivity and mechanical strength. Therefore, use of silver as a primarily filler and epoxy as a host polymer matrix is an effective solution.

Advancement in conductive fillers, development of high aspect ratio silver nanoparticles has the potential to reduce the filler content necessary to obtain useful conductivity and reduce cost. In this research, an advance research on combining conductive filler of silver and Multiwalled Carbon Nanotubes (MWCNT) will be done to investigate the conductivity and mechanical properties.

Carbon Nanotubes (CNT), is one form of carbon, with nano-meter-sized diameter and micrometer-sized length and the atoms are arranged in hexagons, the same arrangement as in graphite [3]. CNTs have unique mechanical, electrical, and electro-chemical properties. Single-Walled Carbon Nanotubes (SWCNT) consist of a single layer which are generally narrower than the MWCNT which consist at least two layers. Although SWCNTs exhibit important electrical properties than MWCNTs, still it is very expensive to produce. CNT have high mechanical strength, unique electrical behavior, low density and compatibility with common composite matrix material [4]. The CNT is capable for reducing the metal content in the ECA, in this case Silver (Ag) which are very expensive thus reducing the cost of ECA.

1.2 PROBLEM STATEMENT

Since lead-based solder is no longer recommended for the interconnection in PCB, ECA is the most convenient material to replace it. ECA is eco-friendly which consist of polymer matrix and metal filler. ECA is suitable to replaced lead-based soldering because it offers numerous advantages over the traditional soldering technology, such as excellent adhesion to most surfaces, lower processing temperature, ease of rework and ability for device miniaturization. As time goes on, there are multiples development of ECA including using various types of polymer matrix and metal filler. There is also further research on using hybrid metal filler such as usage of silver nanoparticles and CNT to achieve better mechanical properties and conductivity [5].

However, until recently, these ECA have been prohibitively expensive and typically less conductive than desired. It relies on metal filler content in the ECA. A high filler content lead to high viscosities, difficult mixing and dispensing, inflated cost from expensive filler, and relatively large minimum dispensing sizes [6]. ECAs is relatively a new technology compared to other technologies, so it does have some limitations and drawbacks including limited impact resistance, increased contact resistance and weak mechanical strength in some climatic conditions [7].

With addition of Silver and CNT as the metal filler of ECAs, some limitations could be overcome. Silver is a precious metal and thus has a high price and it corrodes or oxidizes easily. Silver nanoparticles (AgNP) has been proven to have excellent properties which make them desirable for use biosensors, catalyst, antimicrobial agents, optical limiters, metal adsorbents and advanced composites. Interactions between the AgNP and the CNT surface may occur through strong covalent bonds or weak intermolecular bonds such as $\pi - \pi$ stacking, hydrophobic interactions, hydrogen bonds, or electrostatic attractions [8]. Addition of CNT will reduce the amount of silver metal filler thus could reduce the price of the ECA and its mechanical and electrical performances at different aspect ratio could be studied.

1.3 OBJECTIVES

The objectives of this projects are:

1. To develop Ag-CNT hybrid nanocomposites using varying filler loading of the two conductive filler
2. To evaluate the functional properties of the hybrid nanocomposites

1.4 SCOPE OF PROJECT

The scope covered in this project is as stated below:

1. Formulation of the hybrid composite
2. Fabrication of ECA
3. Electrical properties of ECA
4. Mechanical characterization of ECA
5. Morphological study

1.5 PLANNING

Figure 1.1 illustrates the research activities for PSM 1 which include research title selection, background study, literature review, lab visit, formulation of samples, ECA fabrication, characterization testing, data analysis, report writing and followed by report submission and lastly PSM 1 seminar. The characterization testing only includes for electric conductivity testing.

WEEK ACTIVITIES	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Research Title Selection														
Background Study														
Literature Review														
Lab Visit														
Formulation of Samples														
ECA Fabrication														
Characterization Test • Electrical Conductivity														
Data Analysis														
Report Writing														
Report Submission														
PSM 1 Seminar														

Figure 1.1: Gantt chart detailing research activities and time frame for PSM I

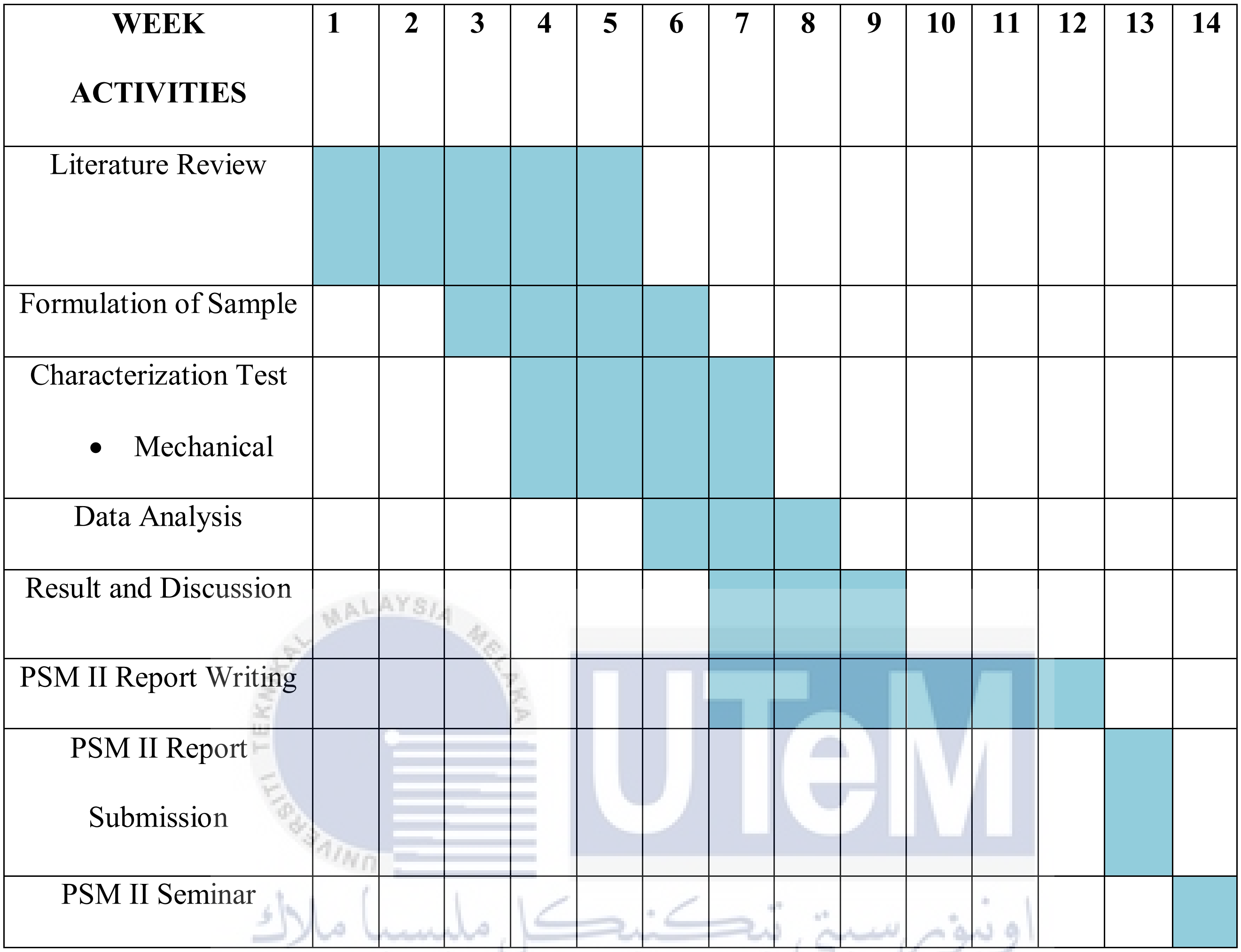


Figure 1.2: Gantt chart detailing research activities and time frame for PSM II

CHAPTER 2

LITERATURE REVIEW

2.1 INRODUCTION

In this chapter, a review on electrically conductive adhesives (ECA) which include type of ECA filler materials, type of Carbon Nanotubes (CNT), mechanical and electrical properties which were reviewed from the previous study.

2.2 ELECTRICALLY CONDUCTIVE ADHESIVES

Electrically conductive adhesives (ECAs) are gaining great interest as potential solder replacement in microelectronics assemblies. The development of the first ECAs goes back to 1950s particularly with Henry Wolfson procuring a patent on "electrically leading concretes containing epoxy and silver. Then it became the foundation from which present day ECAs would be based upon. ECAs are composed of two main components: a polymer matrix and conductive filler material. Basically, there are two types of ECAs, isotropic conductive adhesive (ICA) and anisotropic conductive adhesive (ACA). ICAs typically contain conductive filler concentrations between 20 and 35 vol.%, and the adhesives are conductive in all directions [9]. In ACAs, the volume fractions are normally between 5 and 10 vol.%. The application of ICA is utilized in hybrid applications and surface mount technology while ACA technology is suitable for fine pitch technology such as flat panel display applications, flip chips and fine pitch surface mount device [10]. The advantages and challenges of ECAs are summarized in Table 2.1 below.

Table 2.1: The advantages and disadvantages of ECA's

ADVANTAGES	DISADVANTAGES
Low Processing temperatures	Low Bulk Electrical Conductivity
Fine-Pitch Capabilities	Unstable Contact Resistance
Excellent Adhesion to Numerous Surfaces	Hard to Remove After Cured
Directional Conductivity Possible	Adhesion Strength Needs Improvement
Environmentally Friendly Alternatives	Joint Resistance from Oxidation/Corrosion
Minimal Thermal Fatigue & Stress Cracks	High Ag Content is Expensive
Low Dielectric Constant	Limited Impact Resistance
Works with Non-Solder Components	Environmental Reliability
Less Processing Steps & Operation Cost	Incorrect Spreading from High Viscosity
Higher Flexibility	Longer Curing Time
No Flux or Secondary Underfill Needed	Silver Migration Issue

Various studies are being directed to build up a superior comprehension of the mechanism underlying these issues and to improve the performance of ECAs for electronic applications.

2.2.1 MATRIX

ECAs consist of a polymer binder that provides mechanical strength. Polymers can be classified as either thermosets or thermoplastics. Different polymer is used for different application of ECAs.

a. Thermoplastics

Thermoplastics are high molecular weight materials that can be reshaped upon heating and cooling, since no crosslinking is present in these kinds of materials. Their mechanical properties depend on the type of monomers used and the degree of entanglement of their chains [13]. In the composite industry, thermoplastic resins have an extensive variety of utilizations because they have a high glass transition temperature, the ability to be reshaped and repaired low manufacturing cost long prepreg stability and less processing time compared to thermoset resins. One of the significant disadvantages is under the influence of sustained loading, since they are susceptible to creep rupture.

b. Thermosets

Thermosets are crosslinked polymers and generally have an extensive three-dimensional molecular network structure. Thermosets systems undergo true chemical reactions and form chemical crosslink between polymers chains that resist deformation even at relatively high temperature. The strength and stiffness of thermosets come from the length and density of the crosslinking [14]. Examples of thermosets resins used in composite industry are epoxy and polyester.

b.1 Epoxies

Epoxy networks are typically composed of a resin and a curing agent that react to form a crosslinked thermoset. Epoxy resins are generally derived from the reaction of bisphenol-A with epichlorohydrin to form diglycidyl ether of bisephnol-A (DGEBA) [15] as illustrated in Figure 2.1. The viscosity of epoxy is determined by the reactant's ratio which the ration is between bisphenol-A against epichlorohydrin. Epoxy networks are known to possess outstanding adhesives properties, thermal and dimensional stability, solvent resistance, and high modulus [16].

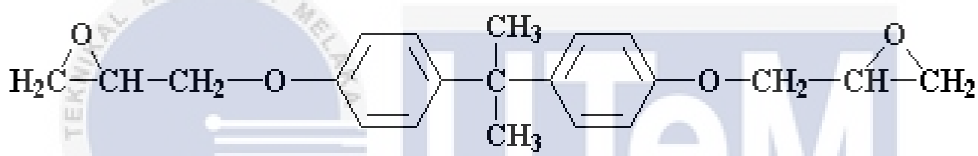


Figure 2.1: Reaction process to produce bisphenol-A epoxy

A wide selection of curing agents is available to react with the epoxide groups to crosslink the epoxy, including those containing amines, amides, novolacs, and carboxylic acids as shown in Figure 2.2. The flexibility offered by epoxy systems has led to their use in such areas as adhesives, paints and coatings, integrated and printed circuit boards, automotive surfaces, and high-performance aircraft components.

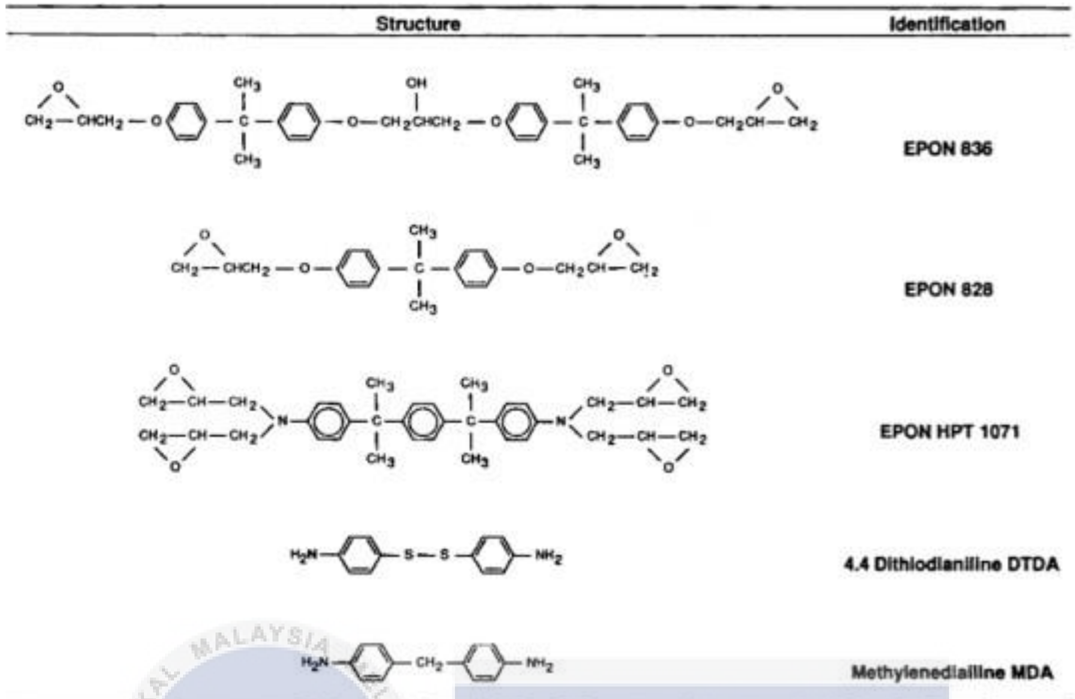


Figure 2.2: Schematic representation of epoxy resin and curing agent chemical structure [34]

However, a major flaw in the application of epoxies is the intrinsic brittleness of the network structure that may occur during low stresses. Brittleness in epoxy systems has been attributed to restricted mobility of the epoxy network caused by the network junction points [17]. The addition of small amount of elastomeric materials into the rigid epoxy enhancing the epoxy toughness and greatly reduced epoxy elastic modulus and thermal stress. Table 2.1 shows the advantage and disadvantage of epoxy.

Table 2.2: Advantages and disadvantages of epoxy [18]

Advantages	Disadvantages
Good moisture and chemical resistance	Longer cure cycles with anhydride hardeners
High purity	Degassing required for two-component systems
Low outgassing	Exotherms in large quantities for amine-curing agents

2.2.2 FILLER FOR ECA COMPOSITES

Filler are added to ECA to make the polymer matrix conductive. The filler is mixed with the polymer epoxy counterpart which forms ECA. There are two types of conductive filler for ECA which are from metal and non-metal material.

2.2.2.1 Gold

Gold is one of the most expensive metallic elements although it has a good electrical and heat conductivity, but copper and gold have a better electrical conductivity. However, since gold is difficult to distort and corrode, in some applications, the utilization of gold is preferable. The resistivity of gold is 0.022 $\mu\Omega$.m at 20°C and thermal conductivity is 310W/mK at 20°C. Gold is greatly malleable which 1 ounce of gold can be rolled into translucent wafer thickness of 0.000013 cm [19].

2.2.2.2 Copper

Copper is one of the metal which has excellent electrical conductivity of 58MS/m which is also offer a low electrical resistance. However it has a poor mechanical properties which the tensile strength is below 225 MPa [20]. Nevertheless, the copper filler is easily to oxidized when subjected to high temperature and humidity which contribute to an increase of electrical resistivity in the ECA. The thermal conductivity of copper also can be considered as good as it can reach to high of $\lambda = 380 \frac{W}{m.K}$

2.2.2.3 Silver

Silver has long been widely used as a filler in ECAs, in spite of its prohibitive cost because of its exceptionally high electrical conductivity 6.25×10^7 S/cm [21] and resistance to oxidation. Silver flakes are typically mechanically processed flakes and its weight percentage must be in the range of 70 wt.% to 90 wt. % to ensure good electrical and mechanical properties of ECA. In nanoparticles, it is known that nanoparticles behave differently and even show different material properties when compared to its bulk component and silver is no different [30], where the high specific surface areas and high surface energies promote oxidation, this is major advantages over other metallic nanofillers. There are few high-aspect silver nanoparticles available at this time, the most common being is pentagonal silver nanowires (PSNW). There are also silver nanosheets which can be high aspect ratio due to their 2-dimensional nature. Compare to another metal fillers, silver has the highest thermal and electrical conductivity at room temperature. However, overloading of silver flakes in ECA contribute to more contact points [11], poor impact strength, increase in viscosity and high material consumption cost [22]. An excess amount of nanoparticles in the composite may even cause a decrease in conductivity in some instances [31].

2.2.2.4 Carbon Nanotube

Carbon is known to be the most versatile element that exist on the earth. CNT was discovered in 1991 by Sumio Iijima. It was named Carbon Nanotube since they have a tubular structure of carbon atom sheets, with a thickness scaled less than a few nanometers. Carbon nanotubes have attracted a lot of researcher in a wide range of fields, not only because of their uniqueness when compared with conventional materials, but also because they are very promising materials in nanotechnology in future technology. CNTs have high conductivity and high aspect ratio which help them to form a network of conductive tubes. Outstanding mechanical properties of CNs are derived from a combination of stiffness, strength, and persistency [23]. Incorporated within a polymer, CNTs transfer their mechanical load to the polymer matrix at a much lower system of weight percentage than carbon black or carbon fibers, leading to more efficient application. CNTs have also been utilized for thermal protection as thermal interface materials.

There are two types of CNT which are Single-Walled Carbon Nanotubes (SWCNT) and Multi-Walled Carbon Nanotubes (MWCNT). SWCNT are seamless cylinders comprised of a layer of graphene. They have unique electronic properties which can change significantly with the chiral vector (Figure 2.3), C = (n, m), the parameter that indicates how the graphene sheet is rolled to form a CNT as shown in Figure 2.2. The SWCNT is also used as a catalyst for direct ethanol or methanol fuel cells [26]. The SWCNT metallic properties are about 1/3 of total SWCNT while another 2/3 are semi-conducting properties if the chiral vectors are equal [27].

(a) (b)

Figure 2.3: Diagram of (a) a single layer of graphite sheet, (b) SWCNT after rolled [30]

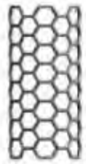
(n, m)	Form of SWNTs	Electrical Conductivity
(n, 0)	 Zigzag	Metallic when n is the multiple of 3, otherwise, semiconducting
(n, n)	 Armchair	Metallic
(n, m) when m ≠ 0, and n	 Chiral	Metallic when (2n+m)/3 is an integer, otherwise, semiconducting

Figure 2.4: Theoretical electronic conductivity of SWCNT depending on roll orientation of the graphene sheet (n, m) [24]

MWCNT consist of multiple rolled layers of graphene. MWCNT exhibit advantages over SWCNT, such as ease of mass production, low cost per unit, and enhance thermal and chemical stability although MWCNT has a structural complexity. In general, the electrical and mechanical properties of SWCNT can change when functionalized. However, intrinsic properties of carbon nanotubes can be preserved by the surface modification of MWCNT where the outer wall of MWCNT is exposed to chemical modifiers. That is why CNTs are used as a non-metal filler for ECA because of their properties compared to other conductive materials as shown in Table 2.2. Figure 2.3 shows the schematic diagram of SWCNT and MWCNT.

Table 2.3: Transport Properties of CNT and other conductive materials [25].

Material	Thermal Conductivity [W/(m.K)]	Electrical Conductivity (S/m)
Carbon Nanotubes	> 3000	$10^6 - 10^7$
Copper	400	6×10^7
Carbon Fiber - Pitch	1,000	$2 - 8.5 \times 10^6$
Carbon Fiber - PAN	8 - 105	$6.5 - 14 \times 10^6$

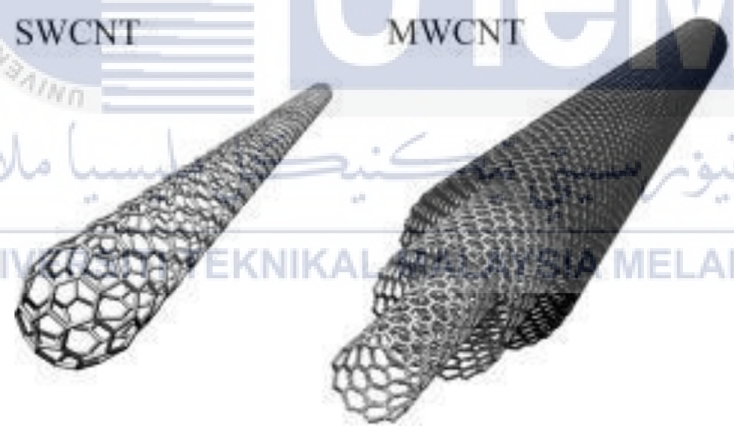


Figure 2.5 : Schematic diagram of SWCNT and MWCNT

Although carbon-based co-fillers such as CNTs offer a plenty of attractive properties that can be utilized by composite materials, there a few challenges that must be first addressed before being able to take full advantage of it. The most common problem is the agglomeration issue of carbon-based filler that occurs when incorporated within the polymer matrix [32][33]. This problem leads to other issues for example increase in viscosity and poor dispersion.

2.3 PROPERTIES OF ELECTRICALLY CONDUCTIVE ADHESIVE

2.3.1 ELECTRICAL PROPERTIES

The electrical properties plays a major role in ECA. The electrical properties of ECA is present due to present of metallic filler. The filler loading, weight percentage and surface area are the factors that affect the resistivity of the ECA. The resistivity of the ECA is an inverse of its electrical conductivity. Among of all conductive metal, Silver has the highest conductivity as shown in Table 2.3. The value of resistivity of silver is the lowest which means that silver has a small capability of resisting electrical current. With a small natural tendency to resist electricity, it has a very high tendency to conduct electricity.

Table 2.4 : The conductivity and resistivity of conductive metal

Material	Resistivity, ρ (Ω.m) at 20°C	Conductivity σ (S/m) at 20°C
Silver	1.59×10^{-8}	6.30×10^{7}
Copper	1.68×10^{-8}	5.98×10^{7}
Gold	2.44×10^{-8}	4.52×10^{7}
Aluminum	2.82×10^{-8}	3.5×10^{7}
Magnesium	4.66×10^{-8}	2.15×10^{7}

CNTs can be highly conducting, and hence can be said to be metallic. Their conductivity has been shown to be a function of their chirality, the degree of twist as well as their diameter. CNTs can be either metallic or semi-conducting in their electrical behavior. Conductivity in MWCNTs is quite complex. Some types of “armchair”-structured CNTs appear to conduct better than other metallic CNTs**.** Furthermore, interwall reactions within multi walled nanotubes have been found to redistribute the current over individual tubes non-uniformly. However, there is no change in current across different parts of metallic single-walled nanotubes. The behavior of the ropes of semi-conducting single walled nanotubes is different, in that the transport current changes abruptly at various positions on the CNTs. A nanotube with a natural junction (where a straight metallic section is joined to a chiral semiconducting section) behaves as a rectifying diode – that is, a half-transistor in a single molecule. It has also recently been reported that single walled nanotubes can route electrical signals at speeds up to 10 GHz when used as interconnects on semi-conducting devices.

Figure 2.6 shows previous study of the conductivity of ECA with silver and MWCNT as the filler. Higher filler loading will increase the electrical conductivity of ECA [35]. Low filler loading will cause a scatter in the resin which makes it difficult to create a conductive path for electrical flow.

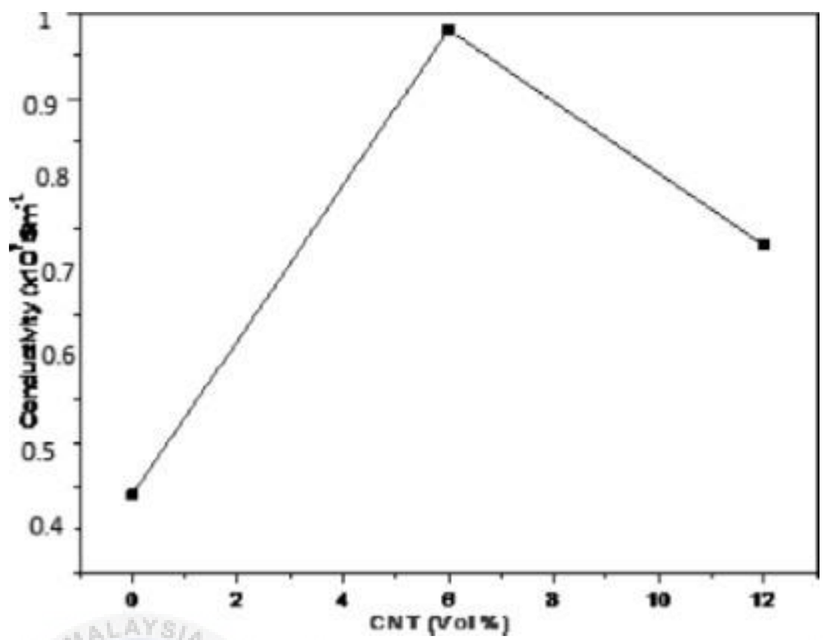


Figure 2.6: The electrical conductivity of ECA with CNT/Ag as metal filler

Table 2.5: The conductivity of ECA

Specimen	Conductivity [s/m]	CNT [mg]	Silver nitrate	CNT vol %	Density [mg/cm^3]
Ag	$0.4 \cdot 10^7$	0	3 gm	0	8.62
Ag/CNT	$0.9 \cdot 10^7$	11	3 gm	6	7.72
Ag/CNT	$0.7 \cdot 10^7$	22	3 gm	12	7.46

Heman, Vimal, Rajesh and Nagesh [37] conducted an experiment on facile and electrical conductivity of CNT reinforced nanosilver composites. The conductivity of ECA drops down as the filler loading more than 6% as it has reached percolation threshold. Percolation threshold happens when there is no significant change occurs as the concentration of the filler increase until a critical concentration V_c is reached, thus the electrical resistivity decrease dramatically [36]. This cause by agglomeration of the filler which increase the contact resistance.

Marq and Demont [38] also investigated about combination of CNT with silver nanoparticle with different silver nanoparticles content. They investigated the electrical conductivity of ECA filler containing silver nanoparticles only, 0.4% vol. DWCNT + AgNP, 0.4% vol. MWCNT +AgNP and 1% vol. MWCNT +AgNP. Based on Figure 2.6, it could be concluded that the higher the volume fraction of silver nanoparticles in the filler the greater the electrical conductivity.

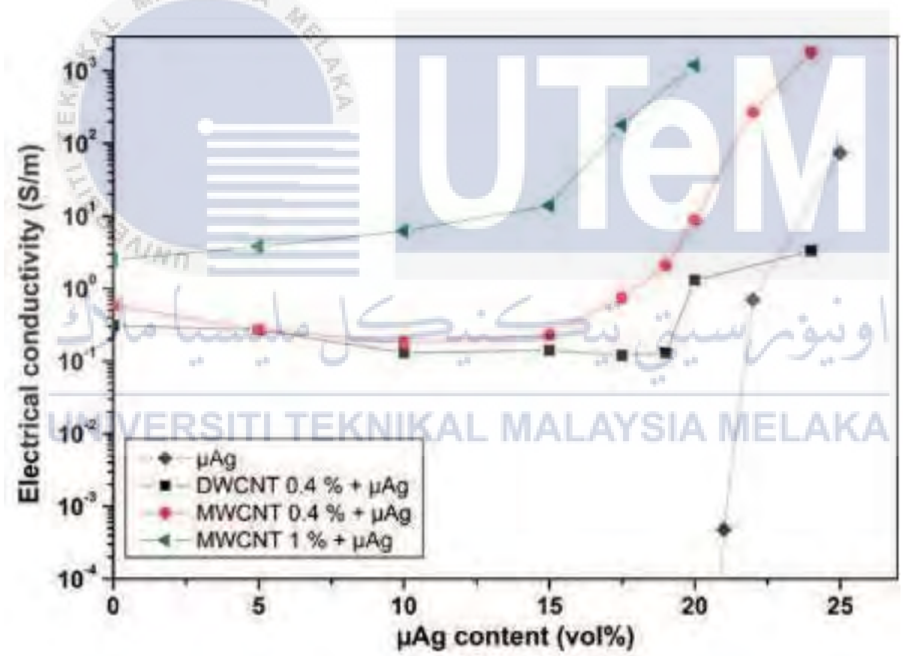


Figure 2.7: Dependence of the dc electrical conductivity on the Ag flakes volume fraction for hybrid composites

2.3.2 MECHANICAL PROPERTIES

Mechanical properties determine the strength of the material toward external force. The mechanical properties of ECA is mostly based on the polymer matrix that had been used to fabricate the ECA. The most common thing to be concerned about ECA in this project are lap shear strength.

For CNT, it can be observed that the tensile strength will increase with the increase of MWCNT content reaching optimum value. At the optimal value of MWCNT in a composite, the ultimate tensile strength and yield strength of composites are enhanced. However too much of CNT content in a composites was found to deteriorate the tensile strength. This is because of difficulties of hydrogen entrapment during the reinforcement addition, thus adding CNTs above the optimal value will make the composites become more brittle.

Jing Li [7] conducted an experiment to measure the volume of resistivity for epoxy/MWCNT composites with different MWCNT loadings. He found that increasing the MWCNT loading content of the composites will increase the volume resistivity as shown in Table 2.5. The loading content of 12 wt.% of MWCNT have the highest value of volume resistivity.

Table 2.6:Measured volume resistivity for epoxy/MWCNT composites with different MWCNT loadings [7].

Loading (wt%)	Volume resistivity	Standard deviation
0	1×10^{14}	-
0.25	1.57×10^{5}	-
0.5	1.92×10^{4}	-
1	534.09	-
2	65.21	7.32
4	9.55	0.81
8	2.16	0.30
12	2.17	0.27

CHAPTER 3

METHODOLOGY

3.1 OVERVIEW OF RESEARCH METHODOLOGY

This chapter describes the experimental work involves in this project, which consist of preparation and fabrication of ECA, type of MWCNT, AgNP, epoxy resin and hardener used, the machine and apparatus used and the material characterization tests on the ECA are described. Below is the summary of the research activities involved in this project, as presented in Figure 3.1:

i. Design of experiment.
ii. Preparation of materials, including the formulation of ECA, sample fabrication, variables and parameters of the experiment which includes:
   a. Materials formulation of the ECA
   b. Fabrication process including, curing process using the oven
   c. Lap shear test using a Universal Test Machine
   d. Electrical conductivity measurement using a 4-point probe
   e. Scanning Electron Microscope (SEM) for surface morphology
iii. Data collection and analysis

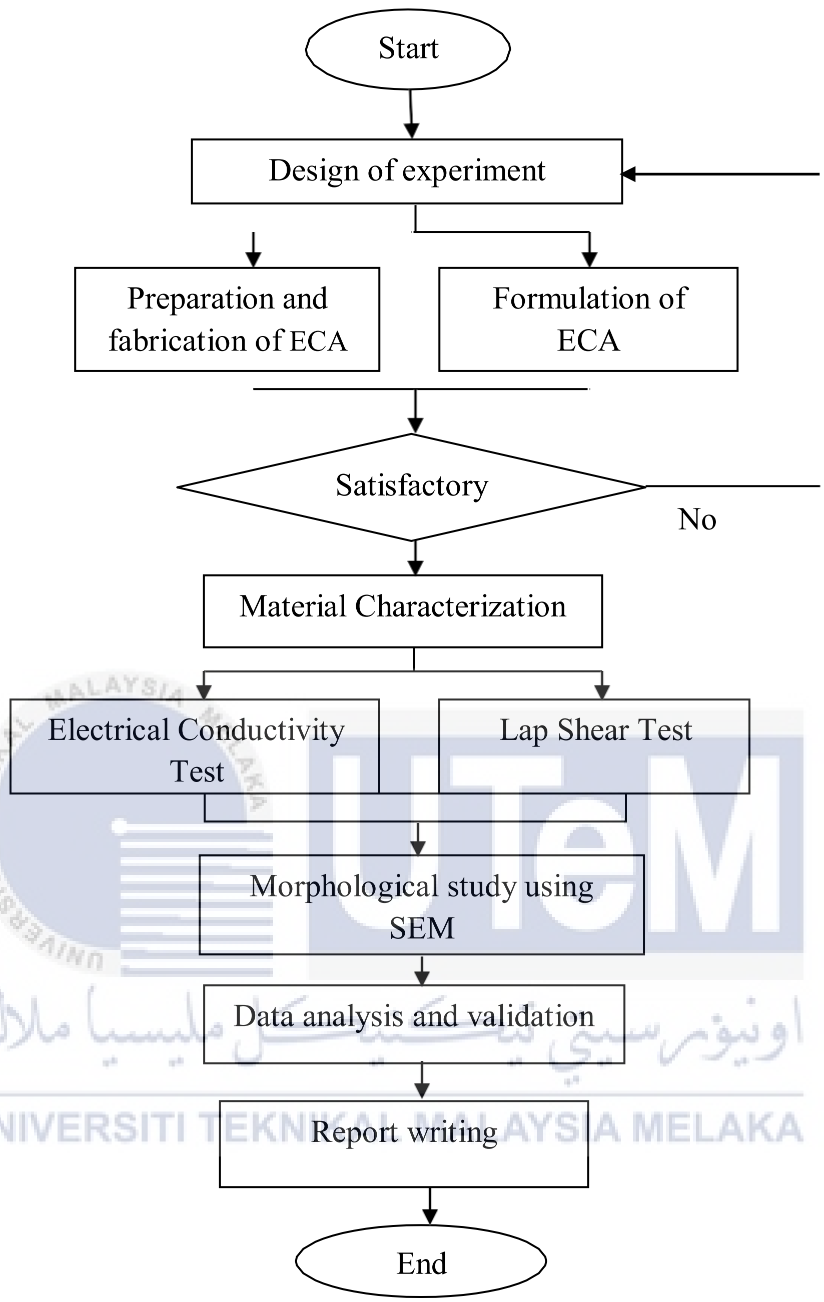


Figure 3.1 : Flow Chart of research

3.2 RAW MATERIALS

Generally in this project, the formulation of the hybrid ECA contain of four part of substances. The first one is the epoxy resin which acts as the polymer matrix of the ECA. In this research project, Epoxy Resin Araldite 506 is used. Next, a hardener is added which is Polyether amine D230 was chosen. The third part is the conductive filler will be added to the filler loading.

3.2.1 Epoxy Embedding Medium, Hardener MNA

The epoxy used as matrix polymer is Epoxy Embedding Medium, Hardener MNA which is supplied by Sigma Aldrich. It is used as the binder for the ECA in this experiment. Table 3.1 shows the specification of the epoxy [39].

Figure 3.2 : Sigma Aldrich Epoxy Embedding Medium, Hardener MNA [39]

Table 3.1 : Specification of Epoxy Embedding Medium, Hardener MNA [39].

Category	Specifications
Appearance	Viscous Liquid
Color	Light Yellow
Flash Point	135 °C
Vapor Pressure	5 mmHg (120 °C)
Density	1.232 g/mL at 25 °C(lit.)

3.2.2 Hardener Polyetheramine D230

The hardener used as the curing agent for the epoxy is supplied by Huntsman Singapore Pte LTD which called JEFFAMINE D-230 Polyether amine [40]. Table 3.2 shows the specification of the hardener as given in the material safety data sheet (MSDS).

Figure 3.3: Huntsman Singapore Pte Ltd JEFFAMINE D-230 Polyetheramine

Table 3.2: Specification of Huntsman Singapore Pte Ltd JEFFAMINE D-230 Polyetheramine [40].

Category	Specification
Viscosity, cSt, 25°C	9.5
Density, g/ml, 25°C	0.948
Flash Point, PMCC, °C	121
Vapor Pressure, mm Hg/°C	1/100

3.2.3 Multi-Walled Carbon Nanotube

The Multi-Wall Carbon Nanotubes (MWCNT) that are used for this experiment is supplied by Nanostructured & Amorphous Materials Inc, USA. The MWCNT has arrange of outer diameter which is from 10nm to 20nm.

Figure 3.4: Nano Armor MWCNT

3.2.4 Sigma-Alrich Silver Flakes

Silver will be added to the metal filler of the ECA obtained from Sigma-Aldrich. The properties of the silver is shown in Table 3.3 [41].

Figure 3.5: Sigma-Aldrich Silver

Table 3.3: Sigma-Aldrich Silver Properties [41].

Properties	**Specification**
Appearances	Flakes
Melting Point	960 °C
Density	10.49 g/cm^3
Resistivity	1.59 µΩ-cm, 20°C

3.3 FORMULATION OF SAMPLE

3.3.1 Electrically Conductive Adhesive Formulation

All of the samples are mixed and blended manually. Before that, all of the raw materials are divided into their weight percentage. The ECA is set to be 5g for every samples. The silver is set to be constant with 10 wt.% from the total weight. The weight percentage of hardener is set to be 30% from total weight of epoxy but it is not included into the total weight of ECA. The filler loading of MWCNT were set to 3 weigh percentage which are 5 wt.%, 6 wt.% and 7 wt.%. The weight percentage for every raw materials for every samples is shown in Table 3.1. All the weight are measured by using weight balance (Figure 3.6).

Table 3.4 : Weight for every raw materials.

Filler Loading (wt%)	**5**	**6**	**7**
Epoxy (g)	4.25	4.2	4.15
Hardener (g)	1.275	1.26	1.245
MWCNT (g)	0.25	0.3	0.35
Silver (g)	0.5	0.5	0.5

The rule of mixture formula is used to calculate the mixture amount needed as given in Equation (3.1):

$$X_c = X_m V_m + X_{f_1} V_{f_1} + X_{f_2} V_{f_2}$$

Where:

c = composite

m = matrix

f_1 = filler 1 (Silver)

f_2 = filler 2 (MWCNT)

In addition, the matrix volume fraction and filler volume fraction is given by Equation (3.2) and (3.3) respectively;

$$\text{Matrix Volume Fraction},\ V_m = \frac{V_m}{V_c}$$

$$\text{Filler Volume Fraction},\ V_f = \frac{V_f}{V_c}$$

To calculate the amount of MWCNT needed, Equation (3.4) is used:

$$\text{MWCNT (g)} = \text{MWCNT (wt.\%)} \times \text{Sample Weight (g)}$$

Equation (3.4) is also used to calculate the amount of Silver.

To calculate the amount of epoxy needed, Equation (3.5) is used:

$$\text{Epoxy (g)} = \text{Sample Weight (g)} - \text{MWCNT (g)} - \text{Silver (g)}$$

To calculate the amount of hardener needed, Equation (3.6) is used:

$$\text{Hardener (g)} = \frac{30}{100} \times \text{Epoxy (g)}$$

Figure 3.6: Weight Balance

Thinky Centrifugal Mixer ARE-310 is used for the mixing process of the raw materials. All of the raw materials are weighed to their own weight percentage together with a 15g container. The 15g container is used because the total weight of all the raw materials mixed are one-third of the mass container. Then the container is inserted into a 150 ml adapter. The adapter is then inserted into the Thinky Centrifugal Mixture. The mixing process is to be undergoes at 2000rpm of speed for about 3 minutes.

Figure 3.7: Thinky Centrifugal Mixer

Figure 3.8: 15g container

Figure 3.9: Adapter

The sample is then imprinted into an acrylic plate layered with Scotch Tape. Then the sample is then sent for curing process in the Memmert Oven. The curing process is set to be in 150°C for about 30 minutes.

Figure 3.10: Memmert Oven

After curing, the sample were left to be cool for 24 hours before being tested for electrical using four-point probe unit and mechanical using a lap shear Universal Testing machine.

3.3.2 SAMPLE PREPARATION FOR ELECTRICAL CHARACTERIZATION (FOUR-POINT PROBE TEST)

For the electrical test method, the testing standard of ASTM F390-11 were referred to as a guideline to measure the sheet resistance (Ω/sq.) of the ECA using four-point probe test unit. A six strip of the ECA was applied onto a 3-mm thick acrylic with dimensions of 45 mm (wide) and 88.9 mm (length) by using printing technique. The strip is 12.7 mm in length and 2 mm wide. The thickness of the ECA was controlled using 2 layers of Scotch tape and spread using a metal sheet for 2 consecutive time.

Figure 3.11: Acrylic plate after layered with Scotch Tape.

Acrylic laser cutting machine was used to cut the acrylic into size for precision. The acrylic used was 3-mm thick thus the laser power used to cut is 50% of the full laser power.

Figure 3.12: Acrylic laser cutting machine

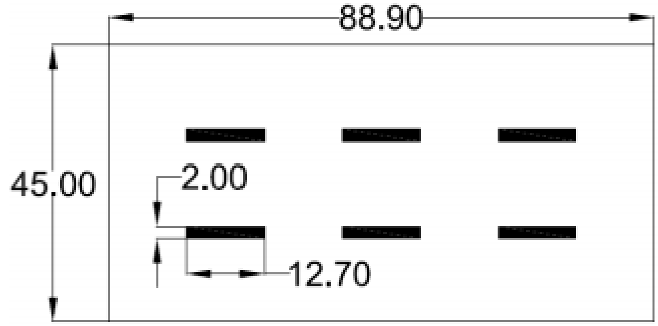


Figure 3.13: Drawing of the Electrical Specimen

3.3.3 SAMPLE PREPARATION FOR MECHANICAL CHRACTERIZATION (LAP SHEAR TEST)

ASTM D1002-10 were used as standard and guideline for the mechanical test. The standard followed includes the cleaning of the sample surface before ECA is applied, the thickness of ECA applied, and the measurement of specimen.

Aluminum sheet with 25.4 mm wide, 101.6 mm length and 1.5 mm thick and the overlap is 12.7 mm thick. The thickness of ECA use is 0.1 mm and to control the thickness, a stemless steel sheet with 0.1mm thick is use as based to lift of side of aluminum and 3 clip is used to hold the specimen in place [42].

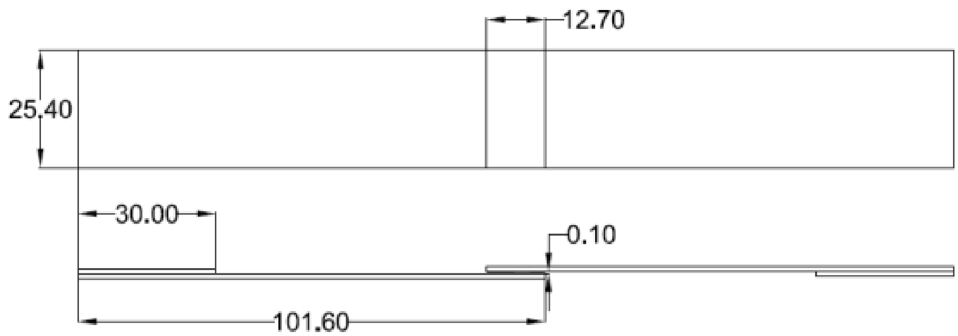


Figure 3.14: Drawing of the Mechanical Specimen

Shearing machine is used to cut the aluminum into the specimen size to ensure that no damage of defect occurred during the process. Any distortion on the edge or bending of specimen could affect the results of conducted test.

3.4 MATERIAL CHARACTERIZATION

3.4.1 MECHANICAL PERFORMANCE

The mechanical performance of ECA will be tested by using a Universal Testing Machine (Figure 3.2) for the lap-shear test. From this test, the stress-strain curve is obtained and the shear strength of the ECA is calculated by using the formula below:

$$\tau = \frac{F}{A}$$

All the samples preparation and test techniques is based on ASTM D1002 standard in tensile loading. Different samples of different type of filler loading is tested and average shear strength is calculated.

Figure 3.15: Universal testing machine for lap shear test

3.4.2 ELECTRICAL PERFORMANCE

Electrical performance test is done by using four-point probe test as shown in Figure 3.3, with the data in the form of resistance per square (Ω/sq.). The ECA is printed as 6 short straight line on insulator substrate by using printing technique and ASTM F390 standard is used as guideline. For each strip, 3 readings are taken and average sheet resistance is calculated.

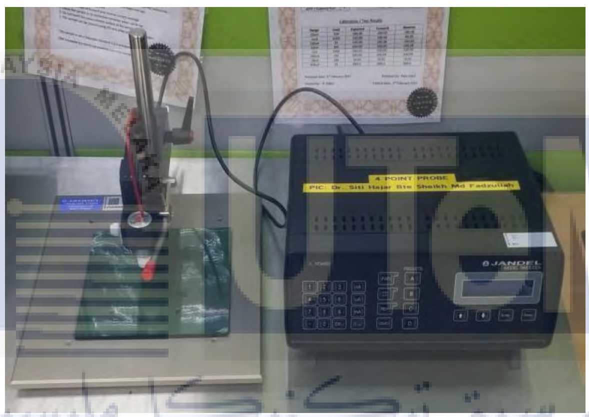


Figure 3.16: Four-point probe for electrical conductivity test

CHAPTER 4

RESULT AND DISCUSSION

4.1 INTRODUCTION

Generally, an ECA need to have a good electrical conductivity and mechanical properties. Both of these properties is essential in order to develop a hybrid conductive composites. From previous study, it can be concluded that the filler contents need to be balanced so it will not surpass the percolation threshold while the epoxy need to be strong enough to provide better adhesion and mechanical properties.

In this chapter, the effects of filler loading containing MWCNT and silver in ECA is presented. The specimen is prepared as stated in previous chapter. For electrical conductivity test, the ECA is printed onto an acrylic in 6 short strips. All the samples are cured in oven for 30 minutes with 150°C and then left to cool down for 24 hours at room temperature.

4.2 ELECTRICAL PERFORMANCE TEST

A high electric conductivity of ECA is very essential since this interconnect material is created to perform the interconnection between component.. That's why the filler type and arrangement of matrix determine the electrical properties of a composite material. The resistivity is totally inverse with the conductivity of ECA which means the lower the resistivity the greater the conductivity by referring from Ohm's Law. Epoxy acts as aninsulator material which promote high electrical resistivity and the conductive filler of MWCNT/Silver is added into the adhesives and reduce the resistivity gradually.

An experiment is conducted by using a standard of ASTM F390-11 by using JANDEL Four-Point probe test. The result is then multiplied with the correction factor that are obtained from the standard.

Table 4.1: Sheet Resistance of ECA

	Sheet Resistance (KΩ.m)		
MWCNT Filler Loading (wt.%)	**Epoxy + Ag + MWCNT**	**Epoxy +MWCNT**	
		Mueezz (2018) [43]	**Wan Ahmad (2018) [44]**
5	13.47± 2.56	10.66 ± 3.19	37.39 ± 9.46
6	11.50 ± 1.29	3.79 ± 1.89	15.32 ± 2.76
7	5.89 ± 0.49	1.367 ± 0.49	2.59 ± 0.35

Table 4.1 shows the graph of sheet resistance as a function of filler loading for the carbon black and MWCNT filled ECA. Figure 4.2 shows the three samples of printed ECA filled with 5 wt.%, 6 wt.%, and 7 wt.% of MWCNT filler loading respectively. The sudden decrease of resistivity between the three samples shows the percolation threshold.

Figure 4.1: Three samples of ECA

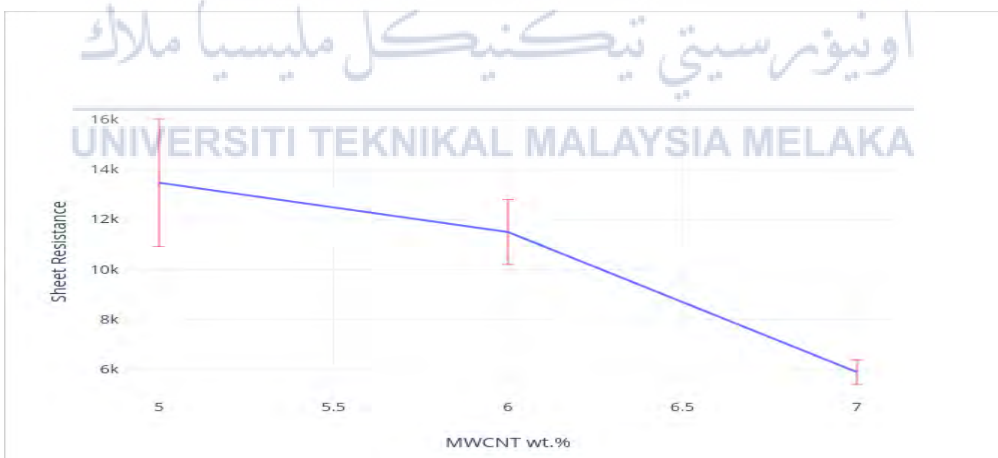


Figure 4.2: Observation of 5 wt.%, 6 wt.% and 7 wt.% MWCNT/Silver

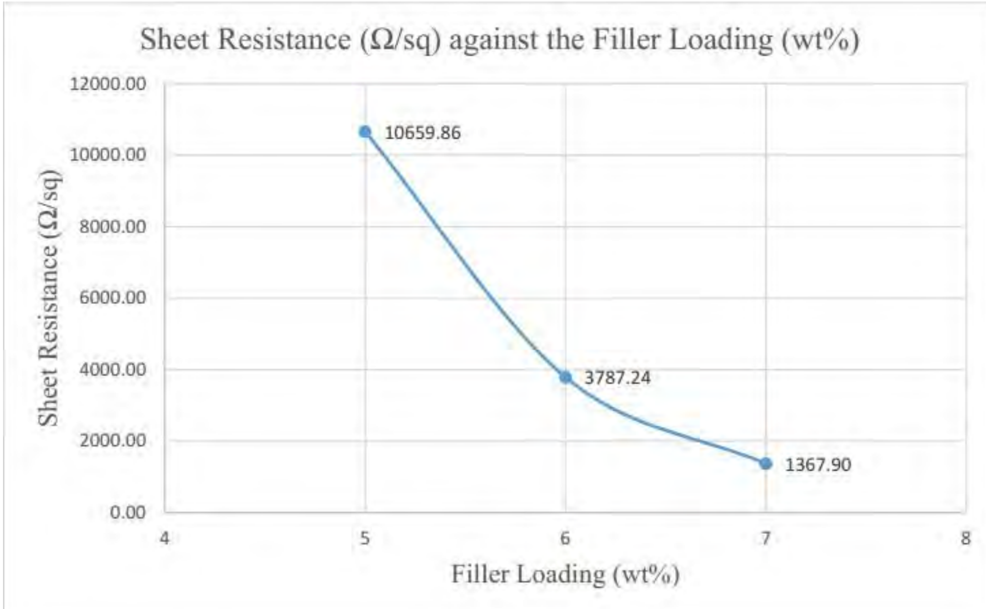


Figure 4.3: Graph of sheet resistance against filler loading normal ECA containing MWCNT

Figure 4.3 shows the graph of volume resistivity which was multiplied by the correction factor, C = 1.9475. Correction factor is a factor that is multiplied with the result to correct for a known amount of systematic error. The result shows that the higher the amount of filler loading in ECA, the lower the volume of resistivity due to increase of contact, an increase of probability of continuous linkage and an enhancement formation of three-dimensional network between MWCNT/Silver filler in ECA [45]. Precaution need to be done so that the filler loading does not surpass the percolation threshold. Moreover, the standard deviation of sheet resistance decrease significantly with an increase of filler loading which indicates to more reliable measurement of sheet resistance obtained.

ECA with high conductive filler loading, hash high total resistance between percolated linkage due to a thin layer of epoxy resin cover the MWCNT/Silver surface, but the total resistivity reduces with shrinkage of epoxy resin after curing process result to conductive filler particles closes together.

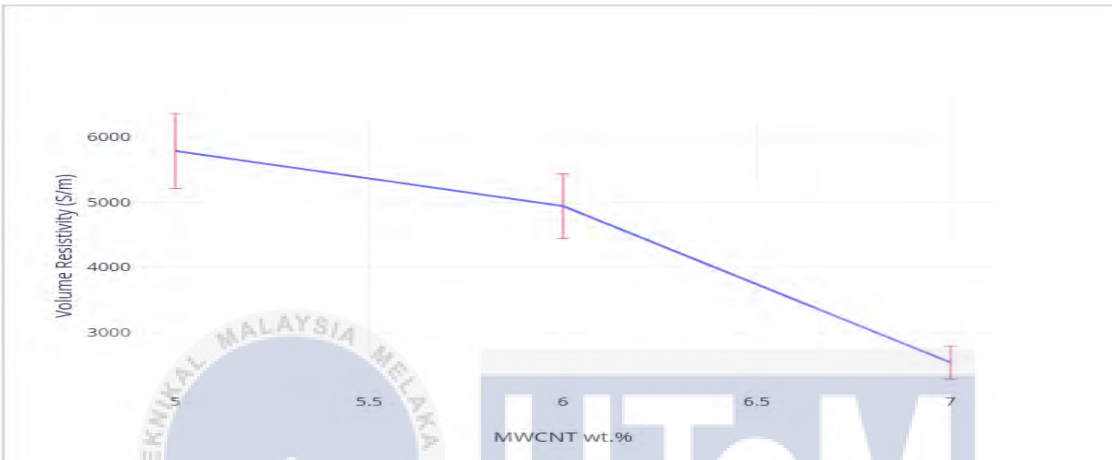


Figure 4.4: Volume Resistivity against Filler Loadings

By comparing the result from a previous study who conducted an experiment investigating the sheet resistance of an ECA containing MWCNT as filler as shown in Figure 4.4 and Figure 4.5, it can be concluded that from this experiment, ECA with filler containing MWCNT/silver has higher resistivity and thus lower conductivity. Hybrid adhesives composites supposedly gives a better conductivity because the presence of metal filler such as silver which naturally have the greatest conductivity. For a 7 wt.% of MWCNT of filler loading, a difference of 23% of the conductivity than normal ECA [Mueez 2018]. This happens because the system of the samples is already saturated when 10 wt.% of Silver mixed with 5 wt.%, 6 wt.% and 7 wt.% of MWCNT, thus it has surpass the percolation threshold.

4.3 MECHANICAL PERFORMANCE TEST

The shear strength of the ECA is to be determined which contributed to the binding strength. The shear of adhesion of the ECA will decrease when increasing the filler loading in the ECA. Increasing the filler loading up to the percolation threshold will yield the composite toughness. Further increase beyond the percolation threshold will result to reduce of reinforcement efficiency [52].

Table 4.2: Shear strength of the ECA filled with MWCNT/Silver

Filler Loading of MWCNT, wt.%	Average Shear Strength (MPa)
5	10.56 ± 1.53
6	8.76 ± 1.19
7	7.02 ± 1.92

Bonding effectiveness is determined by a combination of both adhesive strength and cohesive strength. There are two types of adhesion failure which is adhesive failure and cohesive failure. Adhesive failure is when the failure occurs between the adhesive and substrate where in which the bulk adhesive retained on only one substrate surface. Cohesive failure is a type of failure which occurs within the adhesive that is retained on both substrate surface.

The data from Table 4.2 is collected by conducting the lap shear test in order to study the effect of hybridization of the filler towards the shear stress of the ECA. 5 samples were prepared for each filler loading and it can be observed that the highest shear stress achieved is 10.562 MPa for the 5 wt.% filler loading. Since the addition of MWCNT/Silver filler into the epoxy, it enhances the mechanical properties of ECA and it contributes to an increase of the toughness and resist the formation of crack growth [49]. However, the shear strength of the specimen decreased as the weight percentage of MWCNT is increased. This is because the MWCNT which is high surface energy tend to aggregate resulting to poor dispersion and reduce the mechanical strength in the ECA.

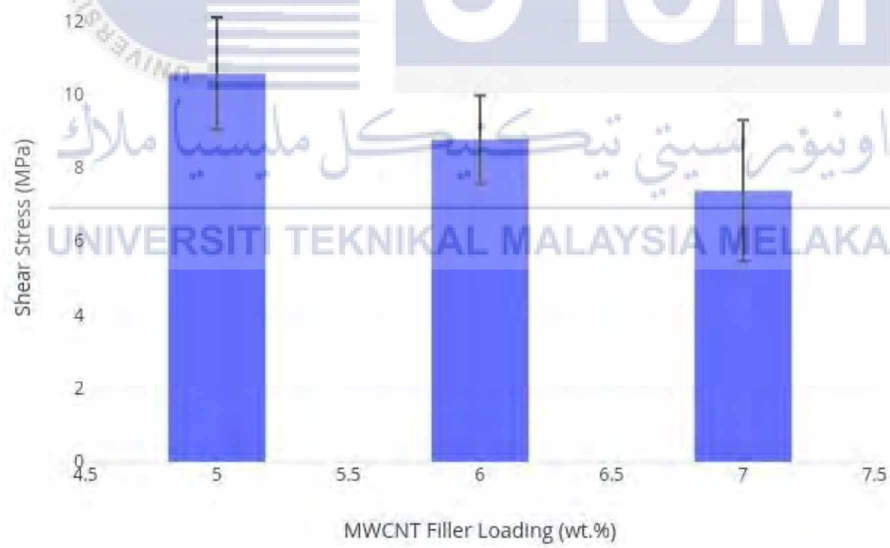


Figure 4.5 : Shear Strength of ECA with different MWCNT Filler Loading

The reason of the observation could be due to the fact at filler loading 5 wt.%, the MWCNT/Silver filler is properly dispersed with the matrix. Plus, the 5 wt.% filler loading of MWCNT has the most amount of polymer matrix inside the ECA which acts as the adhesives. An increase of conductive filler loading in ECA means the volume fraction of epoxy relatives to the total volume ECA reduces [11]. This makes the bond between the conductive filler and the polymer matrix able to transfer load efficiently [46]. In addition, at high MWCNT filler loading, means less surface contact area between epoxy/substrate interface to provide adhesion properties [7].

The shear strength is reduced by 20.47% when compared between the results of ECA with 5 wt.% and 6 wt.% of MWCNT filler loading, while 24.78% of reduction in shear strength between 6 wt.% and 7 wt.%. The ECA with 6 wt.% and 7 wt.% of MWCNT filler loading is poor in load transfer, possibly because of the agglomeration that is formed at the conductive filler. This makes the movement in the ECA are easier to be initiated [47]. An increase of the filler loading in ECA contribute to the increasing of viscosity of ECA prior to curing process which reduce the mobility of MWCNT/Silver in the epoxy and affect the dispersion in the ECA. The agglomeration of MWCNT and Silver could possibly formed a crack which are not good for load transferring capability. By looking at the results, it suggests that as the agglomeration becomes critical, the higher the percentage of decrease of the ECA shear strength.

Table 4.3: Comparison of shear strength with previous study

MWCNT Filler Loading (wt.%)	**Shear Stress (MPa)**		
	Epoxy + Ag + MWCNT	**Epoxy +MWCNT**	
		Mueezz (2018) [43]	**Amin (2018) [48]**
5	10.56 ± 1.53	8.58 ± 1.55	9.55 ± 0.59
6	8.76 ± 1.19	7.67 ± 1.20	7.22 ± 0.50
7	7.026 ± 1.92	5.85 ±2.03	6.34 ± 018

From Table 4.3 it can be concluded that by hybridization of the ECA may result to increase of shear stress of the ECA. For 5 wt.%, an increase of 23% of the shear stress compared to Mueezz (2018) and 10.5% from Amin (2018). However, the trend on the resultant shear strength of the ECA with other studies is similar by using only MWCNT as filler.

4.4 ECA FAILURE ANALYSIS

Adhesive joints may fail adhesively or cohesively. Adhesive failure is interfacial bond failure between the adhesive and the adherend. Cohesive failure occurs when a fracture allows a layer of adhesive to remain on both surfaces [50]. Adhesive mode of failure is observed in this experiment.

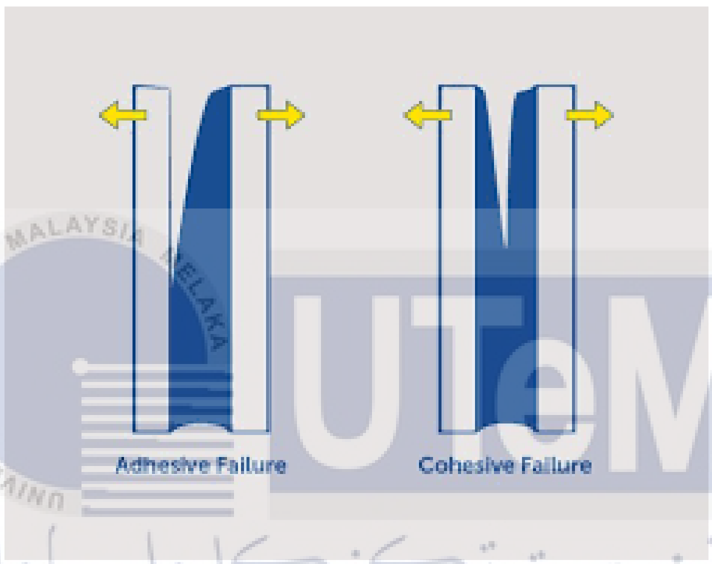


Figure 4.6: Adhesive and cohesive failure illustration.

High shear strength of ECA with adhesive-cohesive failure indicates that there is a high adhesion between ECA/substrate interface as a resulted of large surface area of contact between epoxy/substrate interface, yield to strong mechanical contact [51]. Adhesives failure may happen at high MWCNT filler because of low mechanical interlocking strength between epoxy/substrate interface. Therefore, the ECA bond with adhesive failure have lower shear strength than ECA bond with adhesive-cohesive failure.

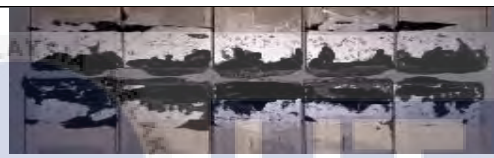
MWCNT filler loading (wt.%)	ECA Failure Behavior	Mode of failure
5		Adhesive-Cohesive
6		Adhesive-Cohesive
7		Adhesive-Cohesive

Figure 4.7: ECA with different MWCNT filler loading mode of failure.

4.5 CHAPTER SUMMARY

In terms of electrical conductivity, the higher the amount of MWCNT filler loading in the ECA, the greater the ECA electrical conductivity performance due to formation of conductive path between the fillers. By comparing the hybrid ECA with normal ECA, the sheet resistance of hybrid ECA is higher than normal ECA for this experiment. Same goes to the value of volume resistivity.

In terms of mechanical strength, an increase of filler loading up to 6 wt.% will result to decrease of shear strength despite contain higher reinforcement by the filler. This is due to aggregation between the fillers and the low weight fraction of polymer matrix. Hence, the adhesion strength between the substrate and ECA is reduced.

CHAPTER 5

CONCLUSION AND RECOMMENDATION FOR FUTURE WORK

5.1 CONCLUSION

The functional properties of hybrid ECA is studied by formulating ECA using MWCNT and silver followed by electrical testing using four-point probe test unit and mechanical testing using universal testing machine. From the experimental work, it is proven that hybrid ECA have better shear strength compared to normal ECA.

The results obtained from the series of electrical and mechanical tests suggest that the percolation threshold of the ECA formulated using epoxy resin with MWCNT/Silver filler is achieved at relatively low weight percentage of MWCNT. Hence, the sheet resistance dropped significantly after 5 wt.% of MWCNT filler loading. Nevertheless, the results obtained from the lap shear test suggests that the shear strength decrease with increasing the filler loading. The filler loading of 5 wt.% of MWCNT has the highest value of shear strength. This shows that agglomeration of filler occurs at high amount of filler loading thus decrease the shear strength of ECA.

Table 5.1: Summary of electrical and mechanical performance test for MWCNT/Silver-filled ECA

Filler loading (wt.%)	**Sheet Resistance (kΩ/sq.)**	**Shear Strength (MPa)**
5	13.47± 2.56	10.56 ± 1.53
6	11.50 ± 1.29	8.76 ± 1.19
7	5.89 ± 0.49	7.026 ± 1.92

From the results obtain in this research, it can be concluded that hybridization does affect the functional properties of ECA. Both electrical and mechanical performance of hybrid ECA has been better than the normal ECA. The addition of silver into MWCNT as the filler for the ECA does influence the ECA properties whereby the lower filler loading is needed to achieve percolation threshold.

5.2 RECOMMENDATION

ECA has been developing throughout the year. It is used for the interconnection technique replacing the more harmful lead solder which has been banned by several organizations. However for hybridization of the ECA, various material could be used to replace silver and MWCNT as the metallic filler. For example, by using different type of CNT and other conductive material. Then, another research could be done to determine percolation threshold of different type of hybrid ECA.

The formulation process of ECA could be further improved to ensure a homogenous distribution of the filler and epoxy in the ECA. For example, during the printing of formulate ECA into the acrylic board, the ECA is not distributed equivalently to every void thus it may affect the amount of sheet resistance or range of sheet resistance between each void from the same samples is not too far.

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