THE EFFECT OF CARBON NANOTUBE ASPECT RATIO ON THE FUNCTIONAL PROPERTIES OF ELECTRICALLY CONDUCTIVE ADHESIVES

ABDUL MUEEZZ BIN ABDUL RAHEEM

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

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ABDUL MUEEZZ BIN ABDUL RAHEEM

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in fulfillment of the requirement for the degree of

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DECLARATION

I declare that this project entitled "The Effect of Carbon Nanotube Aspect Ratio On the Functional Properties of Electrically Conductive Adhesives" is the result of my own work except as cited in the references.

Signature :……………………………………..

Name :……………………………………..

Date :……………………………………..

APPROVAL

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

Signature :…………………………………..

Name :…………………………………..

Date :…………………………………..

DEDICATION

This report is dedicated to my beloved parents.

ABSTRACT

Eliminating lead containing solder in electrical industries has driven the need to develop lead-free conducting material termed Electrically Conductive Adhesive (ECA), since the former interconnect material is high in toxic. Thus, ECA is seen as a substitute material with the advantage of being more environmental friendly interconnect material. ECA is made up of polymer as the binder and filler as the conductive material. Metal fillers such as silver, copper and gold are the most commonly used filler. More recently, non-metallic carbon-based material filler such as carbon nanotubes, carbon black and graphene are extensively studied and developed to be used as ECA conductive filler. In addition, ECA with multiwall carbon nanotubes (MWCNT) is developed to improve the strength and electrical conductivity. Current ECA used in industries has low electrical conductivity, poor impact strength and conductivity fatigue since the filler used are metal filler. This project investigates the effect of carbon nanotubes aspect ratio on the functional properties of electrically conductive adhesive. Generally, with higher aspect ratio of MWCNT filler in ECA, the electrical conductivity is better while as the filler loading increase, the shear strength decrease. Electrical and mechanical samples of ECA with different aspect ratio of the MWCNT filler were prepared and tested with reference to ASTM F390-11 and ASTM D1002 respectively. The ECA were prepared by using solution mixing process before curing in an oven at 100°C for 30 minutes. Here, the two aspect ratio of the MWCNT is 1750 while the second MWCNT aspect ratio is 112.5, with the range of MWCNT filler loading is used in this research, which is 5 wt.%, 6 wt.% and 7 wt.%. The specimens were subjected to electrical test using a four-point probe test unit and mechanical testing by using universal testing machine. By formulating ECA using high aspect ratio MWCNT, lower filler loading is needed to reach the percolation threshold which shows better conductivity compared to low aspect ratio MWCNT. As the filler loading increase, the result suggests lower shear strength of the MWCNT-filled ECA. MWCNT aspect ratio has significant effect on the electrical and mechanical properties of ECA which is caused by the agglomeration and dispersion of the MWCNT in the ECA.

ABSTRAK

Usaha menggantikan pateri berplumbum yang tinggi kandungan toksik di industri elektrikal telah membawa kepada pembangunan pateri bebas plumbum yang dinamakan pelekat konduktif elektrik. Kelebihan pelekat konduktif elektrik ini dilihat sebagai gentian yang lebih mesra alam. Pelekat konduktif elektrik ini diperbuat daripada polimer sebagai perekat dan pengisi sebagai bahan konduktif. Logam pengisi yang biasa digunakan adalah perak, tembaga, dan emas. Baru- baru ini, bahan pengisi seperti karbon nanotube, karbon hitam dan graphene telah dikaji dan dibangunkan secara meluas untuk digunakan sebagai pengisi konduktif didalam pelekat konduktif elektrik. Di samping itu, pelekat konduktif elektrik dengan karbon nanotube berlapis dibangunkan bagi meningkatkan kekuatan dan kekonduksian elektrik. Pelekat konduktif elektrik semasa yang digunakan dalam industri mempunyai kekonduksian elektrik yang rendah, kekuatan impak yang lemah dan kegagalan kekonduksian kerana pengisi yang digunakan adalah bersifat logam. Projek ini menyiasat kesan nisbah aspek karbon nanotube ke atas sifat kefungsian pelekat konduktif elektrik. Pada umumnya, dengan nisbah aspek karbon nanotube yang lebih tinggi digunakan sebagai pengisi didalam pelekat konduktif elektrik, prestasi kekonduksiannya adalah lebih tinggi, manakala kekuatan ricihnya menurun dengan pemuatan pengisian yang menaik. Sampel bagi ujikaji elektrik dan mekanikal pelekat konduktif elektrik dengan nisbah aspek karbon nanotube berlapis yang berbeza disediakan dan diuji dengan merujuk kepada ASTM- F390-11 dan ASTM D1002 masing-masing. Pelekat konduktif elektrik disediakan dengan proses pencampuran sebelum diletakkan didalam ketuhar pada suhu 100 °C selama 30 minit. Nisbah aspek bagi karbon nanotube berlapis yang pertama adalah 1750 manakala nisbah aspek bagi yang kedua pula adalah 112.5 dan nilai pemuatan pengisian yang berbeza digunakan bagi kajian ini iaitu 5% berat, 6% berat dan 7% berat. Sampel elektrikal diuji menggunakan probe empat titik dan sampel makanikal diuji menggunakan mesin ujian sejagat. Dengan merumuskan pelekat konduktif elektrik menggunakan nisbah aspek karbon nanotube yang lebih tinggi, ambang perkolasi dapat dicapai dengan pemuatan pengisisan yang lebih rendah yang menunjuk pengaliran elektrik yang lebih baik. Keputusan kajian ini juga menunjuk semakin meningkat pemuatan pengisian, semakin rendah nilai kekuatan ricih bagi pelekat konduktif elektrik. Nisbah aspek mempunyai kesan terhadap sifat elektrik dan mekanik bagi pelekat konduktif elektrik yang disebabkan oleh pengaglomeratan dan penyebaran karbon nanotube berlapis didalam pelekat konduktif elektrik.

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LIST OF ABBREVIATIONS

3D	Three Dimensional
ACA	Anistropically Conductive Adhesive
CNT	Carbon nanotubes
CVD	Chemical vapor decomposition
ECA	Electrically conductive adhesive
ICA	Isotropically Conductive Adhesive
MWCNT	Multiwall carbon nanotubes
NCA	Non-Conductive Adhesive
PDMS	Polydimethylsiloxane
SEM	Scanning Electron Microscope
SWCNT	Single wall carbon nanotubes
TEM	Transmission electron microscopy
TPU	Thermoplastic polyurethane
UV	Ultra violet

LIST OF SYMBOLS

°C	=	Degree Celcius
k	=	Kelvin
Ω	=	Ohm
sq	=	Square
T_g	=	Glass temperature
g	=	Gram
m	=	Meter
nm	=	Nanometer
µm	=	Micrometer
L	=	Length
OD	=	Outer diameter
V_m	=	Volume of matrix
V_f	=	Volume of fiber
V_c	=	Volume of composite
wt%	=	Weight percentage
mm	=	Milimeter
τ	=	Shear
F	=	Force
A	=	Area
R	=	Resistance
V	=	Voltage
I	=	Current
C	=	Lateral correction factor
Pa	=	Pascal
Mpa	=	Mega Pascal
Gpa	=	Giga Pascal
Tpa	=	Tera Pascal

CHAPTER 1

INTRODUCTION

1.1 Background

The use of lead (Pb) containing solder for assembly of electronic components has been introduced for a long time. Since lead (Pb) is a substance that is high in toxicity, the electronic industries are eliminating or minimizing the usage volume of lead containing solders in response to allow for a better environmental friendly and sustainability industry. It also one of the response toward the international restriction on using Hazardous Substance (RoHS) legislation [1].

The effort to eliminate lead in solder have lead the electrical industries to two alternatives, that is lead-free metal solder alloys and polymer-based electrically conductive adhesive (ECA) [2]. There are two components in ECA which consists of resin or polymer matrix which can be either thermoplastic or thermosetting and a conductive filler typically based from metallic materials. The polymer matrix in electrically conductive adhesive (ECA) provides the mechanical properties such as mechanical strength, adhesion, and impact strength while the conductive filler provides the electrical properties which are relatively different from metal solder, in which the mechanical and electrical properties are provided by only one component [3].

Due to higher capability compared to other materials, high electrical conductivity, and chemical stability, the most commonly used filler in ECA is silver. Other than lowering the processing condition temperature and stress on substrates, ECA also have fine pitch interconnect capability and environmental friendly [4]. Multiwall carbon nanotubes (MWCNT) is another type of filler that is currently under development.

Even though silver is currently the most useable metal filler in ECA, the industry requires a lower processing temperature material to replace silver. Furthermore, there is no current commercialized ECA that is able to overcome the limitations of such materials ; these being lower electrical conductivity, low reliability and capability and poor impact strength [4].

1.2 Problem Statement

Due to the requirements of law to decrease and eliminate the use of hazardous materials, the industries have stop using lead-containing solder. The most common problem with lead-free solder is that a thick layer of intermetallic compounds is formed between the substrate and solder which decrease the electronic components performance significantly [5]. The other problem with lead free metal solder are the processing temperature is high which is more than 180 °C.

There are few problems that limits the usage of ECA in electronic industries such as poor impact strength, low electrical conductivity, conductivity fatigue which means the conductivity of the ECA lowers under increasing temperature and humidity aging [6].

ECA with MWCNT is being developed to improve and overcome all the problems. Thus, the aim of this study is to develop a MWCNT ECA with different aspect ratio with good mechanical and electrical performance at much lower processing temperature.

1.3 Objective

The objectives of pursuing this research topic are:

1. To fabricate the electrically conductive adhesive (ECA) using multi-wall carbon nanotube (MWCNT) with different aspect ratio and filler loading.
2. To study the electrical properties of the MWCNT ECA with different aspect ratio and filler loading.
3. To study the mechanical strength of MWCNT-filled ECA with different aspect ratio and filler loading.

1.4 Scope of Project

The followings are the scope of this research projects:

I. Fabrication of ECA.
II. Electrical characterization using four-point probe test unit.
III. Mechanical characterization using universal testing machine (lap shear test)
IV. Surface morphology study.

1.5 Planning and Execution

Figure 1.1 below illustrates the research activities for PSM 1 that includes the process of research title selection, literature review, designing the experiment, formulation of samples, material characterization testing, data analysis and followed by report writing and report submission and lastly PSM 1 seminar. The material characterization includes electrical and mechanical testing. The research activities in PSM II started with the formulation of sample and followed by the material characterization for electrical and mechanical properties for all sample. Morphological study using Scanning Electron Microscope of each sample is done before all the data is analyzed. Finally, all the data and results are discussed in the report before submission and PSM II seminar. Figure 1.2 shows the Gantt chart of PSM II research activities.

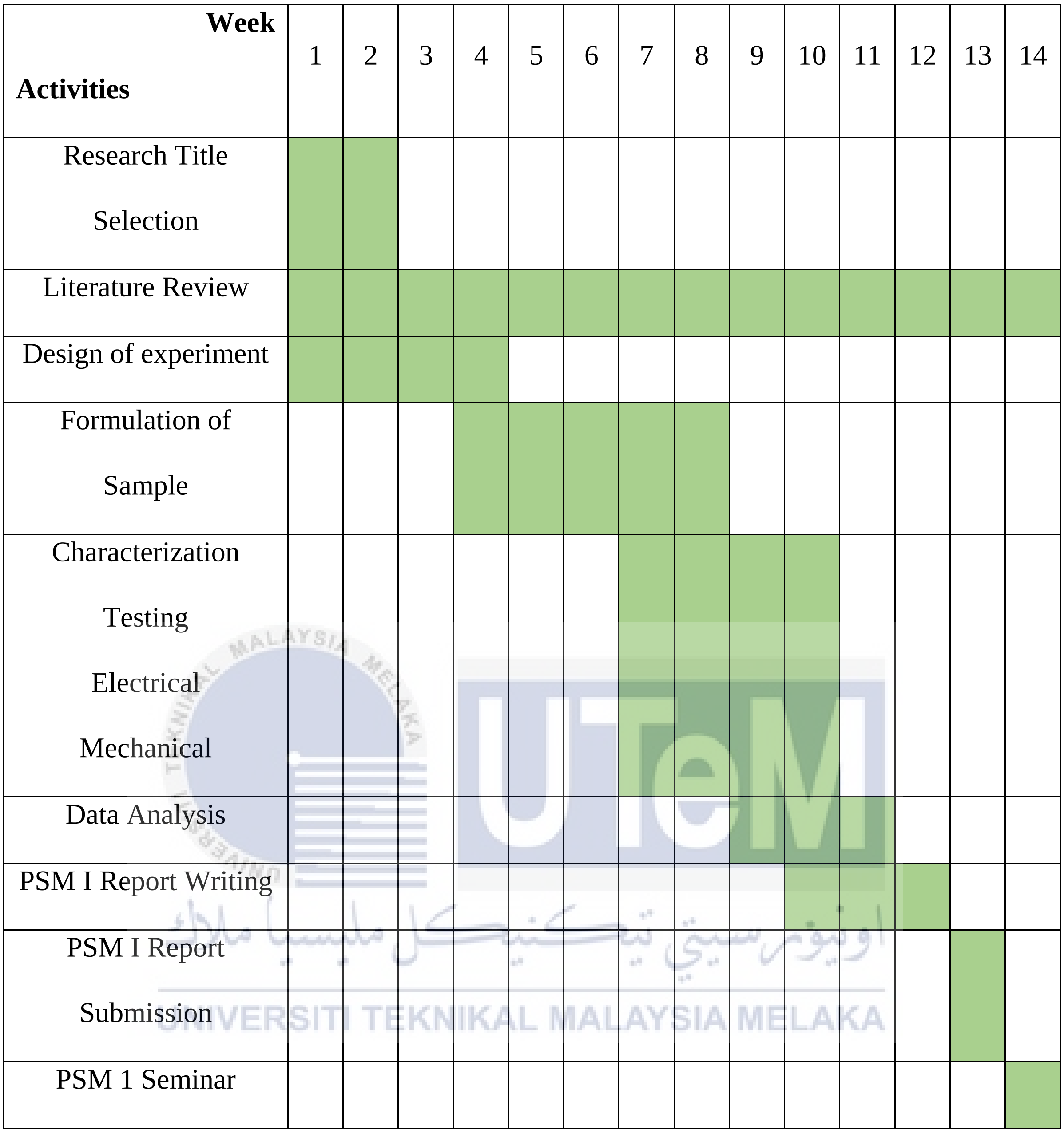

Figure 1.1: Gantt chart detailing research activities and time frame for PSM I

Week / Activities	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Literature Review														
Formulation of Sample														
Characterization Testing Electrical Mechanical														
Morphological Study (SEM)														
Data Analysis														
Result and Discussion														
PSM II Report Writing														
PSM II Report Submission														
PSM II Seminar														

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

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter a review on interconnect material, electrically conductive adhesive, polymers, filler, carbon nanotubes, and the mechanical properties, electrical properties and thermal properties are reviewed from the previous studies on this area.

2.2 Interconnect Material

Interconnect material or commonly term as solder is a metal alloy that can fuse and used to bond electronic connections. In the semiconductor and electronics industries, it is common to use lead (Pb) containing solder as the interconnecting materials of power, signal or transmission. However, due to the amount of toxic produced by lead substance, industries are seeking for other alternative to change for a more environmental friendly interconnecting material [7].

2.2.1 Lead Solder Alloy

Lead solder alloy have been used for many decades in various industries because of the reliability of the materials. It is used for its low melting point, which is 183°C. With the increasing awareness to protect the environment, industries are demanded to reduce or eliminate the use of hazardous material such as lead. Industries are working with researchers to find the most suitable replacement materials for lead.

2.2.2 Lead-Free Solder Alloy

Lead-free metal solder alloy and electrically conductive adhesive (ECA) are the top two focused alternatives to replace lead solder alloy**.** Thermal behavior, wetting capability, processibility, and mechanical properties are the concern of lead-free solder alloys. The most commonly utilized lead-free solder is tin (Sn) due to its inexpensive price. Nonetheless, this material melts at relatively 232°C, which is much higher than those of the lead solder alloy, which melt at relatively 183°C. Moreover, the reliability performance of an electronic components can degrade as a result of much higher processing temperature [7]. Tin/silver (Sn/Ag) and tin/silver/copper (Sn/Ag/Cu) also have higher melting temperature (183°C). These higher melting temperature result in higher solder reflow temperature which can limit the applicability of lead-free solder alloy to a temperature sensitive substrate or boards and increase the energy consumption and processing cost. Therefore, researcher have developed a lower melting point lead-free solder alloys, as shown in Table 2.1 , however the properties of these material are still under further enhancement [2].

Table 2.1: Melting point of lead free solder alloy

Lead free solder alloy	Melting temperature, T_m (°C)
Tin/Indium (Sn/In)	120
Tin/Bismuth (Sn/Bi)	138
Tin/Zinc/Silver/Aluminum/Gallium	189

ECA which is polymer based composite provides several advantage, such as environmental friendliness, mild processing conditions, reduced processing cost, and better capability which can be processed at 150°C, that is significantly better than metallic solder, thus can be regarded as an ideal interconnect material, as an alternative for lead solder alloys. Nanotechnology have been developed progressively in the past few years and polymer-matrix composites which contains inorganic fillers that are in Nano-scale and distributed homogeneously have been the main interest in this field because of their unique characteristic such as thermal conductivity, electrical conductivity and mechanical properties of the material [8].

2.3 Electrical Conductive Adhesive

Electrical conductive adhesive consists of polymer matrix that provides adhesion and mechanical strength also conductive filler that conduct electricity. The level of carbon foot print in the semiconductor industries can be reduced effectively with the use of low processability temperature ECA [1,9,10]. The followings are the advantages of ECA [6, 11]:

I. Lower processing temperature
II. Less energy consumption
III. Finer pitch capability
IV. Higher flexibility
V. Greater fatigue resistance than solder alloy
VI. Use of non-solder able substrate such as glass, TPU, PDMS
VII. Environmental friendly

Classification of ECA which depending on the filler loading are Isotropically Conductive Adhesive (ICA), Anistropically Conductive Adhesive (ACA) and Non-Conductive Adhesive (NCA). Due to the high filler content in ICA, the conductivity of electrical occurs in all x, y, and z direction while in ACA and NCA, the electrical conductivity between the electrodes of the assembly only occurs in z direction because of the low filler loading causing there is insufficient inter-particle contact thus preventing conductivity in x and y direction [7, 9]. Table 2.2 below shows the characteristic of ECA compared to lead containing solder.

Table 2.2: Characteristic of ECA compared to Solder [2].

Characteristic	Sn/Pb solder	ECA
Volume resistivity, Ω.cm	0.000015	0.00035
Typical junction R, mΩ	10-15	<25
Thermal conductivity, W/m.K	30	3.5
Shear strength, psi	>2200	2000
Finest pitch, mil	12	<6-8
Minimum processing temperature, °C	215	150-170
Environmental impact	Negative	Very minor
Thermal fatigue	Yes	Minimal

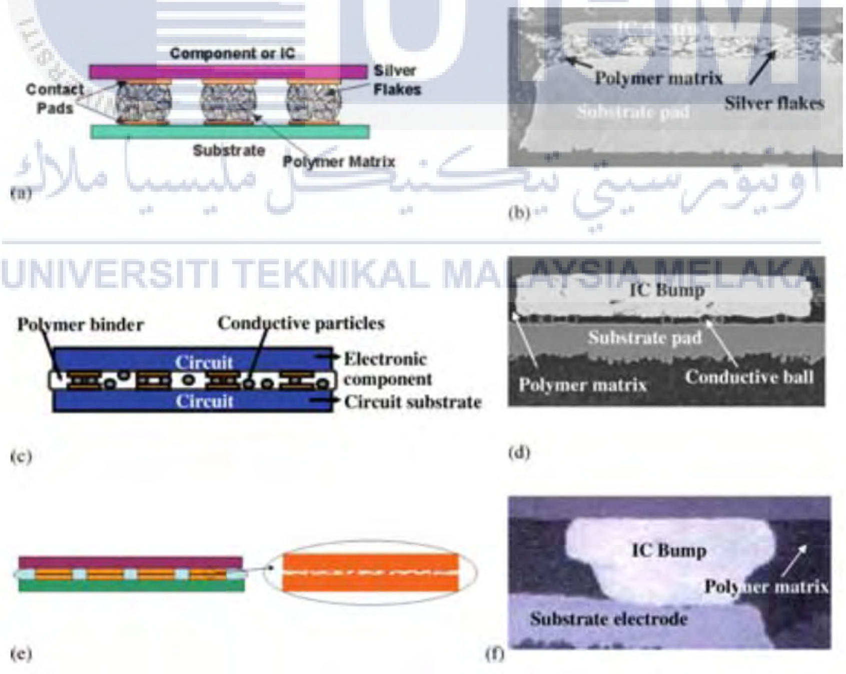

Figure 2.1: Classification of ECA (a, b) ICA (c, d) ACA (e, f) NCA [12].

Figure 2.1 [12] shows the illustration of ICA, ACA and NCA. NCA interconnect method is different from ICA and ACA because it does not contain conductive filler, instead the polymer matrix adhesion is used to bond the pad to the bum with pressure and elevated temperature and the conductivity achieved by the pad and bump contact. Even though ECA consist of higher filler loading, which mean better conductivity, the mechanical strength of the matrix degrades and due to the amount of metallic filler, the conductivity decrease because of corrosion at the bond of component and substrate after exposed to moisture [13, 14].

Electrically conductive adhesive usually understood by researchers by percolation theory. Figure 2.2 shows the relation of volume fraction of filler and the resistivity of the ECA. By gradually increase the volume fraction, the resistivity of the ECA decrease which means better conductivity. Percolation threshold is reached when the volume fraction increase to its critical volume where the conductive filler are in contact and form conductive path between the filler [15, 16].

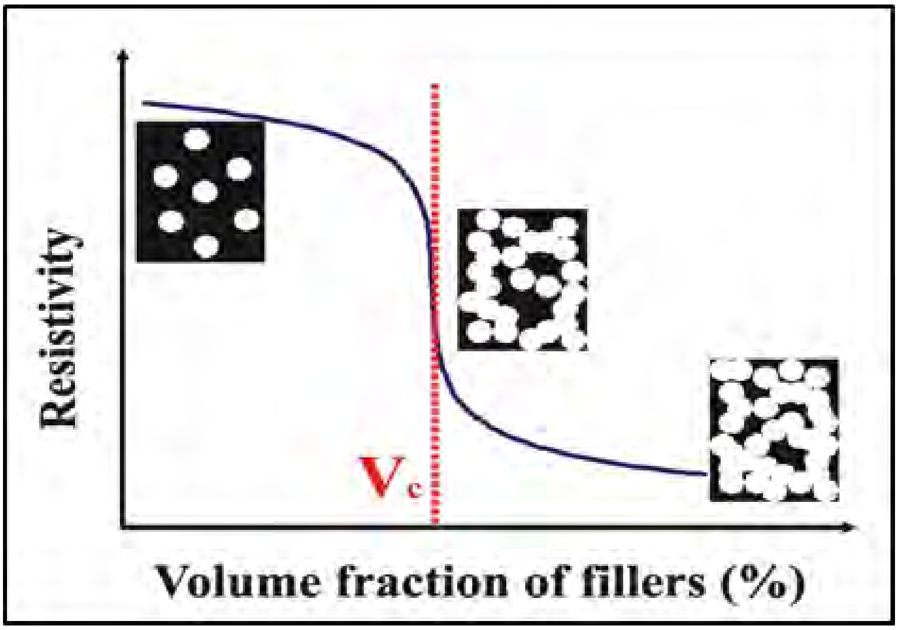

Figure 2.2: Graph of volume fraction of filler against resistivity [15]

2.4 Polymers

Polymer matrix are the material that provides adhesion strength, chemical resistance and corrosion resistance in ECA. There are two types of polymer which is thermoplastic polymer and thermoset polymer and generally cured under high temperature. Table 2.3 show the different type of polymer [9] :

Table 2.3: Classification and examples of polymer

Polymer	Example
Thermoplastic	I. Phenolic epoxy II. Polyimide
Thermoset	I. Epoxy II. Cyanate ester III. Silicone polyurethane

Thermoplastic polymer is a type of polymer that only melt and flow when the temperature is above their glass temperature (T_g) and stay as solid when the temperature is below the T_g. To use thermoplastic polymer as ECA, the polymer must sufficiently have higher T_g to avoid the polymer from undergoing creep and degrades the adhesion strength when thermal cycling associated with typical use but the T_g must be low enough for the ease of processing and preventing from damaging the electronic components during assembly also the high processing temperature will cause sintering and oxidization of the metal filler which decrease the conductivity. Even though thermoplastic is a rework able polymer, the creep effect will cause poor reliability [17]. Thermoset polymer is a type of polymer that have three dimensional (3D) molecular structure. It does not flow at high temperature after curing process because of the structure have interlocked. Specific conditions are needed during curing process to create the 3D structure between the resins and hardeners such as heat, ultra violet (UV) light, microwave, and moisture. Advantages of thermoset polymer are the ability to maintain strength at high temperature and higher adhesion strength. Table 2.4 shows the comparison of different adhesive material.

The viscosity of thermoset polymer is much lower compared to uncured thermoplastic polymer making it easier to be printed at room temperature. Epoxy resin is the most common used thermoset polymer because of the good adhesion, and thermal stability. The disadvantages of thermoset polymer are it is not reversible or rework able compared to thermoplastic polymer [15, 18].

Table 2.4: Adhesive material comparison [2].

Materials	Advantages	Disadvantages
Epoxies	High-temperature use Good moisture and chemical resistance Low outgassing	Longer cure cycles with anhydride hardeners Degassing required for two-component systems Exotherms in large quantities for amine-curing agents
Silicones	Highest purity Stress absorbing High and low temperature stability	Migrate to other circuit elements Low surface energy Swelled by nonpolar solvents
Polyurethanes	Good flexibility at low temperature Stress absorbing Highly versatile chemistry	Lower thermal stability and service temperature than epoxies
Polyamides	Higher temperature stability compared to epoxies High ionic purity Reduced bleed out	Trapped solvent can produce voids under large IC Multi-step curing required to volatilize solvent High-stress materials May absorb moisture in cured condition Cannot be B-staged
Cynate esters	High adhesion strength High thermal stability	High moisture absorption Popcorn susceptibility

2.5 Filler

Fillers are added to electrical conductive adhesive to make the polymer matrix conductive. Few examples of filler include silver (Ag), gold (Au), Copper (Cu), Nickel (Ni), and Carbon. Silver are the most commonly used conductive filler in ECA because silver has the highest electrical and thermal conductivity which is 15.87 nΩ.m and 429 W/m. K and silver have higher conductivity when it is oxidized than other metals. Gold is rarely used in ECA as filler even though it does not oxidize because it is too expensive compare to other metals. The down side of using silver as filler is that silver is electrochemically active. Copper and nickel are not commonly used as ECA filler because it easily oxidize and degrades the conductivity and reliability [15, 17].

Other aspect that is important for the properties of ECA are the size and shape of the conductive filler. To decrease the percolation threshold, higher aspect ratio of the conductive filler is essential to reduce the filler loading volume fraction to achieve the desired electrical properties. Moreover, better mechanical properties can be achieved by reducing the percolation threshold which can lower the loading of filler used.

2.5.1 Carbon Nanotubes

Carbon Nanotube (CNT) was first discovered by Sumio Iijima in 1991. CNT transport electrons in a long length without having any interruption from its own atoms. Carbon nanotubes which generally characterized as Single Wall-Carbon Nanotube (SWCNT) and Multi Wall Carbon Nanotube (MWCNT) are graphite sheet rolled to form a cylindrical shape. SWCNT are a single sheet of graphene rolled into cylinder while MWCNT are a nested or many layers of graphene cylinder. MWCNT may characterized as metallic, whereas SWCNT may be characterized as metallic or semiconductor according to the chirality of the graphene wall [19, 20] .

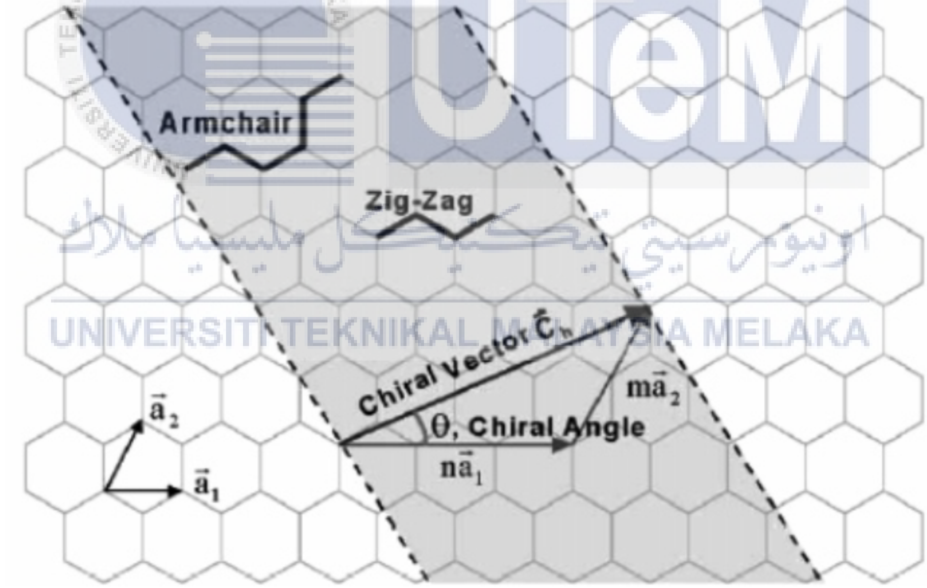

Figure 2.3: Schematic diagram showing how a hexagonal sheet of graphene is rolled to form carbon nanotube [21].

Figure 2.3 shows chirality which is a description of the different way to roll graphene into cylindrical or carbon nanotubes. There are three techniques in producing SWCNT and MWCNT, which is by arc discharge, laser ablation, and chemical vapor decomposition (CVD). Each of these techniques have its own nuances. Arc discharge and laser ablation uses a solid carbon and evaporate it to form host gaseous carbon atom while chemical vapor decomposition catalytically decomposed a gaseous carbon such as hydrocarbon or carbon monoxide. The advantages of CVD are that it is scalable for industry production size and have more control of the geometry of the carbon nanotubes [21]. Generally, carbon nanotube are produced in gases that are composed of hydrogen and a it has been proven that better quality Carbon Nanotubes are produced in pure hydrogen gas [22].

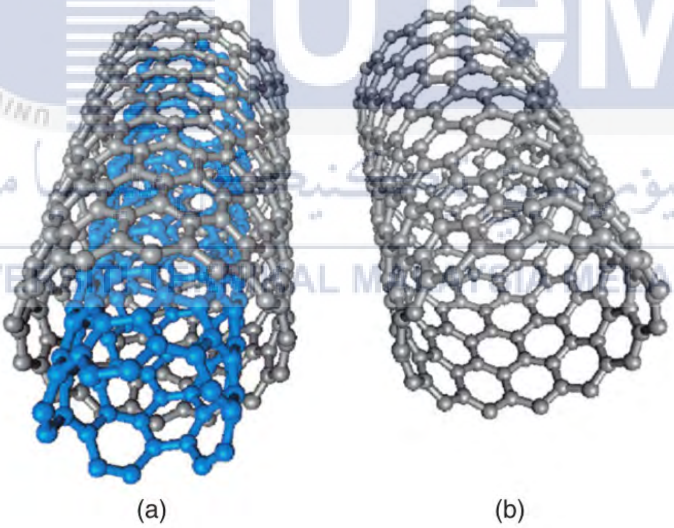

Figure 2.4: Schematic of (a) MWCNT (b) SWCNT [23].

Geometries of carbon nanotubes are characterized into three distinctive geometry character which is armchair, zigzag and chiral as shown in Figure 2.5. The characteristic is classified base on the method of the graphene were rolled into cylindrical shape [23].

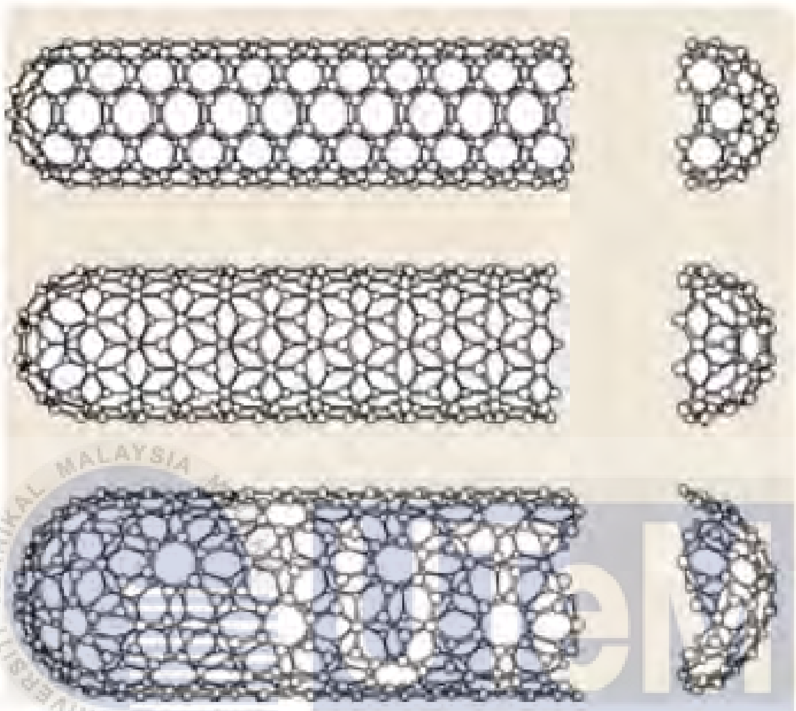

Figure 2.5: Different geometric of CNT [23].

Because of the loading of filler needed to gain the desired level of percolation threshold is significantly low for CNT, it has become the best alternative of filler in ECA. CNT which is a non-metal material that does not corrode can avoid from the ECA conductivity from decreasing and the smaller size which is in range of nanoscale provides better mechanical strength [13]. The electrical conductivity of CNT is 10^4 S/cm while the thermal conductivity maximum value is 6600 W/m. K. The elastic Young's modulus of CNT is approximately 1TPa while the maximum tensile strength is 30GPa [19, 24]. Another advantages of using CNT is that the weight reduction of the electronic component attached to is reduced by 80% [19].

From previous research and theoretical prediction, MWCNT possess better electrical, mechanical and thermal properties compared to SWCNT. The conductivity of MWCNT dramatically increase as the filler loading reaches the percolation threshold. If the filler loading in increased after the percolation threshold, the rate of increment of conductivity decrease due to the agglomeration of the CNT in the ECA.

2.5.2 Carbon Nanotubes Aspect Ratio

Aspect ratio is the length to diameter ratio of material. CNT is well known to have high aspect ratio typically more than 1000. CNT have the potential to agglomerate when it reaches certain filler loading. Any aggregation may decrease the mechanical performance of the ECA. Thus, resulting in inferior properties because it avoiding efficient stress transfer to each nanotube [25]. The agglomeration will affect by decreasing the surface area and agitate the structure of network formed. Properties such as electrical conductivity, mechanical strength and thermal conductivity will be affected by the network structure [26]. As the aspect ratio increase, lower filler loading is need the reach the percolation threshold.

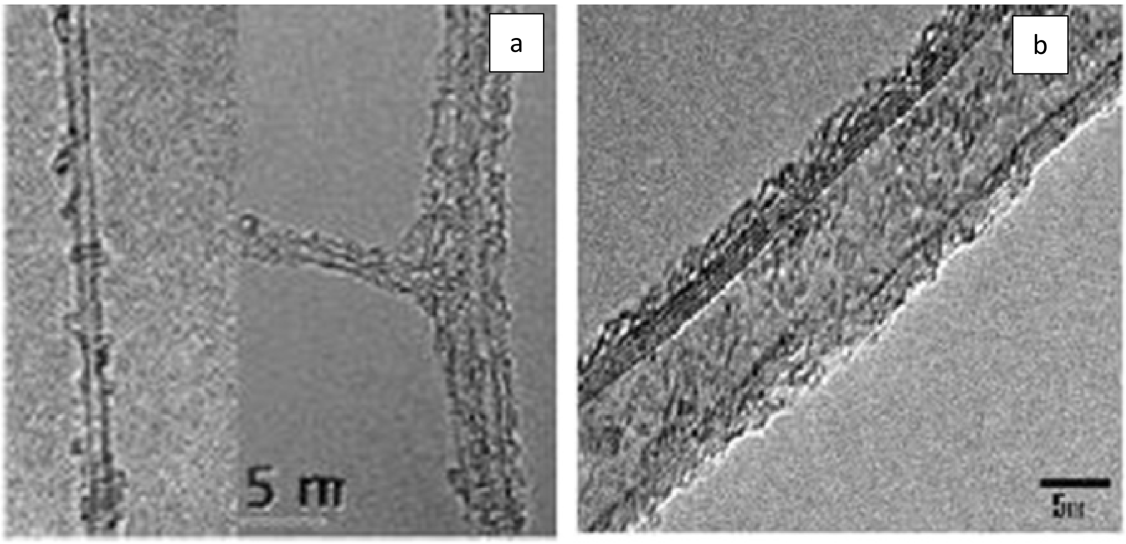

Figure 2.6: Transmission Electron Microscope (TEM) images of (a) SWCNT (b) MWCNT [27].

Previous research has investigated the effect of MWCNT aspect ratio that used as filler in ECA and it is proven that it has an effect on the mechanical and electrical properties of the ECA. Study have showed that higher modulus is achieved with the use of higher aspect ratio MWCNT and it is useful to reduce the rate of fatigue crack growth. However, in a study, it is reported that MWCNT with the same length, but the diameter is decreased to achieve higher aspect ratio will resulting in reduction of the performance efficiency due to the flexibility and entanglement of the thin MWCNT [28]. Figure 2.6 above are the TEM images of SWCNT and MWCNT.

2.6 Properties of Electrically Conductive Adhesive

2.6.1 Mechanical Properties

Mechanical properties determine the strength of the material towards physical abuse. Mechanical properties of a certain material classify the life span and under what circumstances will the material breaks. Example of mechanical properties are tensile strength, yield strength, and ductility.

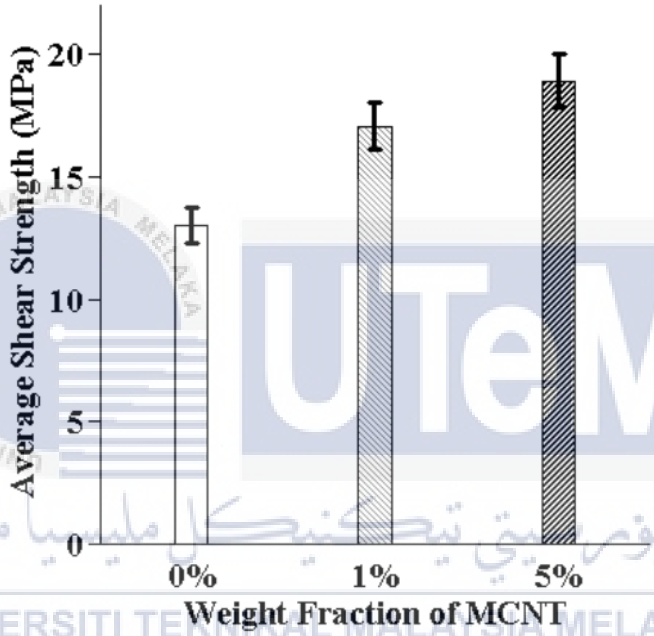

Figure 2.7: Graph of average shear strength with different MWCNT loading in ECA [29].

Figure 2.7 show the average shear strength with different MWCNT loading in ECA reported by Kuang and coworkers that indicates that as the filler loading increase the strength of the ECA increase. This is cause by the bond between the CNT particle are stronger compare to other material [29].

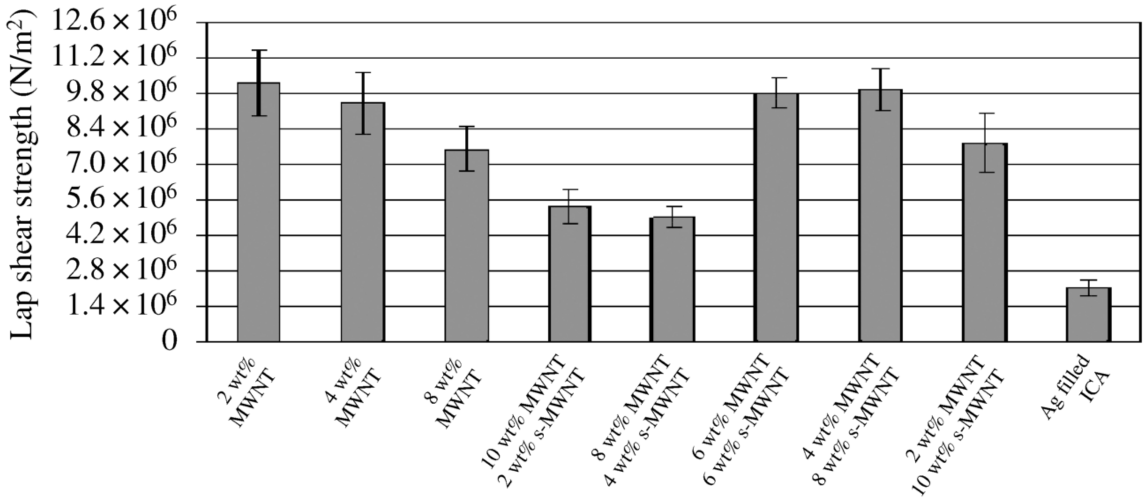

Figure 2.8: Lap shear strength comparison between silver filled ECA using various loading of MWCNT and shatter-milled MWCNT [1].

The data in Figure 2.8 by Li and coworker [1] suggest different trend than those reported by Hsiao and coworker [29] as shown in Figure 2.7. The lower filler loading ECA has better shear strength compare to the higher filler loading. This is because a higher aspect ratio MWCNT is used in this experiment which is 2500 [1]. With higher aspect ratio, the MWCNT tends to agglomerate with lower filler loading thus affecting the ECA mechanical strength. Li also reported that ECA that reinforced with MWCNT has better shear strength compare to silver filled ECA.

2.6.2 Electrical Properties

Electrical properties are the most important properties in classification and identifying of electrical conductive adhesive. The classification is according to the conductivity or resistivity of the materials. The lower the resistivity, the higher the conductivity. As for ECA, the filler used is metal which means it is conductive. However, the conductivity of the filler is depending on the filler loading and shape of the filler. By increasing the filler loading or aspect ratio, the inter-connecting between particle of the filler in ECA is increase thus conductivity is increased. Epoxy have a conductivity of the order 10^{-14} S/cm, depending on the filler to form a cluster that align themselves in the matrix to form a conductive path. Figure 2.9 show the cluster formed in ECA that provide the conductive path.

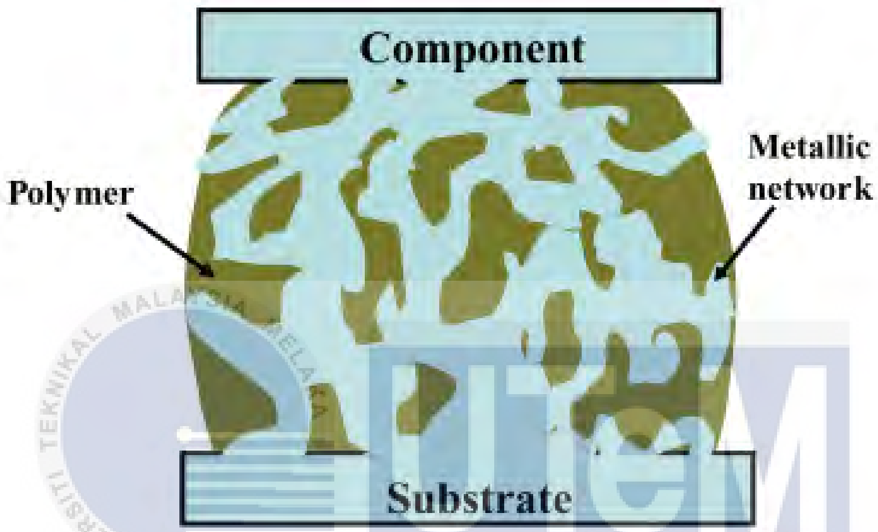

Figure 2.9: Metallic network formed by clustering of filler in ECA [2].

Figure 2.10 indicates that the contact resistance of MWCNT-filled ECA using decrease as the filler loading increases. Lower contact resistance indicates better material conductivity. This is due to the connection between inter-particle of the MWCNT is better thus forming a better conductive path [1].

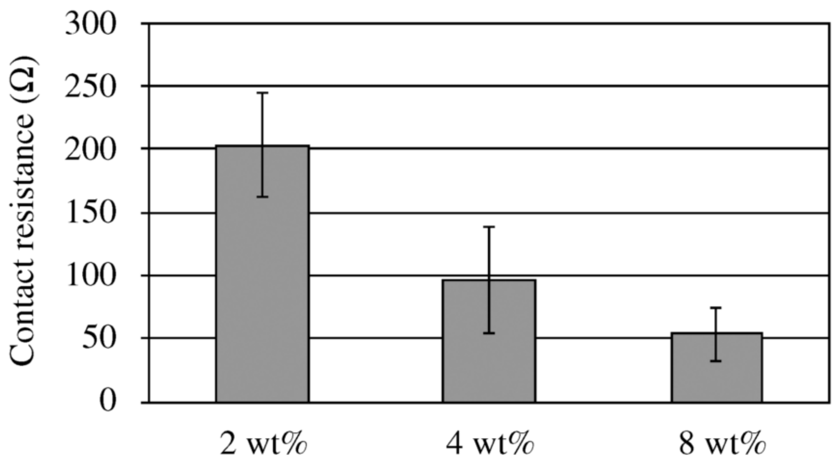

Figure 2.10: Average contact resistance for different filler loading [1].

Figure 2.11 gives the dramatic increase in the ECA conductivity as the filler loading reached the percolation threshold reported by Ayatollahi and coworkers. The graph also indicate that after the percolation threshold and filler loading is increased, the increase in the conductivity decreases and finally show a platue. This is cause by agglomaration of the filler thue increase the contact resistance [28]. Ayatollahi also reported that the conductivity of ECA that reinforced with MWCNT increase as the aspect ratio of the MWCNT increase. Figure 2.12 show the ECA electrical conductivity using different aspect ratio of the MWCNT. Here, it is apparent that the resistance of the ECA decrease with an increase in the aspect ratio.

According to Li and co-workers [1], it is easier for MWCNT with higher aspect ratio to form a link that are conductive compared to larger metal particle with same filler loading. This phenomenon results in a lower percolation threshold of the MWCNT-filled epoxy ECA. In addition, it was also claimed that the intrinsic conductivity of the filler particles and the contact resistance between the filler particles influence the resistance of the ECA. Table 2.5 show the comparison between the intrinsic conductivity of MWCNT and silver filler.

Table 2.5: Intrinsic Resistivity of MWCNT and Silver

Filler	Intrinsic Resistivity (S/cm)
MWCNT	1×10^3
Silver	6.3×10^5

Table 2.5 shows the intrinsic resistivity of MWCNT and silver. Contact resistance (R_c) is influenced by two major factors. First is the constriction resistance (R_{cr}) which occurs during the flow of electron through a small contact area when two conductive fillers are in contact. R_{cr} is inversely proportional to the diameter of the contact area. Second factor is tunneling resistance (R_t) which occurs when only small gap is formed which is less than 10 nm between two conductive filler particles and R_t is proportional to the distance between the conductive filler [1],[30].

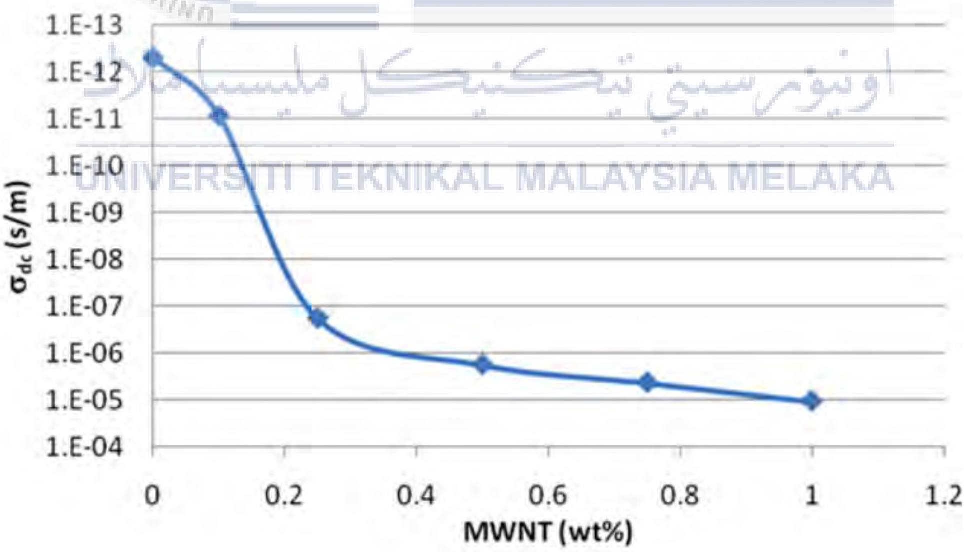

Figure 2.11: Electrical conductivity of ECA with different MWCNT filler loading [28].

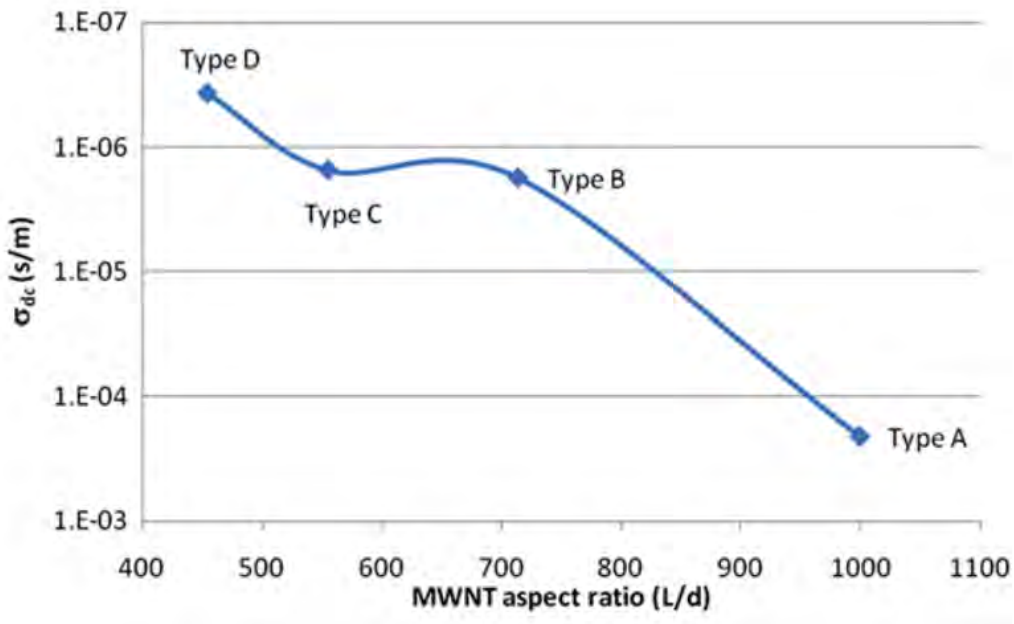

Figure 2.12: Electrical conductivity of different aspect ratio MWCNT (a) 1000 (b) 715 (c) 555 (d) 455 [28].

CHAPTER 3

METHODOLOGY

3.1 Overview of Research Methodology

The detail methodology for this research project include the type of MWCNT, epoxy resin and hardener used, the techniques for the ECA fabrication, the machine and apparatus used and the material characterization tests that are conducted on the ECA are described. Below is a summary of the research activities involved for this project, as follows:

i. Design the process of experiment.
ii. Prepare the procedures, variables and parameters of the experiment.
iii. Listing all the required standards for the related test.
iv. The procedure of preparing ECA using MWCNT as filler.
v. The formulation and fabrication of ECA.
vi. Preparing all the specimen needed for mechanical and electrical test.
vii. Conduct electrical (four-point probe) and mechanical test (lap shear) on all sample to compare the effect of MWCNT aspect ratio in ECA.
viii. Morphological study to know the characteristic of the ECA.

Figure 3.1 show the summary of the methodology of this research from the start of literature review study according to the research title till the final report writing to complete the project.

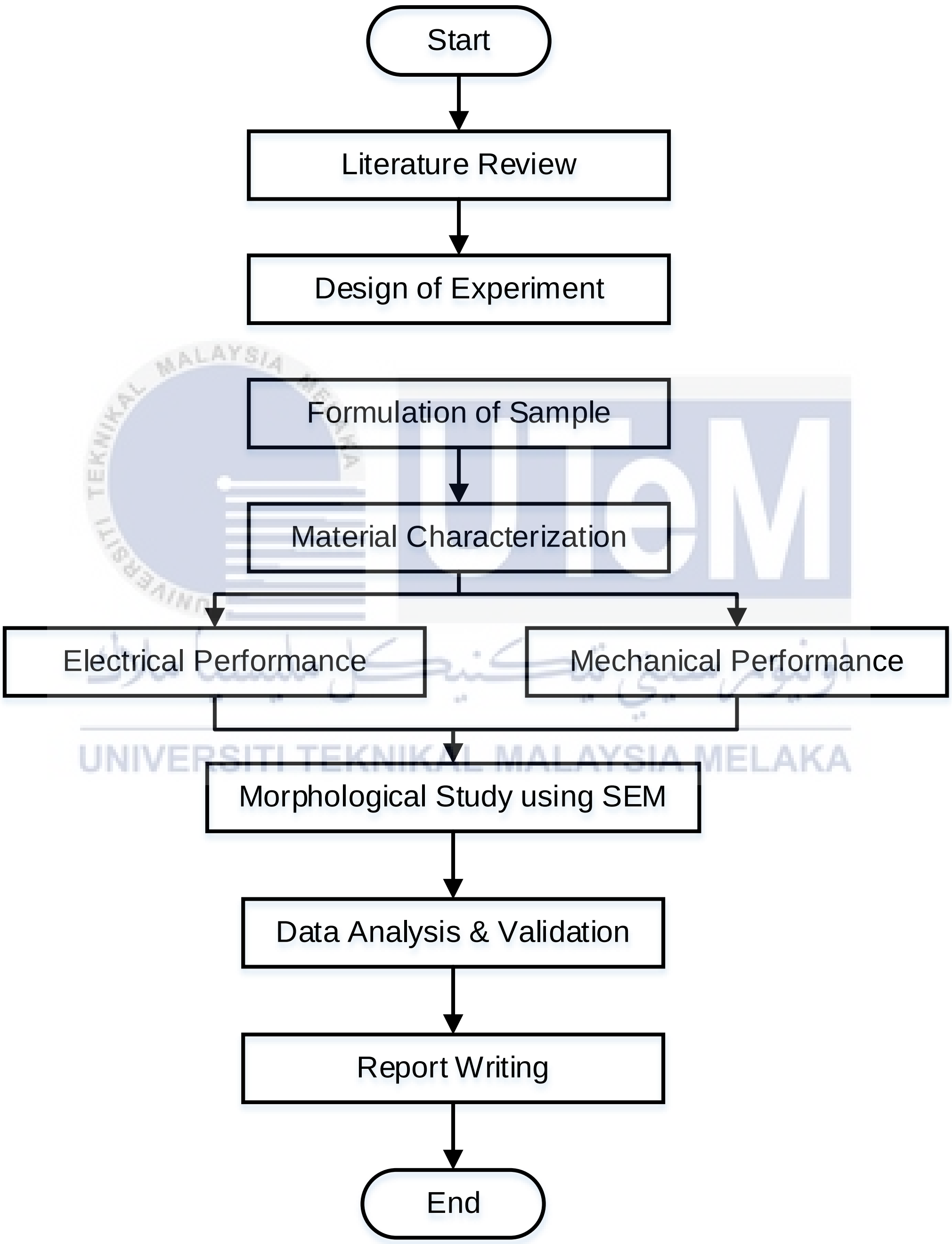

Figure 3.1: Flow Chart of research

3.2 Raw Materials

To formulate an electrically conductive adhesive, there are three parts of substances needed. The first one is the epoxy or resin which is the polymer matrix of the ECA. In this research project, Epoxy Resin Araldite 506 is chosen as the polymer matrix. The second part is the hardener which is thermoset substance. Polyether amine D230 is used as the hardener for this project. The third part is the conductive filer that will be added according to the filler loading and in this research project, MWCNT is used.

3.2.1 Epoxy Resin Araldite 506

The matrix polymer used was an epoxy, named Araldite 506 shown in Figure 3.2 which is supplied by Sigma Aldrich [31]. It is use as the binder for the ECA in this experiment. Table 3.1 shows the specification of the epoxy as given in the material safety data sheet (MSDS).

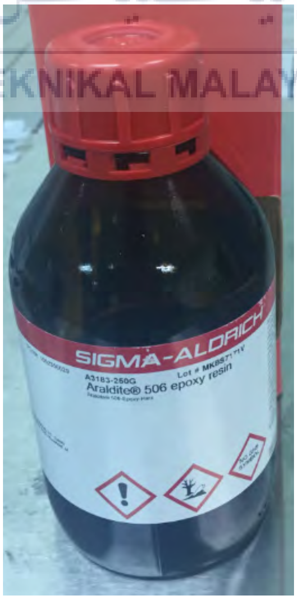

Figure 3.2: Sigma Aldrich Epoxy Resin Araldite 506

Table 3.1: Specification of Sigma Aldrich Epoxy Resin Araldite 506 [31].

Category	Specification
Appearance	Semi-solid melting to a liquid
Color	Colorless
Melting point / Freezing point	15°C - 5°C
Flash point	252°C
Vapor pressure	0.04 hPa at 77°C
Relative density	1168 g/cm^3

3.2.2 Hardener Polyetheramine D230

The hardener shown in Figure 3.3 is used as the curing agent for the epoxy is supplied by Huntsman Singapore Pte LTD which called JEFFAMINE D-230 Polyether amine [32]. 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 [32].

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 Nano Tube

The Multi-Wall Carbon Nanotubes (MWCNT) that are used for this experiment is supplied by Nanostructured & Amorphous Materials Inc, USA. Both high and low aspect ratio MWCNT has the same range of outer diameter which is from 10nm to 20nm as shown in Table 3.3. The different that makes up the aspect ratio is the length. Figure 3.4 show the high aspect ratio MWCNT (HIGH-MWCNT) which is 1750 and the length is ranging from 10µm to 30µm while Figure 3.5 show the low aspect ratio MWCNT (LOW-MWCNT) with length ranging from 0.5 µm to 2 µm and aspect ratio of 112.5 [33].

Table 3.3: MWCNT details and aspect ratio

Nanoamor CNT	Outer diameter (nm)		Length (µm)		Aspect Ratio (L/OD)		
	min	max	min	max	min	max	average
HIGH-MWCNT	10	20	10	30	500	3000	1750
LOW-MWCNT	10	20	0.5	2	25	200	112.5

Figure 3.4: Nano Amor MWCNT with 1750 aspect ratio

Figure 3.5: Nano Amor MWCNT with112.5 aspect ratio

3.3 Formulation of Sample

3.3.1 Electrical Conductive Adhesive Formulation

All the samples were prepared first by blending the epoxy Araldite 506 with JEFFAMINE D-230 Polyetheramine which is the hardener. Before blending, the amount of epoxy used need to be measured using a Mettler Toledo Balance (Figure 3.6). The MWCNT filler loading that are choose for this research are 5 wt.%, 6 wt.%, and 7 wt.%. Table 3.4 below show the weight of each material used to formulate 5 g of ECA according to each filler loading.

Table 3.4: Formulation of sample

Filler loading (wt.%)	**5**	**6**	**7**
Epoxy (g)	4.75	4.7	4.65
Hardener (g)	1.425	1.41	1.395
MWCNT (g)	0.25	0.3	0.35

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

$$X_c = X_m V_m + X_f V_f \tag{3.1}$$

Where:

c = composite

m = matrix

f = fiber

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

$$\text{Matrix volume fraction, } V_m = V_m / V_c \tag{3.2}$$

$$\text{Fiber volume fraction, } V_f = V_f / V_c \tag{3.3}$$

To calculate the amount of MWCNT needed, Equation (3.4) is used, as given below: -

$$\text{MWCNT (g)} = \text{MWCNT (wt.\%)} \times \text{sample weight (g)} \tag{3.4}$$

To calculate the amount of epoxy need, Equation (3.5) is used.

$$\text{Epoxy (g)} = \text{Sample weight (g)} - \text{MWCNT (g)} \tag{3.5}$$

To calculate the amount of hardener need, Equation (3.6) is used.

$$\text{Hardener (g)} = \frac{30}{100} \times \text{Epoxy (g)} \tag{3.6}$$

Figure 3.6: Mettler Toledo Balance

After the hardener is added to the epoxy, it was stirred for 1 minute with constant speed and rotation direction. Then, the amount of MWCNT need is added. The sample was then stirred for 5 minutes to blend the epoxy and MWCNT. The formulated ECA then applied to the specimen for electrical and mechanical and then cured in an Memmert oven (Figure 3.8) for 30 minutes with temperature of 100°C for curing.

Figure 3.7: Process of stirring the epoxy

The stirring process after mixing the epoxy and the hardener is to eliminate the murkiness in the mixture.

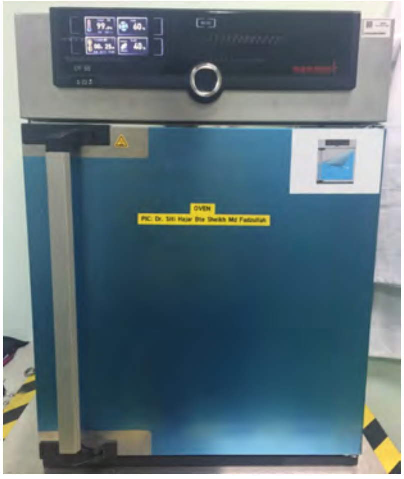

Figure 3.8: Memmert oven

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 Mechanical Specimen Preparation

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 [34].

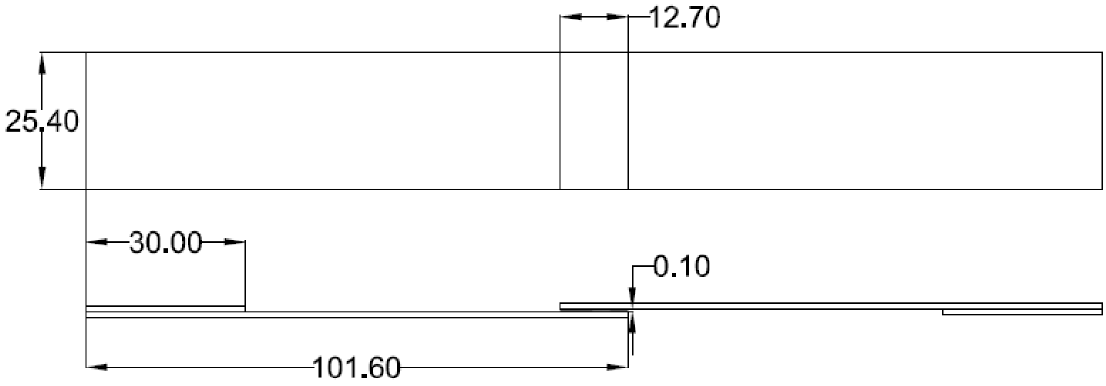

Figure 3.9: Drawing of mechanical specimen

Figure 3.10: Shearing machine

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.

3.3.3 Electrical Specimen Preparation

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.

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.

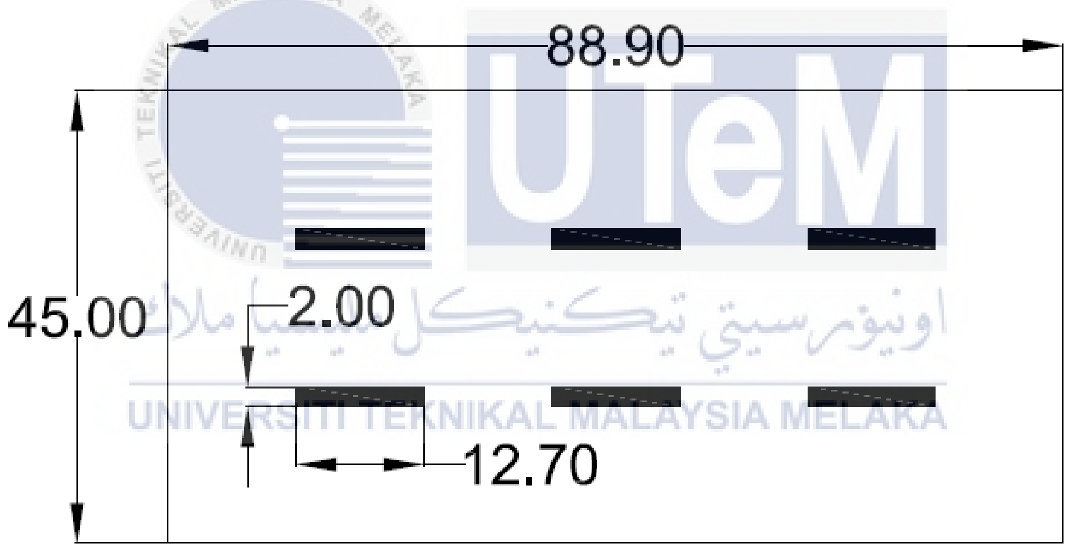

Figure 3.11: Drawing of electrical specimen.

Figure 3.12: Acrylic laser cutting machine.

3.4 Material Characterization

3.4.1 Mechanical Performance

For the mechanical performance test, the specimen will be tested using a Universal Testing Machine (Figure 3.13) for the lap-shear test. The stress-strain curve is obtained from this test and the shear strength of the ECA can be calculated from Equation (3.7):

$$\tau = \frac{F}{A} \tag{3.7}$$

All the sample preparation and test technique is done based on ASTM D1002 [34] standard in tensile loading. For each type of filler loading, 5 samples were prepared and the average shear strength is calculated.

Figure 3.13: Universal testing machine for lap shear test

3.4.2 Electrical Performance

Four-point probe test is used for the electrical performance test, with the data in the form of resistance per square (Ω/sq.) obtained from the test. The ECA is printed as 6 short straight line on insulator substrate by using printing technique and ASTM F390 is used as guideline [35]. For each strip, 3 readings are taken and average sheet resistance is calculated.

From the data obtained, Equation (3.8) is used to calculate the resistance, as follows:

$$R = V/I \qquad (3.8)$$

Following this, the resistance value is then multiplied with the correction factor according to the film shape and will be discussed in the next chapter.

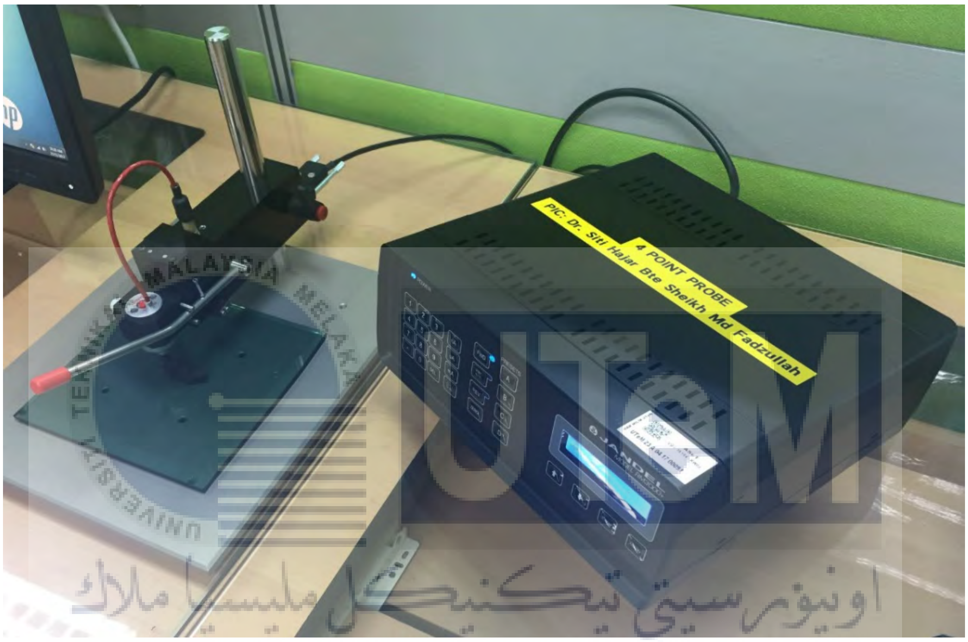

Figure 3.14: Four-point probe for electrical conductivity test

3.5 Surface Morphology Study

Scanning Electron Microscope (SEM) is an imaging machine which operates using a focusing beam with high energy electron to generate signals at the specimen surface is used for the surface morphological study. The presence of air in the chamber may interfere with the scanning process thus the inter-condition barrel was vacuumed. The focal length, level of magnification and brightness of the image need to be adjusted to obtain better and clearer image. The specimen size was also not suitable for SEM thus further preparation of sample is needed. The specimen need to be cut into suitable size and coated with a non-conductive substance to avoid from charging by the electron beam.

For this project, in addition to electrical and mechanical testing, morphological study via (SEM) is also considered to study the effect of different filler loading and aspect ratio on ECA, i.e. analysis on the fractured surface of the specimens following lap shear test. The purpose of this analysis is to determine the point and cause of failure to the ECA such as presence of agglomeration of the MWCNT with varying filler loading and aspect ratio.

Figure 3.15: Scanning Electron Microscope (SEM)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

In general, it is essential for ECA to have good electrical and mechanical properties. From the literature review, it can be summarized that the filler contents need to be sufficient to conduct electricity while the epoxy need to be strong enough to provide better adhesion and mechanical properties. It is crucial to test the electrical and the mechanical effect that are caused by the filler loading and aspect ratio of the MWCNT as filler. The aspect ratio and filler loading plays an important role in determining the mechanical and electrical performance of ECA.

In this chapter, the effects of MWCNT aspect ratio as filler in ECA is presented. All specimen is prepared as stated in previous chapter and mechanical and electrical test are conducted. For electrical conductivity test, the ECA is printed onto an acrylic in 6 short strips while for mechanical test, 5 samples were prepared for each filler loading. All the samples were cured in an oven for 30 minutes at temperature of 100°C and then left to cool down for 24 hours at room temperature.

4.2 Electrical Characterization of MWCNT-Filled ECA with Varying Filler Loading and Aspect Ratio

Better flow of electrical charge in a material indicates that the material exhibits a better electrical conductivity. The type of filler and orientation inside a matrix will determine the electrical characteristic of a composite material. A cluster is formed when the matrix which is an insulator, traversed by the conductive filler when it is added. Due to the interconnecting filler particle, a conductive path is formed when the cluster aligned throughout the matrix [36].

As the aspect ratio of filler increase, the conductivity generally increases. Excluded volume concept is used to describe this trend which is the volume around an object as the overlapping of two similar object is to be avoided when the center of the object is not allowed to enter. As the two MWCNT particle excluded volume overlapping, a conducting link may be formed. The percolation threshold decreases as a result of decreasing excluded volume. This indicates that at lower loadings, better conductivity is achieved. A few research has proven that decreasing excluded volume is caused by increase in aspect ratio [28, 37].

In this study, the property measured using a four-point probe is in terms of the material's sheet resistance, that is multiplied with the correction factor obtained from ASTM F390-11, depending on the shape of the film strip [35]. Table 4.1 show the lateral correction factor extracted from the ASTM F390-11.

Table 4.1: Table of lateral correction factor for rectangular thin film [35].

w/S	l/w = 1	l/w = 2	l/w = 3	l/w = 4
1.00	….	….	0.9988	0.9994
1.25	….	….	1.2467	1.2248
1.50	….	1.4788	1.4893	1.4893
1.75	….	1.7196	1.7238	1.7238
2.00	….	1.9454	1.9475	1.9475
2.50	….	2.3532	2.3541	2.3541
3.00	2.4575	2.7000	2.7005	2.7005
4.00	3.1137	3.2246	3.2248	3.2248
5.00	3.5098	3.5749	3.5750	3.5750
7.50	4.0095	4.0361	4.0362	4.0362
10.00	4.2209	4.2357	4.2357	4.2357
15.00	4.3882	4.3947	4.3947	4.3947
20.00	4.4516	4.4553	4.4553	4.4553
40.00	4.5190	4.5129	4.5129	4.5129
∞	4.5324	4.5324	4.5324	4.5324

Table 4.2: Sheet resistance of high and low aspect ratio MWCNT ECA.

Filler Loading (wt.%)	Sheet Resistance (kΩ/sq.)	
	High aspect ratio	Low aspect ratio
5	10.66 ± 3.19	180.87 ± 48.70
6	3.79 ± 1.89	143.40 ± 45.84
7	1.367 ± 0.49	77.33 ± 51.15

Figure 4.1 shows the graph of sheet resistance as a function of filler loading for the MWCNT-filled ECA, using high and low aspect ratio MWCNT. In addition, visual observation of the printed MWCNT-filled ECA with 5, 6 and 7 wt. % of MWCNT filler loading of high and low aspect ratio following electrical conductivity tests are given in Figures 4.2 and 4.3 respectively. The sudden decrease in the resistance for both high and low aspect ratios between the 5 wt.%, 6 wt.% and 7 wt.% indicate that the percolation threshold is achieved [28]. Lower filler loading is required to achieve the threshold for the ECA with high MWCNT aspect ratio [13]. As the filler loading increase beyond 7 wt.%, the level of conductivity increment is smaller. This is caused by the agglomeration of the MWCNT that are not dispersed properly, therefore affecting the bridge particle interconnection structure [38].

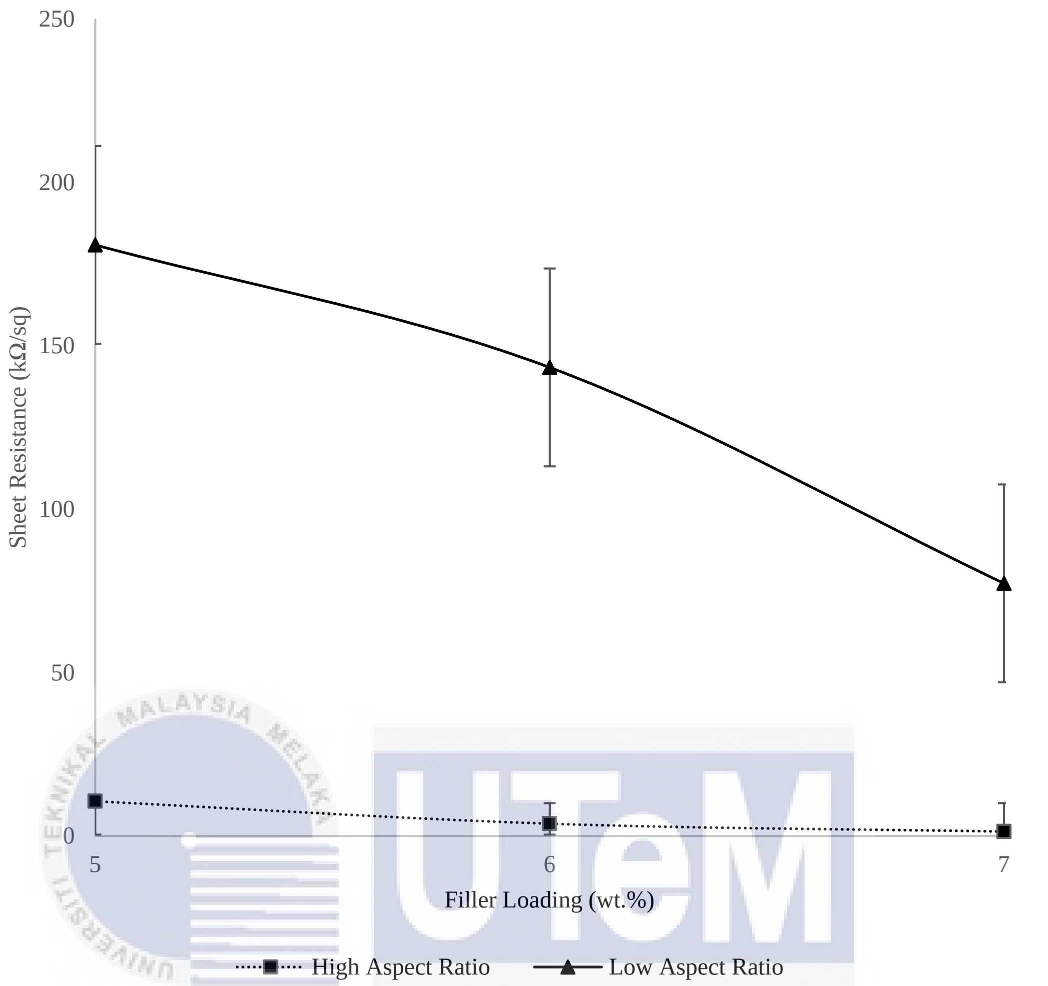

Figure 4.1: Sheet resistance against filler loading of high and low aspect ratio MWCNT ECA.

With lower aspect ratio, percolation threshold is achieved at higher filler loading which indicates that the resistance is higher compare to high aspect ratio MWCNT-filled ECA of the same filler loading. The trend of increasing electrical conductivity with increasing aspect ratio can be explained with excluded volume concept stated before. By formulating ECA using high aspect ratio MWCNT, higher conductivity can be achieved with lower filler loading compared to low aspect ratio MWCNT.

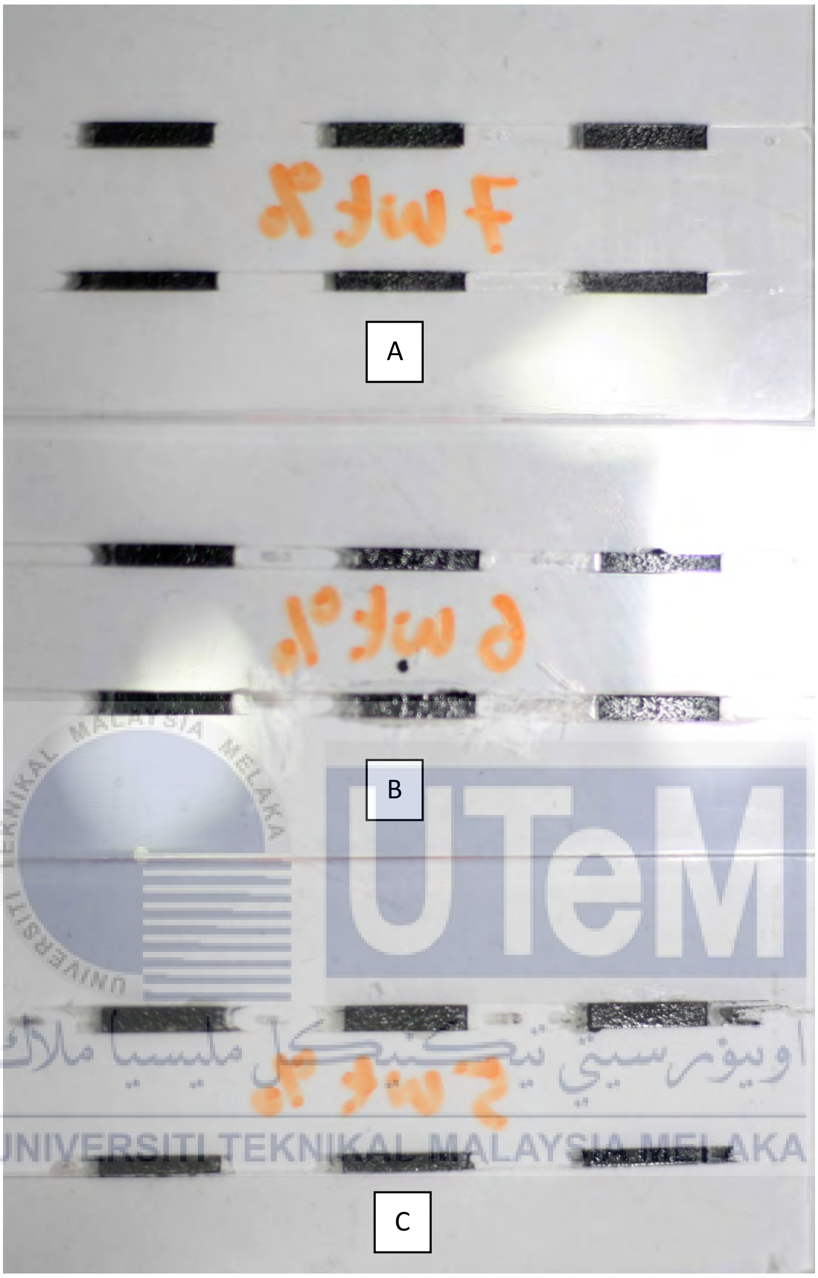

Figure 4.2: Observation of high aspect ratio MWCNT-filled ECA sample with (a) 7 wt.% (b) 6 wt.%. (c) 5 wt.%.

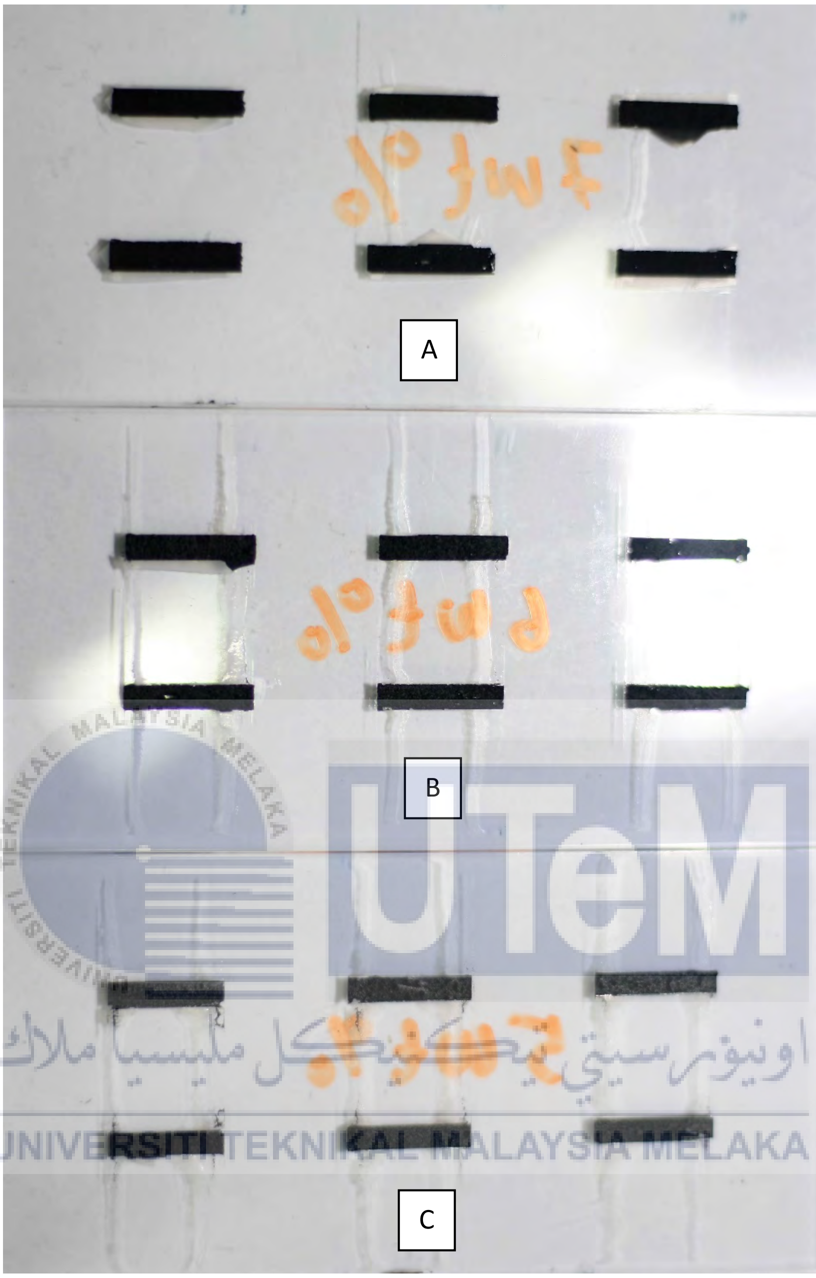

Figure 4.3: Observation of low aspect ratio MWCNT-filled ECA sample with (a) 7 wt.% (b) 6 wt.%. (c) 5 wt.%.

The contact resistance obtained from this research is higher compared to commercially available metal filled ECA. However, the percolation threshold for MWCNT-filled ECA is much lower compared to metal-filled ECA. Table 4.3 below shows the comparison between the different types of ECA.

Table 4.3: Comparison between MWCNT-filled ECA and metal-filled ECA.

Type of ECA	Percolation threshold
High aspect ratio MWCNT-filled ECA	Less than 7 wt.%
Low aspect ratio MWCNT-filled ECA	Less than 5 wt.%
Metal-filled ECA	Above 25 wt.%

During the curing process, ECA shrink and the force decrease the distance between the metal particles which increase the contact area diameter and improve conductivity of the ECA. However, shrinking of ECA does not significantly affect the distance between the MWCNT particles due to lack of crosslinking between the epoxy and MWCNT. Therefore, the contact resistance of metal-filled ECA is lower compared to MWCNT-filled ECA but the percolation threshold of MWCNT-filled ECA is lower that metal-filled ECA [1].

4.3 Mechanical Characterization of MWCNT-Filled ECA with Varying Filler Loading and Aspect Ratio

The binding strength of ECA is the shear strength, which is a critical aspect. Generally, with increasing MWCNT filler loading, the shear of adhesion decrease. The proliferation of filler into the matrix is caused by the decrease in mechanical strength [13]. Moreover, the shear strength of the ECA is far greater than the minimum strength required for ECA and the decrease is very small.

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 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.

To study the impact of different MWCNT aspect ratio in the ECA, lap shear test was performed and for each filler loading, 5 sample were prepared. Table 4.4 present the results following the lap shear test for the ECAs with high aspect ratio MWCNT at varying filler loading. From the table, it can be observed that the highest shear stress achieved is 8.58 MPa for the 5 wt.% filler loading. The shear strength of the specimen decreased as the filler loading of the high aspect ratio MWCNT is increased.

Table 4.4: Shear strength of the ECA filled with MWCNT of high and low aspect ratio.

Filler Loading (wt.%)	Strength (MPa)	
	ECA with high aspect ratio	ECA with low aspect ratio
5	8.58 ± 1.55	9.87 ± 1.63
6	7.67 ± 1.20	7.57 ± 0.75
7	5.85 ± 2.03	10.11 ± 1.93

The shear strength of each filler loading MWCNT ECA with high and low aspect ratio is shown in Figure 4.4. It is apparent that the ECA with 5 wt.% filler loading has higher shear strength compared to those of 6 wt.% and 7 wt.% filler loading, for the high aspect ratio. The reason for such observation could be due to the fact that at filler loading of 5 wt.%, the MWCNT is properly dispersed with the matrix, while the ECA of 6 wt.% and 7 wt.% could possibly have agglomerated MWCNT and formed crack which are not good for load transferring capability [38]. The shear strength is reduced by 11.28% when compared between the results of ECA with filler loading of 5 wt.% and 6 wt.%, while 26.89% of reduction in shear strength when compared between 6 wt.% and 7 wt. %. These results suggest that as the agglomeration become critical, the percent of decrease in the ECA shear strength is higher [1, 28].

For the case of ECA with low aspect ratio of the MWCNT, the results obtained is slightly off-trend. The stress is reduced by 26.34% between filler loading range of 5 wt.% and 6 wt.% but show an increase by 28.74% at filler loading of 7 wt.%, compared to 6 wt.%. These could possibly be due to the distribution of MWCNT in the ECA which is not homogeneously dispersed thus affecting the shear strength of the sample.

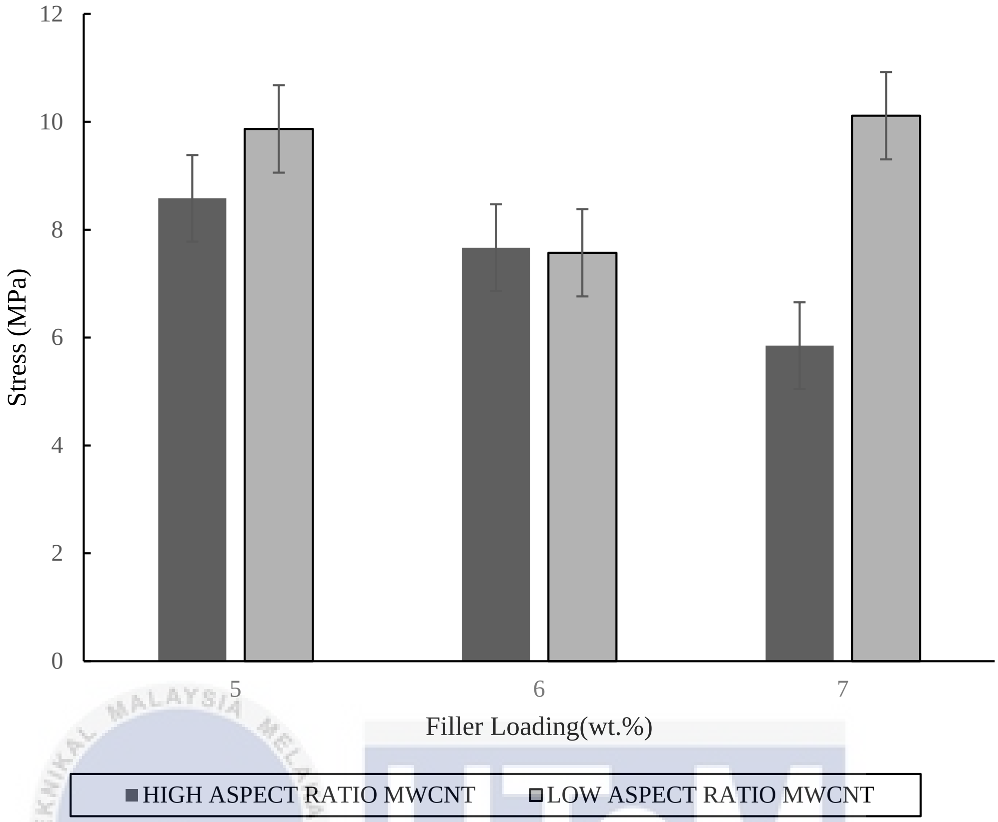

Figure 4.4: Shear strength against ECA with different aspect ratio and filler loading of the MWCNT.

From Figure 4.4, at filler loading of 5 wt.%, there is 15% difference in the shear strength between the low aspect ratio and high aspect ratio MWCNT-filled ECA. However, at increasing filler loading of 6 wt.%, there is a much smaller difference of only 1.24%. From the literature, Li and coworker [1] reported that a commercially available silver filled ECA shear strength is 2.1 MPa. Such comparison indicate that much higher mechanical strength is achieved when using a nanocarbon-based material as a conductive filler for the ECA.

Figures 4.5, 4.6 and 4.7 show the surface of the samples fabricated using high aspect ratio MWCNT-filled ECA with varying filler loading of 5 wt.%, 6 wt.% and 7 wt. % following the lap shear test respectively. For the ECA with filler loading of 5 wt.% and 6 wt.%, the observation suggest cohesive and adhesive failure since some ECA are retained on both sides of the substrate, while for the 7 wt.%, the observation suggest adhesive failure since the ECA are retained only on one side of the substrate [28].

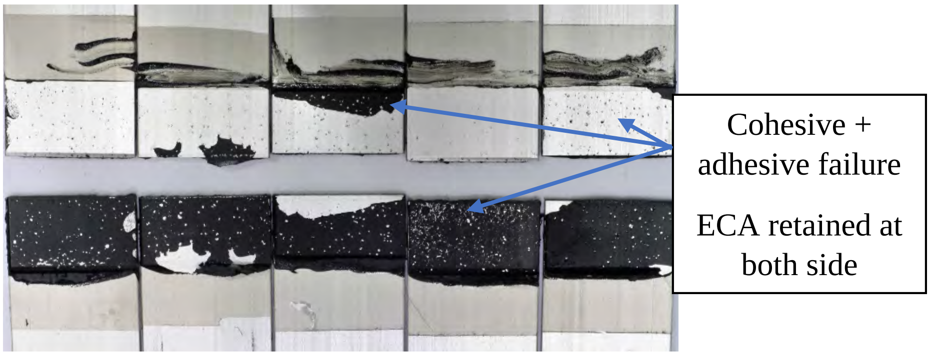

Figure 4.5: 5 wt.% high aspect ratio MWCNT ECA mechanical test samples.

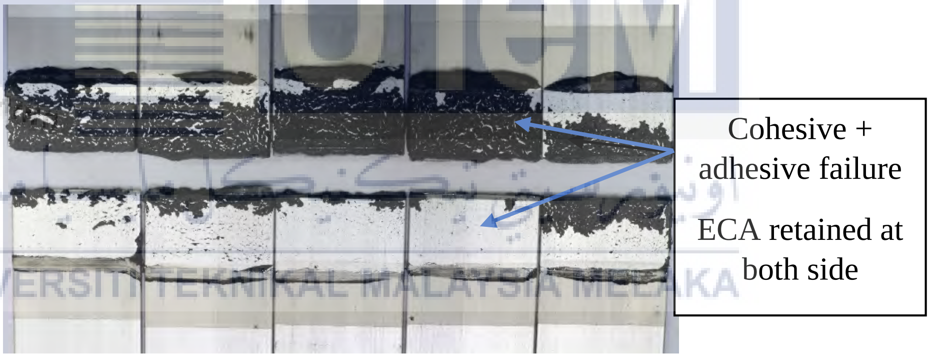

Figure 4.6: 6 wt.% high aspect ratio MWCNT ECA mechanical test samples.

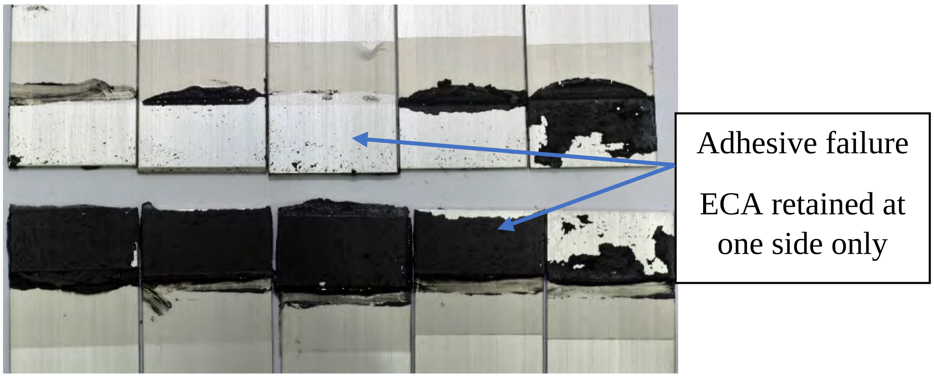

Figure 4.7: 7 wt.% high aspect ratio MWCNT ECA mechanical test samples.

Figures 4.8, 4.9 and 4.10 show the surface of the samples low aspect ratio MWCNT-filled ECA with varying filler loading of 5 wt.%, 6 wt.% and 7 wt. % following the lap shear test respectively. All the samples show adhesive and cohesive failure trend since ECA is retained on both side of the samples.

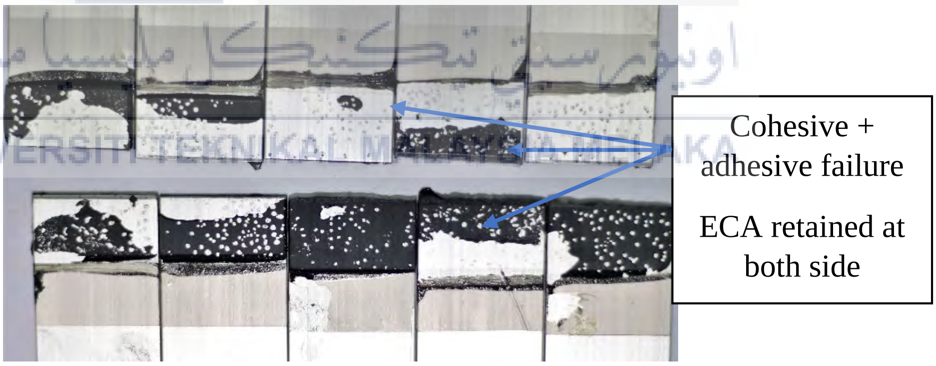

Figure 4.8: 5 wt.% low aspect ratio MWCNT ECA mechanical test samples.

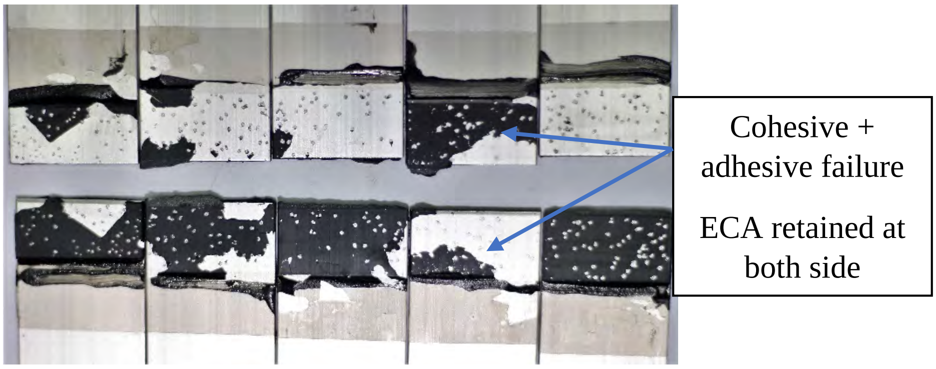

Figure 4.9: 6 wt.% low aspect ratio MWCNT ECA mechanical test samples.

Figure 4.10: 7 wt.% low aspect ratio MWCNT ECA mechanical test samples.

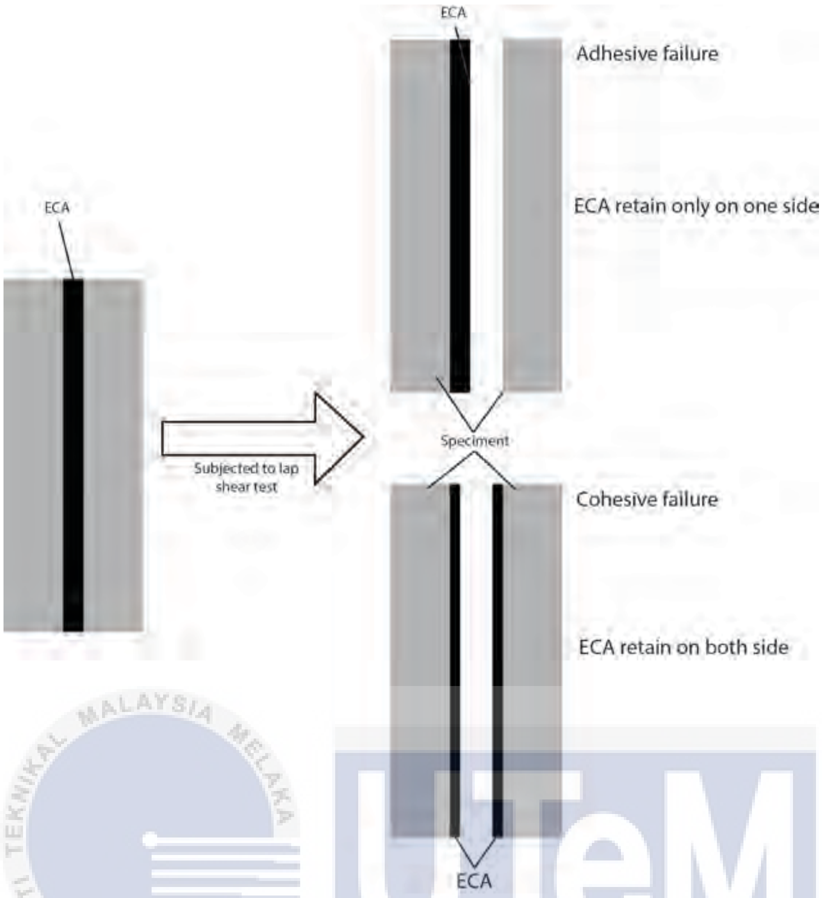

Figure 4.11: Adhesive and cohesive failure illustration.

To better understand the failure mechanism in adhesive, the difference between adhesive and cohesive failure is shown in Figure 4.11. Failure occurs between ECA and specimen for adhesive failure which indicate that the bond between ECA and specimen is weak while for cohesive failure, it occurs within the ECA which makes the ECA retain on both side.

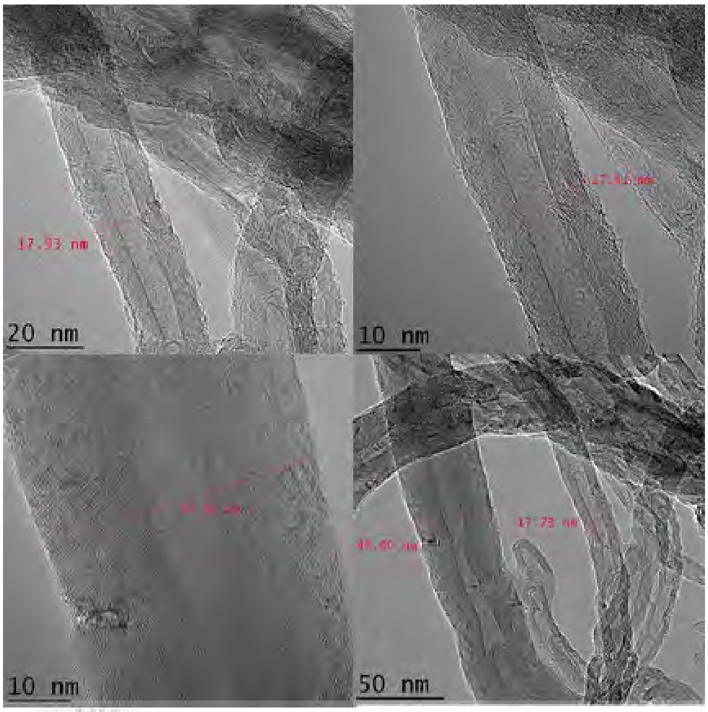

Figure 4.12: TEM image showing the high aspect ratio MWCNT diameter.

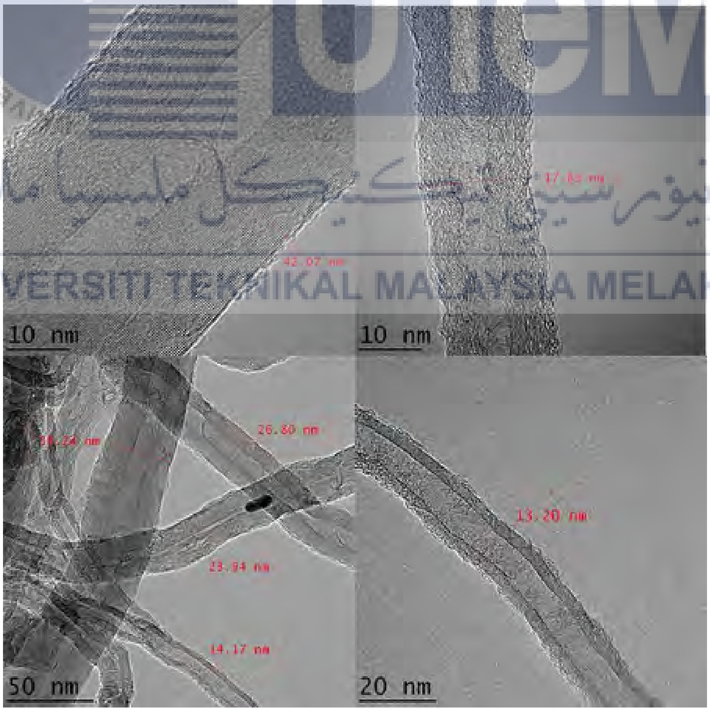

Figure 4.13: TEM image showing the low aspect ratio MWCNT diameter.

According to the MSDS provided by Nanoamor, the high and low aspect ratio MWCNT is reported to have minimum and maximum outer diameter of 10 nm and 20 nm respectively [33]. However, from the transmission electron microscopy (TEM) image as shown in Figure 4.12 and 4.13, some MWCNT have larger diameter than reported in the datasheet. Hence this may affect the aspect ratio of the MWCNT.

Figure 4.14 and 4.15 shows the distribution of the high aspect ratio MWCNT under Scanning Electron Microscope (SEM). The ECA with 7 wt.% of MWCNT filler loading show better distribution of the MWCNT compared to the ECA with only 5 wt.% filler loading. The ECA with MWCNT of 7 wt.% filler loading exhibit more homogeneous distribution in the ECA, hence formed better conductive pathway between the MWCNT particles, which results in lower sheet resistance [39].

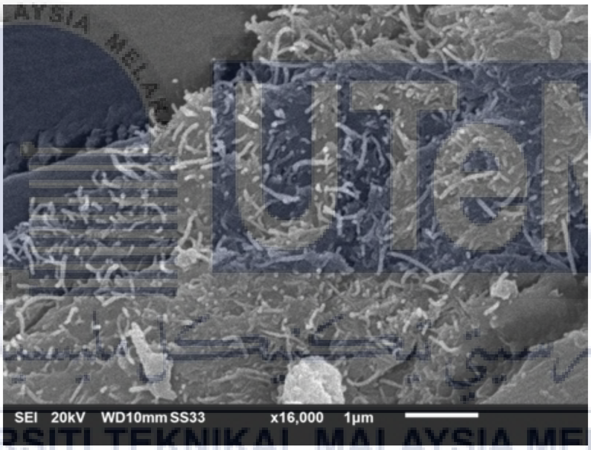

Figure 4.14: 5 wt.% high aspect ratio MWCNT distribution in ECA image obtained using SEM.

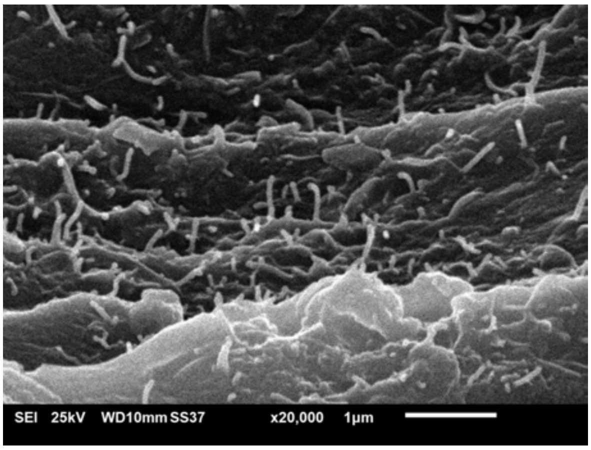

Figure 4.15: 7 wt.% high aspect ratio MWCNT distribution in ECA image obtained using SEM.

The fractured surface of 5 wt.% MWCNT-filled ECA is rougher compared to those of the 7 wt.%, as shown in Figure 4.16 and 4.17 for the high aspect ratio MWCNT-filled ECA and same as for low aspect ratio MWCNT-filled ECA as shown in Figure 4.18 and 4.19. The ECA with 5 wt.% MWCNT exhibit better adhesion compared to those of the 7 wt.% ECA, which is obtained from the lap shear test results. All the SEM micrograph are from top view of sample.

Such observation proves that cohesive failure occurs at 5 wt.% while adhesive failure occurs at 7 wt.% which correlates to the MWCNT distribution in the ECA. Clearly, better distribution of MWCNT in ECA with MWCNT filler loading of 7 wt.% results in better conductivity and adhesion between the epoxy matrix and the MWCNT conductive filler. However, at higher filler loading, the adhesion strength between the epoxy matrix to the substrate surface is decreased. Visual observation of the high aspect ratio MWCNT-filled ECA with the low aspect ratio MWCNT-filled ECA suggest that the high aspect ratio has rougher surface for both filler loading. This could possibly be caused by the amount of MWCNT added into the ECA that correlates with the aspect ratio of the MWCNT with same filler loading since the filler loading is determined by weight percentage.

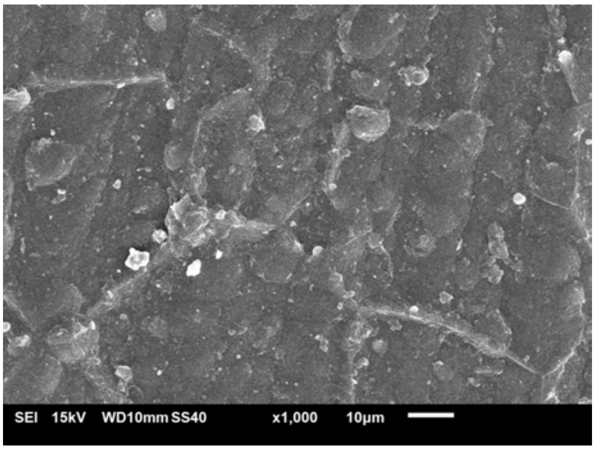

Figure 4.16: SEM micrograph showing the fractured surface of ECA containing 5 wt.% of MWCNT (high aspect ratio) at x1,000 (top view of sample).

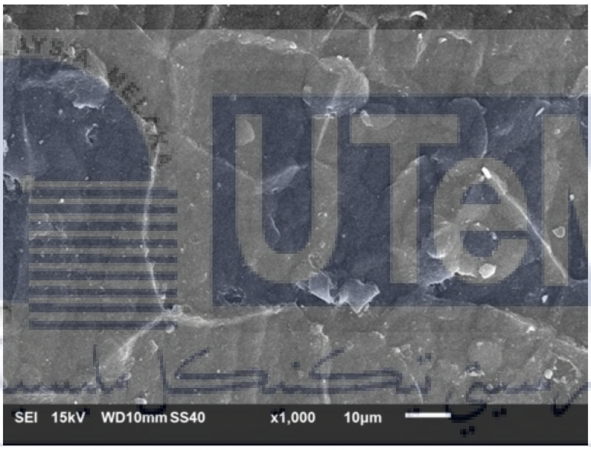

Figure 4.17: SEM micrograph showing the fractured surface of ECA containing 7 wt.% of MWCNT (high aspect ratio) at x1,000 (top view of sample).

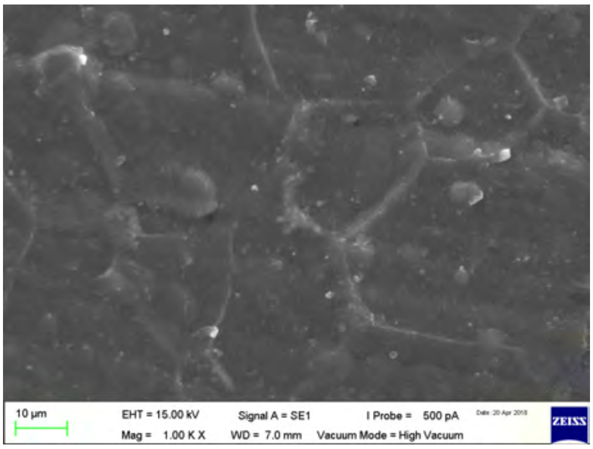

Figure 4.18: SEM micrograph showing the fractured surface of ECA containing 5 wt.% of MWCNT (low aspect ratio) at x1,000 (top view of sample).

Figure 4.19: SEM micrograph showing the fractured surface of ECA containing 7 wt.% of MWCNT (low aspect ratio) at x1,000 (top view of sample).

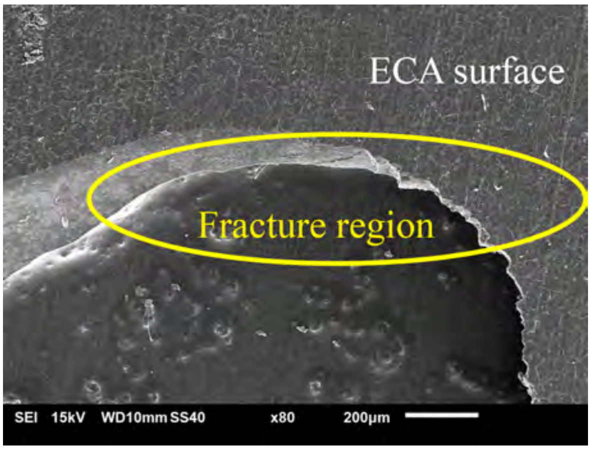

Figure 4.20: SEM micrograph showing fractured region of the ECA with 5 wt.% MWCNT filler loading (high aspect ratio top view of sample).

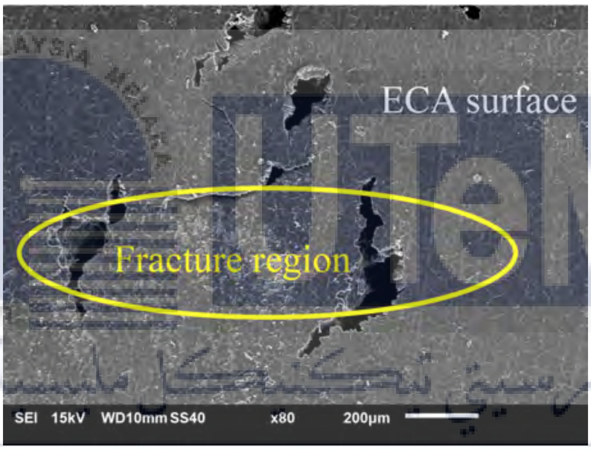

Figure 4.21: SEM micrograph showing fractured region of the ECA with 7 wt.% MWCNT filler loading (high aspect ratio top view of sample).

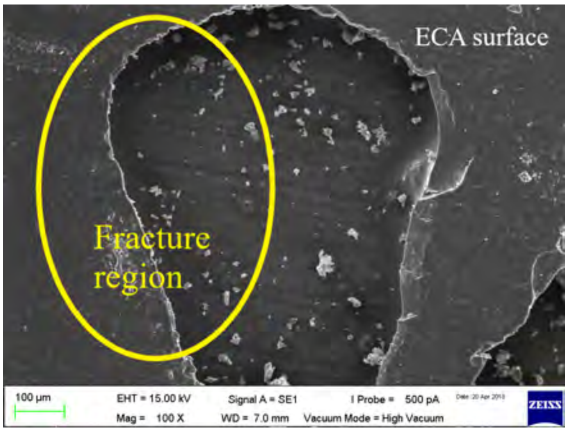

Figure 4.22: SEM micrograph showing fractured region of the ECA with 5 wt.% MWCNT filler loading (low aspect ratio top view of sample).

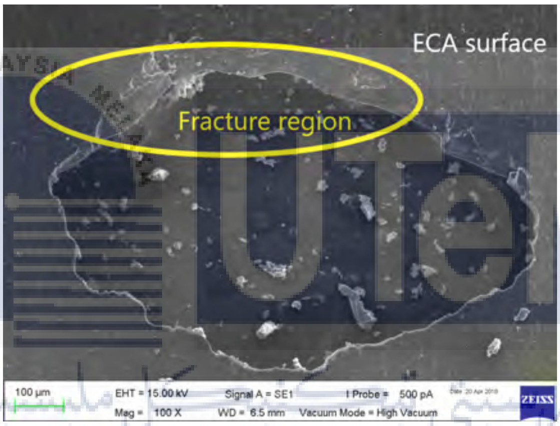

Figure 4.23: SEM micrograph showing fractured region of the ECA with 7 wt.% MWCNT filler loading (low aspect ratio top view of sample).

There is a variation in the fractured region for high aspect ratio MWCNT-filled ECA. For the 5 wt.% MWCNT-filled ECA, the fractured region is larger and smooth while fractured region for 7 wt.% MWCNT-filled ECA is smaller and rougher, as shown in Figure 4.20 and 4.21 since the 5 wt.% and 7 wt.% have different type of failure which is combination of cohesive and adhesive failure and adhesive failure, respectively. From the lap shear test, both the 5 wt.% and 7 wt.% with low aspect ratio MWCNT-filled ECA have combination of cohesive and adhesive failure, with the fractured region as shown in Figure 4.22 and 4.23.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The effect of MWCNT aspect ratio on the functional properties of ECA is studied by formulating ECA using different aspect ratio which is 1750 (high aspect ratio MWCNT) and 112.5 (low aspect ratio MWCNT) followed by electrical testing using four-point probe test unit and mechanical testing using universal testing machine. From the experimental work, it is evident that ECA filled with higher aspect ratio MWCNT have better conductivity compared to low aspect ratio MWCNT-filled 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 filler is achieved at relatively low filler loading of the MWCNT for high aspect ratio MWCNT filled ECA. In addition, results obtained from lap shear test suggests that the shear strength decrease with increasing filler loading, in passing from 5 wt.% to 7 wt.%. These results suggest that as the agglomeration become critical, the percent of decrease in the ECA shear strength is more apparent. However, there is some deviation in the data for the case of 7 wt.% low aspect ratio MWCNT-filled ECA and testing that resulted in a scatter in the data. Such observation could be attributed by the manual mixing process at the formulation stage, in which the MWCNT is not homogeneously dispersed in the ECA. Such observations are summarized in Table 5.1.

Table 5.1: Summary of electrical and mechanical performance test for high and low aspect ratio MWCNT-filled ECA.

Filler Loading	High aspect ratio filled ECA		Low aspect ratio filled ECA	
	Sheet Resistance (kΩ/sq.)	Stress (MPa)	Sheet Resistance (kΩ/sq.)	Stress (MPa)
5	10.66 ± 3.19	8.5810 ± 1.5544	180.87 ± 48.70	9.8680 ± 1.6346
6	3.79 ± 1.89	7.6664 ± 1.2006	143.40 ± 45.84	7.5710 ± 0.7536
7	1.367 ± 0.49	5.8494 ± 2.0265	77.33 ± 51.15	10.1127 ± 1.9359

As the filler loading increase, the sheet resistance of both types of MWCNT-filled ECA is decrease thus indicating better conductivity. Higher aspect ratio MWCNT- filled ECA has better conductivity compare to low aspect ratio MWCNT-filled ECA because the percolation threshold is achieved at lower filler loading. For the mechanical properties of both high and low aspect ratios MWCNT-filled ECA, the higher MWCNT-filled ECA has better shear strength compare to low aspect ratio. Moreover, these results show better shear strength compared to silver-filled ECA.

From the results obtain in this research, it can be concluded that the aspect ratio of multi-walled carbon nanotube affects the functional properties of electrically conductive adhesive. The distribution of MWCNT in ECA and the excluded volume are the key factors which influence the material properties, whereby as the aspect ratio increase, lower filler loading is needed to achieve percolation threshold.

5.2 Recommendation

Electrically conductive adhesive offers various advantages compared to lead containing solder. The most important advantage is that ECA is environmentally friendly. Even though ECA has been used commercially especially metal-filled ECA, there are more rooms for improvement to be explored to enhance the potential of non-metal-filled ECA. For example, the effect of using MWCNT and SWCNT in ECA and the filler loading needed to achieve percolation threshold and better performance compared to commercially available ECA.

The formulation process of ECA could be further improved to ensure a homogeneous distribution of the filler and epoxy in the ECA is achieved to avoid agglomeration of the MWCNT that degrades the reliability performance of the ECA, thus producing better electrical and mechanical properties ECA. Lastly, research on the curing method and condition could be done as it plays and important role in determining the reliability of the ECA produced.

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