THE FUNCTIONAL PROPERTIES OF SILVER/CARBON NANOTUBE HYBRID COMPOSITES

WAN ZULHILMI BIN WAN SAIFUL BAHRIN

A report submitted

in fulfillment of the requirement for the degree of

Bachelor of Mechanical Engineering (Hons)

Faculty of Mechanical Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2019

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.

ACKNOWLEDGEMENT

Firstly, I would like to take this opportunity to express my sincere acknowledgement to my supervisor, Dr. Siti Hajar Binti Sheikh Md. Fadzullah from the Faculty of Mechanical Engineering of Universiti Teknikal Malaysia Melaka (UTeM) for her valuable time and energy, and her supervision, support, and encouragement towards the completion of this project.

I would also like to express my greatest gratitude to Muhamad Muaz Bin Nasaruddin, an MSc student from the Faculty of Mechanical Engineering for his advice, consultations and suggestions throughout this project, which give me a clear vision on how the research project should be conducted. Special thanks to my friend Sow for his commitment and co-operation in completing this project. Special thanks to Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka (UTeM) for the financial support throughout this project.

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

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

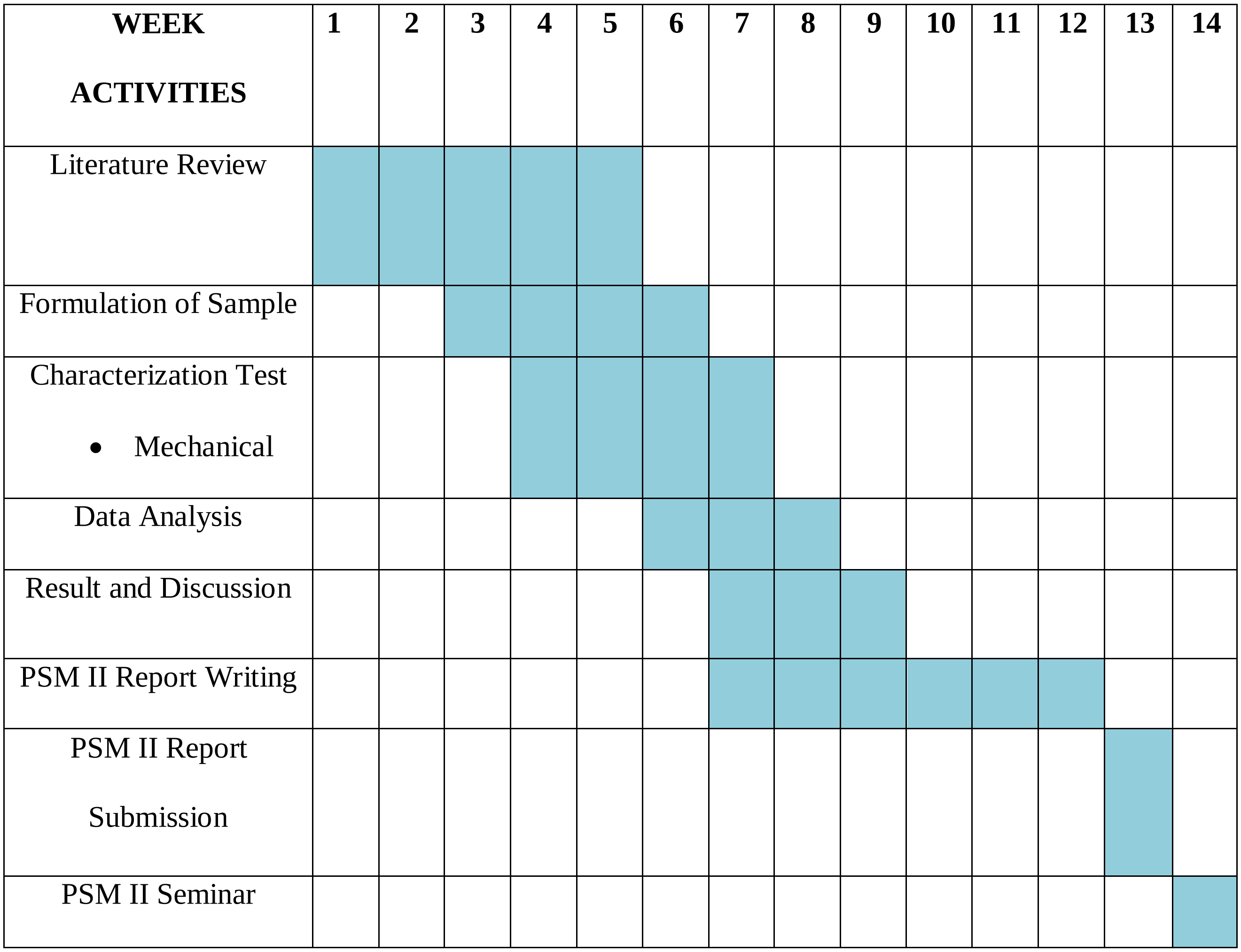

Figure 1.2: Gantt chart detailing research activities and time frame for PSM II

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.