A STUDY OF CARBON NANOTUBES (CNTs) BASED ISOTROPIC CONDUCTIVE ADHESIVES (ICAs) AS ELECTRONIC INTERCONNECT MATERIAL

By

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ABSTRACT

A STUDY OF CARBON NANOTUBES (CNTs)

BASED ISOTROPIC CONDUCTIVE ADHESIVES (ICAs)

AS ELECTRONIC INTERCONNECT MATERIAL

LIM SEOW PHENG

The study of carbon nano-tubes (CNTs) based isotropic conductive adhesives as an environmental friendly electronics interconnect material is currently being considered a possible 'drop-in' bonding material for conventional lead-free solder material. An isotropic conductive adhesive (ICA) requires 25-30% volume fraction of conductive fillers to ensure electrical conductivity, but with these high volume fraction will degrades the mechanical properties of polymer/conductive filler matrix.

The research project aims to develop a multiwall carbon nano-tubes (MWCNTs) based isotropic conductive adhesives (ICAs) as opposed to conventional silver particle/flakes based ICAs. In term of electrical properties, previous research has shown that MWCNTs was able to decrease the bulk resistivity just by replacing certain amount of silver flakes in ICAs. The study showed that 37% improvement in bulk resistivity after 3wt% of MWCNTs replaced with silver flakes in the conventional ICAs. In term of mechanical properties, it was also found that 27.2% increase in hardness with a replacement of 3wt% MWCNTs with the silver flakes in ICAs. In addition, the results from the study showed that MWCNTs able to improve the impact performance of ICAs. For the system that contained 3wt% MWCNTs, the drop test results showed zero percentage of failure.

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APPROVAL SHEET

I certify that, this dissertation entitled **"A STUDY OF CARBON NANOTUBES (CNTs) BASED ISOTROPIC CONDUCTIVE ADHESIVES (ICAs) AS ELECTRONIC INTERCONNECT MATERIAL"** was prepared by LIM SEOW PHENG and submitted in partial fulfillment of the requirements for the degree of Master of Engineering Science at Universiti Tunku Abdul Rahman.

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It is hereby certified that **LIM SEOW PHENG** (ID No:**11UEM06211**) has completed this dissertation entitled **" A STUDY OF CARBON NANOTUBES (CNTs) BASED ISOTROPIC CONDUCTIVE ADHESIVES (ICAs) AS ELECTRONIC INTERCONNECT MATERIAL"** under the supervision of ASSOCIATE PROFESSOR DR RAJKUMAR DURAIRAJ (supervisor) from Department of Mechanical and Material Engineering, Faculty of Engineering and Science and ASSOCIATE PROFESSOR DR LIANG MENG SUAN (Co-Supervisor) from Department of Mechanical and Material Engineering, Faculty of Engineering and Science.

I understand that the University will upload softcopy of my thesis in pdf format into UTAR Institutional Repository, which may be made accessible to UTAR community and public.

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DECLARATION

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

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LIST OF PUBLICATION

1. R. Durairaj, Lam Wai Man, Kau Chee Leong, Liew Jian Ping, N. N. Ekere and Lim Seow Pheng, "Rheological Characterisation of Diglycidylether of Bisphenol-A (DGEBA) and Polyurethane (PU) Based Isotropic Conductive Adhesives", Intech, pp.23-38, Feb 2013, ISBN 980-953-307-924-5

2. R. Durairaj, Lam Wai Man, Liew Jian Ping, Lim Seow Pheng, and Ramesh T. Subramaniam, "Rheology and Processability of Diglycidylether of bisphenol-A (DGEBA) and Polyurethane (PU) based Isotropic Conductive Adhesives Filled with Different Size-distributed Silver Flakes and Silver Particles Engineering Letters, Volume 21 Issue 3, August 2013, pp. 143-148. (*SCOPUS Cited Publication*)

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LIST OF ABBREVIATIONS

ICAs	Isotropic Conductive Adhesives
ECA	Electrical Conductive Adhesives
ACA	Anisotropic Conductive Adhesive
CNTs	Carbon nanotubes
SWNTs	Single-walled nano-tubes
MWCNTs	Mutli wall carbon nano-tubes
SDNPs	Silver dispersion nano-particles
SSNPs	Synthesized silver nano-particles
Sn	Tin
Au	Gold
Ni	Nickel
Ag	Silver
Cu	Copper
C	Carbon
Pb	Lead
DGEBA	Diglycidyl Ether of Bisphenol-A
PCB	Printed Circuit Board
PU	Polyurethane

RoHS	Restriction of Hazardous Substances
WEEE	Waste from Electronic and Electrical Equipment
ROHS	Restriction of the use of hazardous substances in electrical and electronic equipment
NCMS	National Center for Manufacturing Sciences
LCD	Liquid crystal display
BGA	Ball grid array
s/m	Siemens per meter
TPa	Tera Pascal
Ωcm	Ohm centimeter
Ωm	Ohm meter
wt%	Weight percentage
ρ (rho)	Resistivity
˚C	Degree Celsius
RH	Relative humidity
LMPA	low-melting-point alloy fillers
Ω/square (Rs)	Sheet resistance
HV	Vickers Pyramid Number
DPH	Diamond Pyramid Hardness

F	Force
A	Surface area
Kgf	kilograms-force
mm	Millimetres
nm	Nanometres
µm	Micrometer
SEM	Scanning Electron Microscope
AFM	Atomic force microscope

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CHAPTER

CHAPTER 1

1.0 INTRODUCTION

1.1 Importance and challenges of electrical conductive adhesives (ECAs)

Legislations have been proposed to reduce or eliminate the use of lead (Pb) in electronic products due to their short and long term environmental impact. The two main directives are the European Union (EU) legislation 'Waste from Electronic and Electrical Equipment (WEEE) and 'Restriction of the use of hazardous substances in electrical and electronic equipment' (ROHS) directive, which is aimed at reduction or complete removal of Pb in electronic products (RoHS Regulations, 2006). The conventional bonding medium used in the assembly of the electronic product is tin-lead (Sn/Pb) solder. The two most promising alternative to Sn/Pb based solder is the lead-free solder and electrical conductive adhesives (ECAs). ECAs consist of polymer resin such as thermoplastics and thermosets and conductive fillers such as silver, copper, gold, and nickel. The polymer resin contributes to the mechanical properties meanwhile the conductive fillers provide the electrical conductivity.

The advantage of ECAs over Pb-solder is that it can be cured at lower temperature, which reduces the production of volatile organic compound and lowers the thermal stresses experience by the chip and substrate. ECAs are gaining wide use in ball grid array (BGA) and flip-chip assembly for various application such as liquid crystal display (LCD) and smart card applications due to lower processing temperature and environmentally friendly bonding

medium. Despite its lower processing temperature, the ECAs are still plagued by lower conductivity and poor mechanical performance with respect to impact strength. Optimising the performance of ECAs with respect to electrical and mechanical still remains a challenge in the electronic manufacturing industry.

1.2 Introduction to electrical conductive adhesives (ECAs)

The electrical conductive adhesives (ECAs) are classified into two types: (i) anisotropically conductive adhesives (ACAs) and (ii) isotropic conductive adhesives (ICAs). In the ACA, the filler loading is usually between 5 to 10wt%. The electrical contact is usually achieved through a combination of temperature and pressure. Due to lower filler loadings, the ACA conduction is mainly restricted in the z-direction. Their application is mainly used in the assembly of flat panel display. One of the main difference of ACAs and ICAs is the filler loading of the latter which is around 60-80wt% of the overall system. In addition, the high filler loading contributes to the conductivity in the x, y and z directions. The ICAs are seen a possible replacement for lead or lead-free solder pastes.

As mentioned earlier, the uniqueness of the ICAs is that it consists of two components, which is the polymer resin and conductive fillers. As mentioned earlier, the mechanical properties such impact strength is from the cured polymer resin meanwhile the filler materials contributes to the electrical conductivity. This is achieved through shrinkage experience by the polymer

resin during the curing process that enables the contact between the conductive fillers. The primary conductive filler is silver flakes (Wong and Lu, 2000).

1.3 Carbon nano-tubes (CNTs) based isotropic conductive adhesives (ICAs)

The carbon nanotube (CNTs) was developed by Sumio Iijima of NEC, Japan in 1991 (Iijima S., 1991). The structure of carbon nano-tubes are known to have a long aspect ratio and low density. The CNTs have a potential to reach the percolation threshold at a lower volume fraction as opposed to silver flakes. Previous work to incorporate CNT in the epoxy system has shown increase in the mechanical and electrical properties (Wu et al., 2006).

This research project aims to develop a multi-wall carbon nanotubes based ICAs. In addition, there is a need to understand the effect of incorporating CNTs in the existing mixture of polymer and silver flakes systems on the electrical conductivity and mechanical reliability.

1.4 Problem statement

The aims of the research project are to develop a multi-wall carbon nano-tubes (MWCNTs) based isotropic conductive adhesives (ICAs) that have satisfactory electrical conductivity and desirable mechanical strength that can be potentially used for solder replacement in the assembly of electronic devices. A comparative study was carried with silver flakes and silver nano-particles based ICAs. This study has three objectives, as follows:

1. To study the effect of incorporating MWCNTs to the existing polymer resin and silver flakes to the electrical conductivity of Isotropic Conductive Adhesives (ICAs).
2. To investigate the mechanical properties of MWCNTs based ICAs.
3. To investigate the effect of thermal aging on the mechanical and electrical properties of MWCNTs based ICAs.

In order to achieve the aims and objectives of the research, the following are the research questions:

- Could the addition of multi-wall carbon nano-tubes (MWCNTs) improve the electrical conductivity/lower the resistivity of isotropic conductive adhesives (ICAs)?
- How many percentages of MWCNTs must be added to enhance the mechanical properties of the isotropic conductive adhesives?

- What is the effect of thermal aging process on the mechanical and subsequently the electrical properties of MWCNT based ICAs and conventional ICAs?

1.5 Overview of the Thesis

Chapter 1 provides the introduction to the study, the aim and objectives of the work, and presents an overview of the thesis. Chapter 2 presents a literature review of carbon nano-tubes and general review on CNTs based ICA. In addition, chapter 2 also described constituent of ICA. Chapter 3 presents a description of methodology of this research, sample preparation for electrical and mechanical test, and materials used in the formulation of ICAs. Furthermore, electrical and mechanical test method were presented in this chapter.

Chapter 4 focuses on results and discussion of the experimental work conducted in this research, which is divided into three sub section. The first section presents the results and discussion of electrical conductivity studies on conventional ICAs and MWCNTs based ICAs. This section start with investigation finding the most suitable curing temperature to cure adhesives in this research, following by electrical conductivity studies of formulated ICAs (system 1 - 6), and continue with study the effect of replacing nano-sized silver particles with silver flakes in term of bulk resistivity, and end with

investigation on effect of different volume fraction of MWCNTs to bulk resistivity (system 7a- 7j).

The second section presents the results and discussion of mechanical properties on conventional ICAs and MWCNTs based ICAs. This section presented the investigations on mechanical properties such as Vickers Micro Hardness and drop test for both conventional ICAs and MWCNTs based ICAs. Besides, Study on effect of different volume fraction of MWCNTs in Drop Test and Vickers Micro hardness was also presented in this section.

The third section presents the results and discussion on thermal aging studies of ICAs. This section presented regarding thermal aging on electrical and mechanical properties for conventional ICAs and MWCNTs based ICAs. Thermal aging studies only focus on conventional ICAs (system 1 and system 2) and MWCNTs based ICAs (system 6). The reason is system 1, system 2 and system 6 showed the lowest bulk resistivity in electrical conductivity test. The Chapter 5 presents the main conclusions from the study and the suggestions for further work.

CHAPTER 2

2.0 LITERATURE REVIEW

2.1 Introduction to Carbon nano-tubes (CNTs)

The carbon nano-tube (CNTs) has shown to have a good mechanical and electrical property which has attracted its usage in wide range of applications. As mentioned earlier, the low density and high aspect ratio of CNTs could be an ideal candidate for polymer nanocomposites. The typical dimension of CNTs consists of diameter ranging from 1 to 50 nm and length in nano or micron scale depending on the applications. The basic structure of CNTs is shown in Figure 2.1.

Carbon nano-tubes are classified into two, first is known as single-walled carbon nano-tubes (SWCNTs) and second is known as multi-walled carbon nano-tubes (MWCNTs). These SCWNTS and MWCNTs basic building block is graphene. Different chiralities can be created by changing the direction in the roll-up. Further, several SWCNTs can be layered onto another to produce a multi wall walled carbon nanotube (MWCNT), as shown in Figure 2.1.

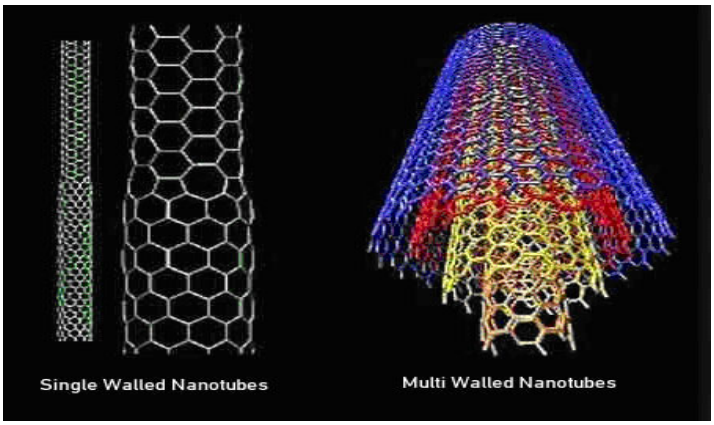

Figure 2.1 Basic structures of CNTs (Gauri , 2012).

By changing the rolling angle of graphene sheet, different tubes chiralities was created, the tubes chiralities included Armchair, Zigzag, and Chiral.

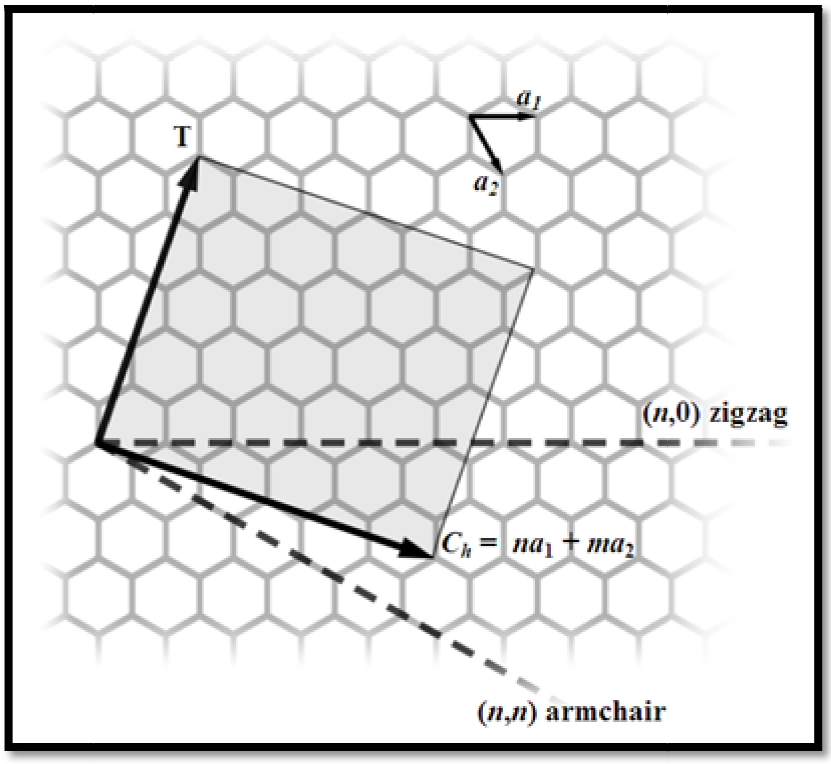

Figure 2.2 Figure 2.2 Nanotube naming scheme (Kebes, 2005).

Based on Figure 2.2, the (*n*,*m*) represents the coordinate system used to shows how the graphene sheet is wrapped. The number of unit vectors along the two

directions in the honeycomb lattice of the graphene sheet is denoted by the n and m. The nano tubes are known as zig zag if the m = 0 and armchair nano tubes if the n = m. Otherwise it is known as chiral. The vector ($\mathbf{C}_h$) within infinite graphene sheet shows how to "roll up" the sheet of graphene to produce nanotube. **T** denotes the tube axis, and $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit vectors of graphene in real space (Kebes, 2005).

2.1.1 Conductivity properties of carbon nano-tubes (CNTs)

The electrical conductivity of CNTs depends on the combination of n and m, which represents the structural parameters. The n and m shows the extent the nano tubes can be twisted. The degree of twist and chirality can result in the carbon nano-tubes to highly conducting. The CNTs depending on the twist can be either exhibit metallic or semi-conducting electrical behaviour. The inter-wall reaction within multiwall carbon nano-tubes will also play a role in the redistribution of the current over the individual tubes.

Previous study by Tans et al. (1997) showed that SWCNTs showed metallic and semiconducting behaviour. The study showed that the conductivity measured at room temperature was about 10^5 to 10^6 S/m for metallic nano-tubes meanwhile semiconducting nano-tubes was about 10 S/m. Another study by Odom et al. (1998) and Wildoer et al. (1998) confirmed this percolation threshold through their work in scanning tunnelling spectroscopy. They

concluded that electrical properties depend on the nanotube diameter and helicity. Another study by Kim et al. (1998), Fischer et al. (1997) and Bozhko et al. (1998) found that the conductivity of SWCNTs vary from 1 x 10^4 S/m to 3 x 10^6 S/m at room temperature. They concluded that the conductivity depends on the level of entanglement and in-plane conductivity. For the MWCNTs, Ebbesen et al. (1996) reported a conductivity ranging between 20 and 2 x 10^7 S/m. The study also showed that the helicity plays an important role in the conductivity.

2.1.2 Mechanical properties of carbon nano-tubes

The single sheet of graphite structure which has individual carbon atom connected to each other forms a honeycomb lattice. The carbon atom in this honeycomb lattice is connected to one another through a strong chemical bond to neighboring carbon atoms. These strong bonds results in graphite sheet with high elastic modulus which contributes to the overall mechanical properties of the systems which incorporate them. A study by Treacy et al. (1996) measured that Young's modulus of SWCNTs is 1 TPa. Another study by Krishnan et al. (1998) showed that the range of Young's modulus is 1.22 TPa to 1.26 TPa.

2.1.3 Aspect ratio of carbon nano-tubes

CNTs are known for the high aspect ratio which contribute high percolation threshold with lower filler loading in order to achieve electrical conductivity. Due this low filler loading, the mechanical performance such as impact strength, hardness and fracture strength of the polymer matrix could be preserved.

2.2 Review of CNTs based ICA

A study by Li et al. (2010) developed conductive adhesives filled with MWCNTs. The study showed that the percolation threshold for the electrical conductivity was at 3wt% of MWCNTs. By adding the 3wt%, the study showed a similar electrical conductivity with solder. In addition, the study also recommended that the ultrasonic mixing process should be used to disperse the MWCNTs within the epoxy system.

In another study by Qian et al. (2000), an 80% of shear strength of the polystyrene/CNT matrix was retained by incorporating 0.8wt% of CNT. Meanwhile, a conventional metal filled/polymer system could only retain less than 28% of the shear strength. The study showed that poor dispersability of the CNT within the polymer matrix contributed to the crack between the CNT/polymer interfaces. The study also recommended that functionalizing the

surface of MWCNTs could form a strong chemical bond with polymer resin.

In a study by Lin et al. (2004), effect of replacing certain weight percent of silver flakes with CNTs on the electrical conductivity was reported. The study found that for 66.5% silver filled conductive adhesives measured a resistivity of $10^4\ \Omega\cdot cm$ but by replacing the existing silver flakes with 0.27wt% CNT, the resistivity dropped to $10^{-3}\ \Omega\cdot cm$.

2.3 Review of silver nano-sized particles based ICA

Nano-sized silver particle have been used as secondary filler along with the micro sized silver particles in the ICAs in order to enhance the electrical and mechanical properties of ICAs. In a study by Li et al. (2010), adding about 2.5 wt% of nano-sized silver particles increased the resistivity of the composite. But near to threshold value, the nano-sized particles helped to build a conductive pathway with the micro size silver particles resulting in a drop in resistivity. This seem to indicate that addition of nano-particles contribute to the drop of resistivity relatively due to the presence of larger particles. The larger number of nano-sized particles will be able to fill up the holes between the large particles providing a conductive pathway. But it should be noted that the presence of this nano-size particles may also increase the contact resistance between the particles thus net resistivity measured could be higher than the conductive adhesives with silver flakes.

2.4 Constituent of ICAs

ICA consists of two elements, first elements are polymer resin and second elements are conductive filler. As mention earlier, the resin provides the mechanical properties meanwhile the filler provide the conductive pathway for the flow of current in the ICAs.

The common used conductive filler was Ag, Au, Ni, Cu and carbon in various forms. Among those conductive filler, Ag (silver) either silver flakes or silver particle was the most efficient conductive filler for ICAs in term of the conductivity and reliability of the silver element. In year 1991, an investigation by Lyons (1991) stated that two types of polymers can be used as the adhesive resins, thermosets and thermoplastic comprises of epoxies, polyimides, silicones and acrylic adhesives.

2.4.1 Conductive Filler

The filler must be able to conduct electricity. Silver is the most common used conductive filler due to its ability conduct electricity even after oxidation and good electrical conductor. Silver is the most conductive of the frequently used metals, although it is also expensive. Some researchers have explored the use of copper or other low-cost materials instead of silver, but their results have largely proved unsatisfactory.

Another important attribute of silver is that it can be easily precipitated through chemical method to form different shapes and sizes (Shimada et al., 2000). The precipitated silver flakes is usually pre-treated with organic lubricant to ensure good disperse ability within the polymer matrix, which in return affect the flow property and electrical conductivity (Wong et al., 2006).

Phuapradit et al. (2002) presented a review of blending of silver flakes and particles with wide range of size distribution and its effect on rheology and electrical properties. The overlapping of the flakes (usually in disk shapes) can provide better electrical conductivity. In addition, the overlapping of the irregular shaped flakes will also create voids which could be filled by nano-sized particles or CNTs. Voids to a certain extent in ICAs will degrade the mechanical and electrical performance. A study by Kottaus et al. (1997) studied the influence of adding highly porous Ag powder to fill the voids between the flakes. The results from the study showed improvement in the thermal and mechanical properties of the ICA system. Further modification has been done to the filler systems in the ICAs through the incorporation of low-melting-point alloy fillers (LMPA) and silver flakes as the conductive filler (Lu and Wong, 2000). During the thermal curing process, the LMPA filler melts to form a network of conductive path along with the silver flakes and the substrate.

2.4.2 Resins: Thermoplastics and Thermosets

Lyons (1991) studied the influence of resin materials on the properties of ICAs. Two types of polymers can be used as the adhesive resins: thermosets and thermoplastics. Lyons summarized that thermoset materials do not flow at high temperatures due to the interlocked cross-linked structure after cure. They are materials that are initially monomers, which polymerize during curing (hardening) process. Three-dimensional cross-linked molecular structures are formed after curing as a result of the physical links or branch points that tie the polymer chains together. The relative number of branch points is called the cross-link density, and materials with high cross-link densities tend to be stiffer but more brittle. The degree of chemical conversion at which the cross-link structure first forms is called the gel point and the phenomenon is known as gelation.

Thermoplastic materials consist of long polymer chains that have few side branches, and the chains are not physically linked. They can flow at a high temperature since they do not process the cross-link network structures that prevent flow of thermoset polymers. High temperature engineering thermoplastics have been introduced that rival the performance of thermoset. They can withstand the temperatures of soldering operations without physical deformation and flow because they possess exceptionally rigid chain high molecular weight structures that resist large scale molecular motion until very high temperatures. They are amorphous glasses, such as polyetherimide and polyethersulfone.

Thermoset epoxy resins are the most common polymer matrices used for conductive adhesives. The epoxies based on the diglycidylether of bisphenol-A (DGEBA), which is synthesized through a reaction between bisphenol A and epichlorohydrin, are the common materials for liquid adhesives. DGEBA epoxy has an epoxide functionality of 2 for its average molecular weight of 380. Modification to the base resin usually consists of varying the epoxy equivalent weight or increasing the viscosity. The main ingredients of an epoxy system consist of the resin and the hardener. Sometimes an accelerator is added to facilitate curing, leading to the desired reaction products at desired temperatures. Notice the bisphenol A resin contains active three-member rings. Ring opening reactions with hardeners produce highly cross-linked structures in a curing process. Several of hardeners have been found effective, resulting in different rates of curing, different reaction products and product properties. They can be grouped into three major categories: catalytic (Lewis acids and bases), amines (aliphatic and aromatic), and anhydrides. In the case of anhydrides, tertiary amine accelerators, or catalysts, are added to promote curing.

Klosterman et al. (1996) reported that aliphatic amines generally cure rapidly and can react at low temperatures. Elevated temperature cures are often required of aromatic amines, as the functional groups are tied to more rigid moieties. Epoxy curing involves sequential opening of the three-member rings. Each can form two chemical bonds with hardeners. Therefore, the original DGEBA molecule theoretically serves as a cross-linking point, connecting four branches. The viscosity of the resin first decreases as temperature increases.

Meanwhile, as the extent of cure reaction increases, the polymeric structure becomes cross-linked. At the gel point, the increased cross-linking causes the material viscosity to rise greatly and further flow is prohibited. As a consequence, the system cures and stiffens, and the material is no longer process able (Klosterman et al., 1996).

CHAPTER 3

3.0 MATERIALS AND METHODS

3.1 Methodology

This chapter presents a description of the methodology, materials used experimental equipment, and parameters used for different parts of the study. In this study, the variation of volume fraction in ICAs with three types of fillers (silver flakes, mixture silver nano-particles with silver flakes and mixture of silver flakes and MWCNTs) are investigated.

Based on the flow chart (Figure 3.1), systems with different volume fraction of conductive filler and polymer resin were formulated/mixed based on the composition Table 3.3, 3.4 and 3.5 (section 3.3). Systems were prepared into several forms of specimens for mechanical and electrical tests. Specimens were cured in the curing furnace for 60 minutes with specific temperature and then following by mechanical, electrical and thermal aging studies of ICAs.

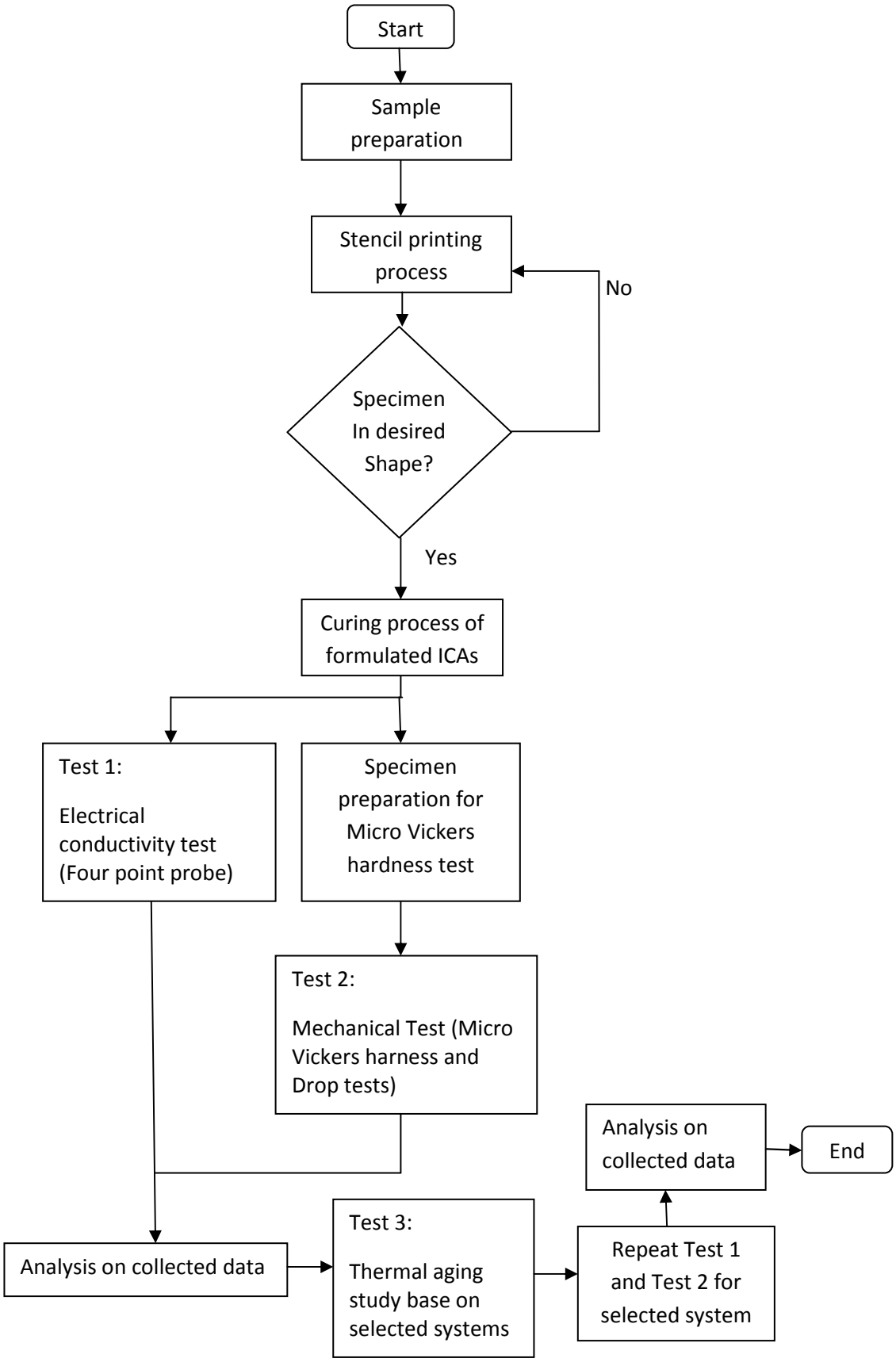

Figure 3.1 Flow chart

3.2 Sample investigated

In this section, ICAs with composition as shown in Table 3.3, Table 3.4 and Table 3.5 were mixed and stirred by a metal stick in a beaker as shown in Figure 3.2 for 20 minutes to make sure the conductive filler and polymer resin was mixed and dispersed uniformly and completely.

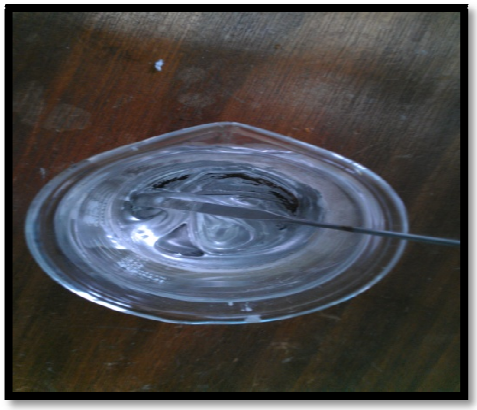

Figure 3.2 ICAs mixed and stirred in a beaker.

The mechanical and electrical properties of the formulated conventional isotropic conductive adhesives with different volume fraction of conductive filler were being benchmark against the MWCNTs based ICAs. The different volume fractions of MWCNTs were added in ICAs as replacement for silver flakes.

In order to prolong shelf life and enhanced the lifetimes of the ICAs in electronics devices, thermal aging process of ICAs under specific condition was studies, the formulated ICAs was stored in a curing furnace under condition 85°C and 85 RH for 600 hour in this project in order to studies the effect of thermal aging process to the mechanical and electrical properties of

ICAs, for every 100 hours, the mechanical and electrical properties of ICAs was measured and studies.

Curing temperature was an important issue in electrical conductivity for ICAs. During the curing process, conductive filler and polymer resin in ICAs cured shrinkage and dense completely only in the critical curing temperature. In order to achieve the top electrical performance of ICAs, the different curing temperature such as 180℃, 200℃, 220℃ and 240℃ was used to cure the selected ICAs (system 1, 2 and 6) to determine the suitable curing temperature for ICAs and the curing period was set to 1 hour in this studies.

Table 3.1 shows the materials used in the formulation of ICAs. Table 3.2 shows the parameter to be investigated and Table 3.3, Table 3.4 and Table 3.5 show the sample investigated in this study.

Table 3.1 Individual chemical components utilised in the formulation of ICAs.

Materials	Materials name	Manufacturer
Resin	Diglycidylether of bisphenol-A (DGEBA)	Sigma Aldrich
Curing agent	Ethylene diamine	Merck & Co.
Conductive filler 1	a) Silver flakes	Inframat® advanced materials
Conductive filler 2	a) Silver dispersion nano-particles (SDNPs)	Sigma Aldrich
	b) Synthesized silver nano-particles (SSNPs)	Lab synthesis
	c) Multi wall carbon nano-tubes (MWCNTs)	Nanostructured & Amorphous Materials

Table 3.2 Parameter investigated.

Conductive filler 1	Conductive filler 2	Sized of conductive filler	Volume fraction of conductive filler	Curing temperature
Silver flakes		5-8 μm	0.6 and 0.8	180°C, 200°C, 220°C and 240°C.
	SDNPs	10 nm and 20 nm		
	SSNPs	10-20 nm		
	MWCNTs	Outside diameter: 8-15 nm Inside diameter: 3-5 nm Length: 10-50 μm 99% carbon basic		

From Table 3.2, conductive filler 1 as the main filler in ICAs, conductive filler 2 which is secondary filler as a replacement to the conductive filler 1. For example, 57wt% of silver flakes as main conductive filler and 3wt% of the silver flakes was replace by 3wt% MWCNTs which is secondary conductive filler, and the rest was the 40wt% of the epoxy resin.

Table 3.3 Sample investigated (Conventional ICAs).

System	Epoxy resin	Conductive filler 1	Curing temperature
System 1	DGEBA= 40 wt%	Silver flakes= 60wt%	180°C, 200°C, 220°C and 240°C
System 2	DGEBA= 20 wt%	Silver flakes= 80wt%	180°C,200°C, 220°C and 240°C

Table 3.4 Sample investigated (Reinforce ICAs with nano-size filler).

System	Epoxy resin	Conductive filler 1	Conductive filler 2	Curing temperature
System 3	DGEBA= 40wt%	Silver flakes= 54wt%	SDNPs = 6wt% Size =10nm	220°C
System 4	DGEBA= 40wt%	Silver flakes= 54wt%	SDNPs = 6wt% Size =20nm	220°C
System 5	DGEBA= 40wt%	Silver flakes= 54wt%	SSNPs = 6wt% Size =10-20nm	220°C
System 6	DGEBA= 40wt%	Silver flakes= 57wt%	MWCNTs =3wt%	180°C,200°C , 220°C and 240°C

Table 3.3 shows the sample composition of system 1 and system 2 which is conventional ICAs. Table 3.4 shows the sample composition for system 3 to system 6 which reinforce with nano-size filler.

Table 3.5 Sample investigated (Reinforce ICAs with different volume fraction of MWCNTs).

System	Epoxy resin	Conductive filler 1	Conductive filler 2	Curing temperature
System 7a	DGEBA= 40wt%	Silver flakes= 59.7 wt%	MWCNTs = 0.3wt%	220°C
System 7b	DGEBA= 40wt%	Silver flakes= 59.4 wt%	MWCNTs = 0.6wt%	220°C
System 7c	DGEBA= 40wt%	Silver flakes= 59.1 wt%	MWCNTs = 0.9wt%	220°C
System 7d	DGEBA= 40wt%	Silver flakes= 58.8 wt%	MWCNTs = 1.2wt%	220°C
System 7e	DGEBA= 40wt%	Silver flakes= 58.5 wt%	MWCNTs= 1.5wt%	220°C
System 7f	DGEBA= 40wt%	Silver flakes= 58.2 wt%	MWCNTs = 1.8wt%	220°C
System 7g	DGEBA= 40wt%	Silver flakes= 57.9 wt%	MWCNTs = 2.1wt%	220°C
System 7h	DGEBA= 40wt%	Silver flakes= 57.6 wt%	MWCNTs = 2.4wt%	220°C
System 7i	DGEBA= 40wt%	Silver flakes= 57.3 wt%	MWCNTs = 2.7wt%	220°C
System 7j	DGEBA= 40wt%	Silver flakes= 57.0 wt%	MWCNTs = 3.0wt%	220°C

The volume fraction of the MWCNTs was increased 0.3 wt% for each increment in ICAs, as shows in Table 3.5. Please note that for all the system in this study, 5 wt% of the curing agent (Ethylene diamine) were added into the ICAs to reduce the curing time and helps in reducing the curing temperature of the ICAs during the curing process.

3.3 Electrical resistivity test method of ICAs

Electrical resistivity (also known as resistivity, specific electrical resistance, or volume resistivity) measures the extent to which a material may restrict the flow of electrical current through its body. A better conductivity is achieved when the measured resistivity is low. The symbol that denotes resistivity is commonly represented by the Greek letter ρ (rho). The SI unit of electrical resistivity is the ohm·metre (Ω·m).

3.3.1 Test vehicle board and stencil printing process

Test vehicle board were designed and prepared for resistivity test as shows in Figure 3.3. Test vehicle board was created by PCB which two copper strings at the sides and a 5mm gap between the copper, this gap was designed for printing process of ICAs in resistivity measurement.

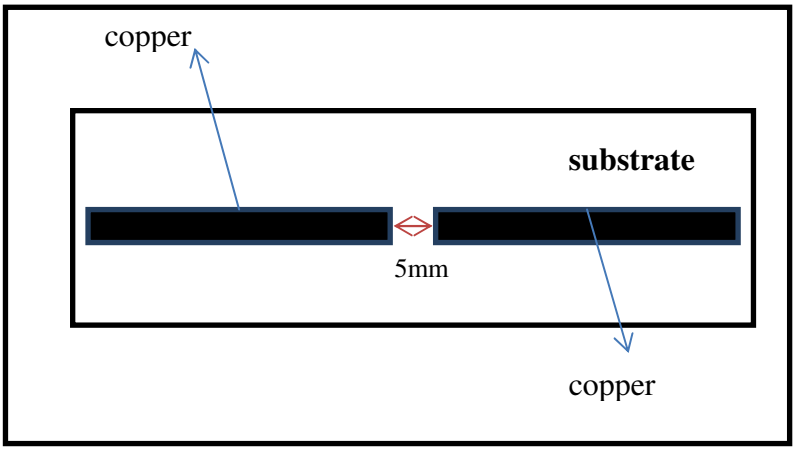

Figure 3.3 Test vehicle board for ICA resistivity test.

The formulated ICAs in half solid or paste form was printed on the test vehicle board as showed in Figure 3.5. Printing stencil with aperture in the middle, thickness 0.10 mm and diameter 10 mm was designed and prepared for the printing process as shown in Figure 3.4. The functions of this printing stencil are to confirm or make sure the size and volume that printed on the test vehicle board was constant and consistent for every sample in resistivity measurement.

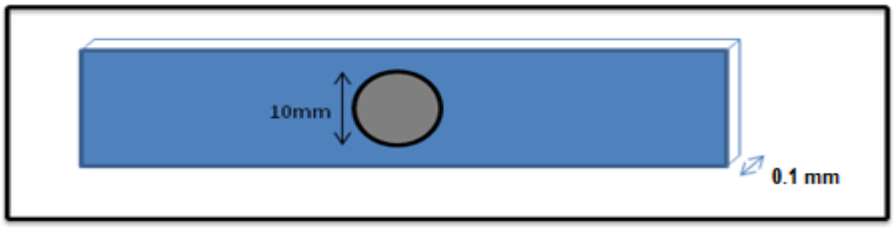

Figure 3.4 Schematic of printing stencil.

According to a study by Durairaj et al. (2008), the printing process is widely used method in the electronic manufacturing industry to transfer the pastes (solder pastes and conductive adhesives) to substrates. Due to the complexity of the process, the printer, stencil, environment and solder paste flow behaviour is seen as major parameters that must be controlled.

Formulated ICAs were stencilled onto the test vehicle board like Figure 3.5 showed. After the printing process, the ICAs on the test vehicle board then were cured in the curing furnace for 60 minutes and the measurement of sheet resistivity of ICAs were taken by the four point probe.

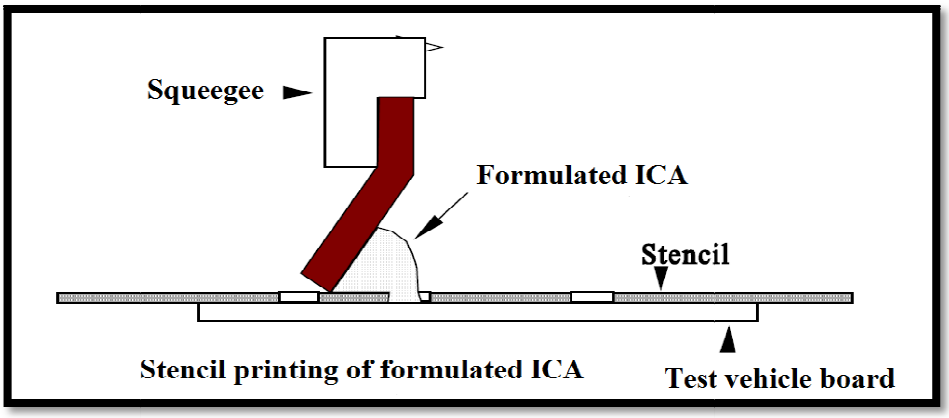

Figure 3.5 Formulated ICAs were stencilled onto test vehicle board (Durairaj, R, 2008)

3.3.2 Four point probe

In this study, the resistivity's of the ICAs were measured by instrument namely four point probes. A four point probe is a simple but commonly used equipment to measure the resistivity of conducting samples. The schematic representation of the Four-Point Probe is showed in Figure 3.6.

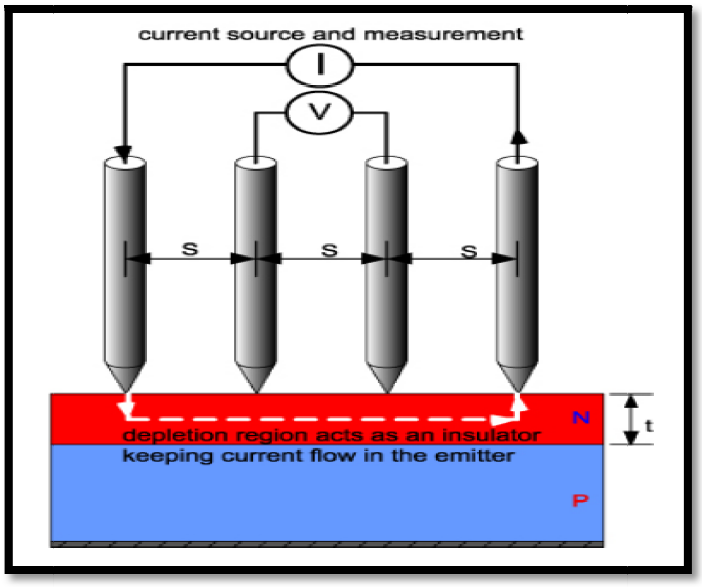

Figure 3.6 Schematic of the Four-Point Probe.

The theory behind four point probe is a fixed current injected into the wafer through the two outer probes, and a voltage is measured between the two inner probes. The spacing between the four probes is 1.6 mm. Four point probes that used in this study are from *KeithLink Technology Co., Ltd.* as showed in Figure 3.7.

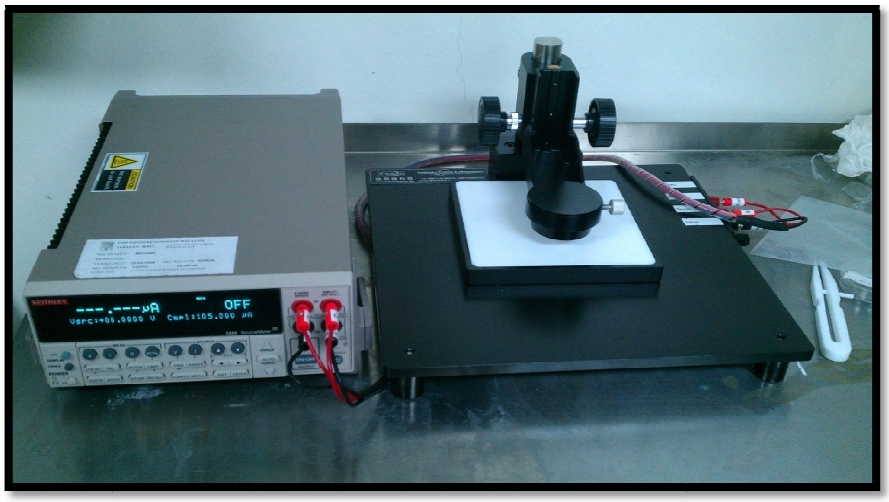

Figure 3.7 Four point probe from KeithLink Technology Co., Ltd.

According to Four-Point Probe theory, if probes with uniform spacing *s* (1.6 mm) are placed on an infinite slab material, then the resistivity, ρ, is given by:

$$\rho = 2\pi s \left(\frac{V}{I}\right) \qquad \text{for } t >> s \qquad (1)$$

and

$$\rho = \frac{\pi}{\text{In}2}(t)\left(\frac{V}{I}\right) \qquad \text{for } s >> t, \qquad (2)$$

with *t* representing the thickness of the thin film. For shallow layers, the above equation gives the sheet resistance as:

$$Rs = \frac{\rho}{t} = \frac{\pi}{\ln 2}\left(\frac{V}{I}\right) = 4.532\left(\frac{V}{I}\right) \qquad \text{for } s >> t. \qquad (3)$$

From equation (2) and (3) above, $\frac{\pi}{\ln 2} = 4.532$ was a constant value which is the correction factor of the four point probes. The recorded measured resistance from four point probes , $\left(\frac{V}{I}\right)$ were multiply by 4.532. This product is the sheet resistance in units' Ω/square of the film under measurement. From equation (2), the sheet resistance multiply by the film thickness, in cm, the bulk resistivity of the film, in Ω.cm will be obtain. The results and finding on the bulk resistivity in unit's Ω.m of the formulated ICAs were reported in following chapter.

3.4 Mechanical and reliability test method

Mechanical properties such as hardness and toughness of the ICAs were being investigated in this study. The reliability of any conductive adhesive joint is a critical issue that must be considered carefully before the adhesives can be widely used in a production setting. Poor electrical and mechanical stability upon exposure to environmental aging conditions, such as elevated temperature and humidity aging, and poor reliability in impact situation, are several major concerns that exist in the ICAs. In most cases, reliability testing is often accelerated by increasing load/stress, humidity, temperature, etc. to simulate environmental influence factors and cyclic thermal loads, shock tests, etc.

Hardness test of the formulated ICAs in this study were investigated by an instruments called Vickers micro hardness tester. The formulated ICAs joint with copper board (PCB) in this study was investigated by drop test. Besides, thermal aging experiment were conducted for investigate the effect of the temperature and humidity response to the formulated ICAs.

3.4.1 Vickers micro hardness test of ICAs

The Vickers hardness test was developed in 1921 by Robert L. Smith and George E. Sandland. One of the uniqueness of the Vickers test is that the calculations of the hardness are independent of the size of the indenter. This in return enables the indenter to be used for wide range materials irrespective of the hardness. The underlying principle in the measurement of the hardness of a particular material is to understand the ability of material to resist plastic deformation from a standard source which in this case the indenter. The unit of hardness given by the test is known as the *Vickers Pyramid Number (HV) or Diamond Pyramid Hardness (DPH).*

Manufacturer for the Vickers micro hardness tester is *CV instrument* and the standard were EN-ISO 6507 and ASTM E384, Figure 3.8 showed the Vickers micro hardness tester that used to studies the hardness of the formulated ICAs.

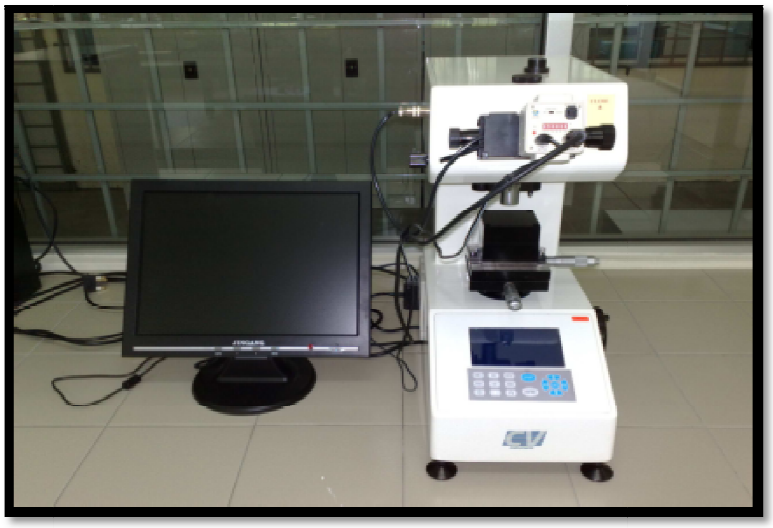

Figure 3.8 Vickers Micro Hardness Tester.

Regarding to the Vickers micro hardness indenter, it was decided that the indenter shape should be capable of producing geometrically similar impressions, irrespective of size, the impression should have well-defined points of measurement, and the indenter should have high resistance to self-deformation. A diamond in the form of a square-based pyramid satisfied these conditions. It had been established that the ideal size of a *Brinell* impression was 3/8 of the ball diameter. As two tangents to the circle at the ends of a chord 3d/8 long intersect at 136°, it was decided to use this as the included angle of the indenter, giving an angle to the horizontal plane of 22° on each side. The angle was varied experimentally and it was found that the hardness value obtained on a homogeneous piece of material remained constant, irrespective of load (UK Calibrations.co.uk, 1924).

The HV number is then calculated by the ratio *F/A* where *F* is the force applied to the diamond in kilograms-force and *A* is the surface area of the resulting indentation in square millimetres. *A* can be determined by the formula given:

$$A = \frac{d^2}{2 \sin (136^0/2)} \quad (4)$$

Which can be approximated to,

$$A \approx \frac{d^2}{1.8544} \quad (5)$$

Where *d* is the average length of the diagonal left by the indenter in millimetres. Hence,

$$HV = \frac{F}{A} \approx \frac{1.8544F}{d^2} \quad (6)$$

Where F is in kgf and d is in millimetres.

From equation (4), (5) and (6) above, *d* was the length measured from the mark which in square in shape created by the Vickers micro hardness indenter when force, *F* applying on the surface of the measured material through indenter. From Figure 3.9, side view shown the schematic of the indenter applying force on the surface of material, and the upper view shown square mark with d_1 and d_2 created by the indenter. From equation (4), (5) and (6), d^2 was the product of multiply d_1 and d_2. The indenter load in term force, F applying on the tested specimen in this study was set to 25 kgf.

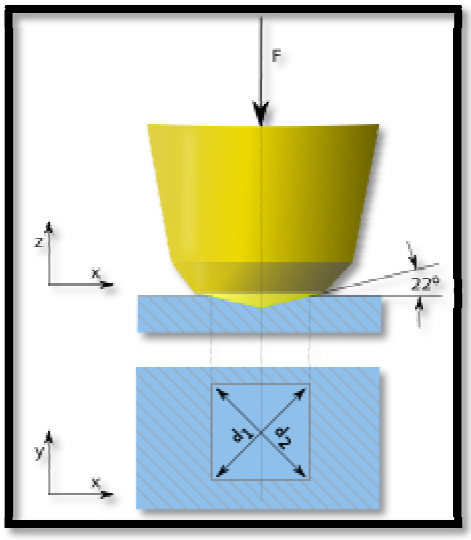

Figure 3.9 Schematic of indenter and square mark.

From the explanations above, the hardness value can be calculated manually by using formula (4), (5) and (6), since d_1 and d_2 obtained. As an alternative way, the hardness reading can be taken from screen on the Vickers micro hardness machine when measuring the hardness of ICAs. Hardness reading taken from the Vickers micro hardness machine was preferred to save time and avoid calculation error. The results and finding of the ICAs hardness in unit's HV were reported in following chapter.

3.4.2 Specimen preparation for Vickers micro hardness test

Before undergoing for the hardness test, specimen for this test must gone through mounting process for keeping the substrate help up straight and have a flat surface for hardness measuring process. Figure 3.9.1 shows the powder that is used in the preparation for the mounting of specimen. The mounting process of specimen was according to ASTM E3-11.

Figure 3.9.1 Powder for specimen mounting.

Formulated ICAs were arrange in sandwich form and then cured in the curing furnace for 60 minutes under specific temperature and gone through the specimen mounting process.

Sandwich form mean two copper plates at two side and ICAs in the middle like Figure 3.9.2 showed. The benefits arrange the formulated ICAs in sandwich form were minimizing the air bubble (voids) in the ICAs and save materials because only small amount of ICAs needed arrange in this sandwich form. Air bubble/voids in the ICAs will degrade the mechanical performance of ICAs as showed in Figure 3.9.3.

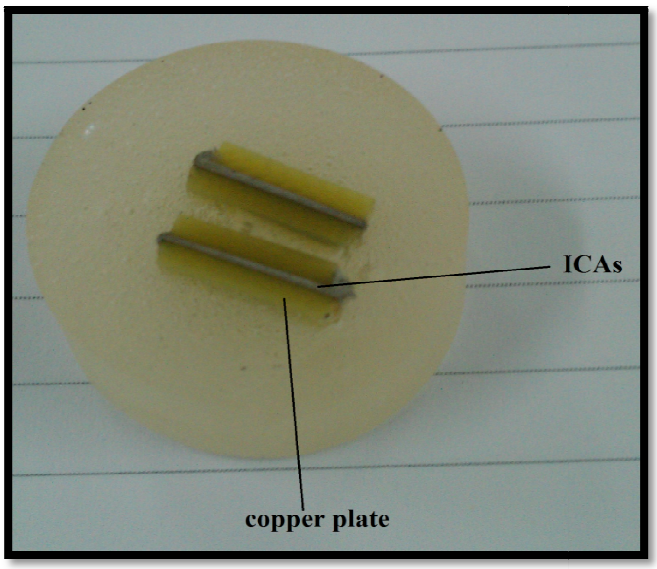

Figure 3.9.2Mounted specimen in sandwich form.

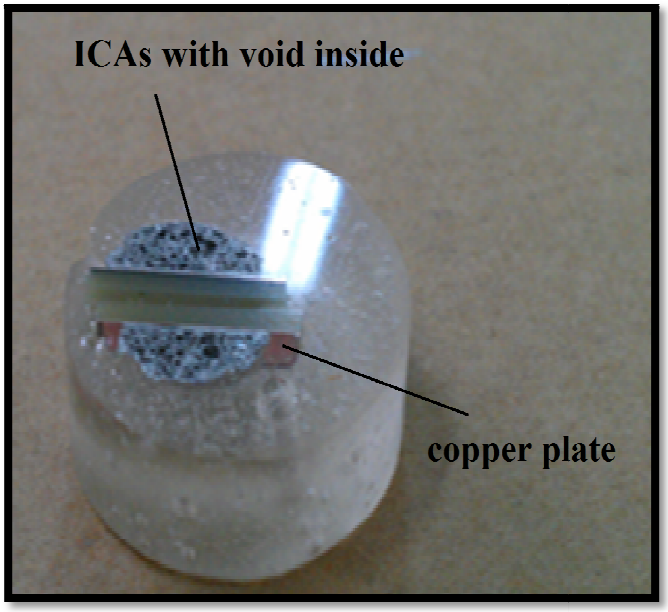

Figure 3.9.3 Mounted specimen with voids inside.

Mounted specimen were grinding and polishing by grinder in order to obtain flat and uniform surface for Vickers micro hardness measurements. Mounted specimen showed in Figure 3.9.2 was ready for the Vickers hardness test. Results and finding were reported on following chapter.

3.4.3 Drop test of ICAs

In this studies, drop test of the formulated ICAs was carried out to investigate the impact performance of the ICAs joint with the printed circuit board (PCB). The drop test was design by the National Center for Manufacturing Sciences (NCMS), United States. The purpose of the test is to simulate the influence of impact on electronic products.

The setup of the drop test is relatively simple, as shown in Figure 3.9.4. The sample which consists of cured conductive adhesives on copper substrates is dropped onto a hard surface from a height of 1.5 m. This test will be repeated 6 times to ensure repeatability of the results.

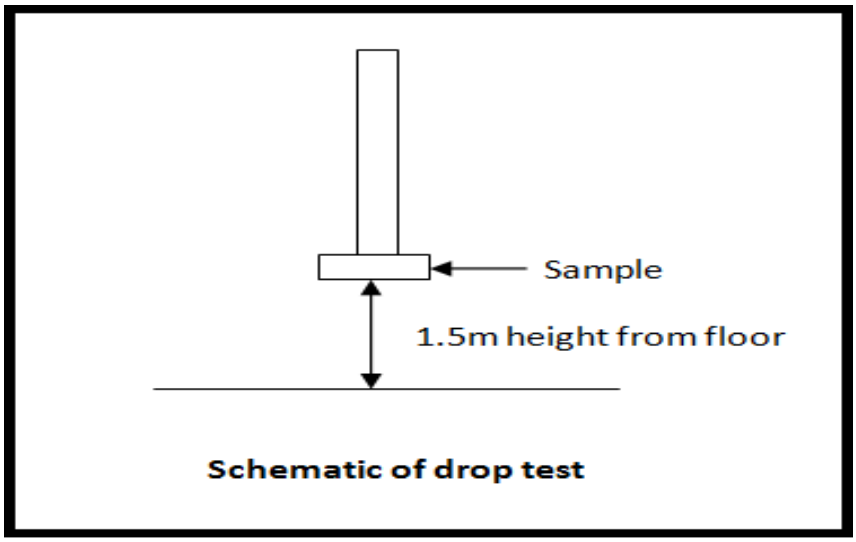

Figure 3.9.4 Schematic of the drop test.

3.4.4 Specimen preparation for Drop Test

Formulated ICAs were printed on PCB and cured in the curing furnace for 60 minutes under specific temperature. The PCB adherents' had dimensions of 120 x 120 x 1.2 mm. A sample of the PCB that used in this drop test was showed in Figure 3.9.5. The formulated ICAs were printed on the PCB as showed in Figure 3.9.6.

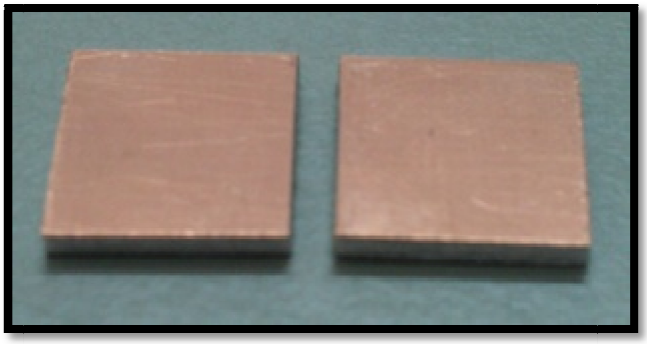

Figure 3.9.5 Sample of PCB for drop test.

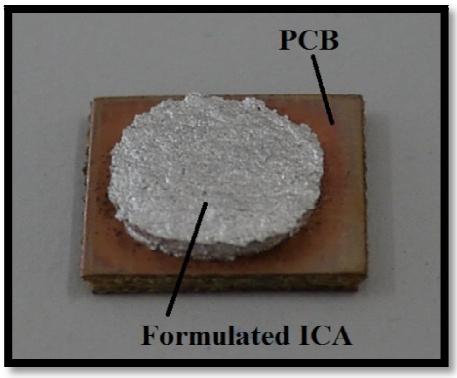

Figure 3.9.6 ICA printed on the PCB.

The same stencil printing techniques on previous section 3.3.1 were used on specimen preparation for drop test. The different in this stencil printing process compare to previous section is the formulated ICAs were printed on square shape PCB with dimension 120 x 120 x 1.2 mm (width, length ,thickness) for drop test studies, while the ICAs printed on the test vehicle board on section 3.3.1 is for electrical resistivity studies.

Specimen showed in Figure 3.9.6 was ready for the drop test experiment. The experiment was started by dropping the drop test specimen from 1.5m from the floor onto hard surface and the condition of specimen was observed. Drop test results were divided into two conditions, pass or fail. The condition of pass and fail were shows in Table 3.6.

Each specimen must gone through six drops for this experiment, and any of the drop meet the fail condition, no further drop for the specimen, the specimen consider fail in the drop test results. Either the specimen passing all the six drop and meet the requirement of pass condition, the specimen consider pass in the drop test results.

Table 3.6 Condition of pass and fail for drop test experiment.

Condition of results	
Pass	**Fail**
1. Tested specimen without popping out from PCB.	1. Tested specimen popping out from PCB.
2. Without crack or fracture on tested specimen.	2. Crack or fracture on tested specimen.

The results for drop test were reported in percentage of failure, eight specimens for each system were prepared for the drop test experiment. The formula used to calculate the percentage of failure given by:

$$\text{Percentage of failure} = \frac{\text{Number of specimen fail}}{\text{Total specimen}} \times 100\% \qquad (7)$$

From equation (7) above, number of specimen fail represent to total amount of fail specimens in the drop test experiment. For example, three of the specimens fail out of total eight specimens. Therefore, percentage of failure for the specimen tested was 37.5%.

3.4.5 Thermal Aging of ICAs

Thermal aging on the selected formulated system was conducted to investigate the electrical and mechanical stability properties upon exposure to environmental aging conditions, such as elevated temperature and humidity aging. In these studies, selected formulated ICAs were aged on a curing furnace for 600 hours under condition 85^0C and 85% RH.

Selection on formulated systems for the thermal aging experiment were based on the electrical resistivity of the system, only three lowest resistivity systems had been chosen from the overall system. System 1, 2 and 6 were selected for the thermal aging experiment because showing the lowest resistivity among entire system in this study. The selected systems were prepared in the required specimen for mechanical and electrical test, and cured in the furnace under condition of 220^0C. The mechanical and electrical measurements of selected systems for non-thermal aging were taken and proceed to thermal aging process.

The mechanical and electrical properties of the aged ICAs was measured for every 100 hours until 600 hours. The mechanical properties were measured through the Vickers hardness test and electrical properties were measured by the four point probes. The measurement methods were mention in previous section. The measurements taken during the thermal aging process were plotted in graph form for comparisons purpose. The results and discussions of the

thermal aging process were reported on the chapter 4.

CHAPTER 4

4.0 RESULTS AND DISCUSSION

4.1 Results and discussion (Electrical conductivity studies on conventional ICAs and MWCNTs based ICAs.)

4.1.1 Effect of bulk resistivity on curing temperature of ICAs

In order to determine a suitable curing temperature, the formulated sample labelled as system 1, system 2 and system 6 was cured at 180 ^{0}C, 200 ^{0}C, 220 ^{0}C, and 240 ^{0}C, the bulk resistivity was measured respectively, as showed in Figure 4.1, Figure 4.1.1 and Figure 4.1.2. Result in Figure 4.1 shows that curing temperature for system 1 at 220 ^{0}C obtained the lowest bulk resistivity when compared with other curing temperatures. This indicates that curing temperature, 220^{0}C is the critical curing temperature for this system which attained at 60wt% of silver flakes.

System 2 was formulated with 20wt% of DGEBA and 80wt% of silver flakes. From Figure 4.1.1, it showed that 200 ^{0}C is the critical curing temperature for this system. The lower bulk resistivity was achieved due to higher concentration of silver flakes.

System 6 was formulated with 40wt% of DGEBA, 57wt% of silver flakes and 3 wt% of MWCNTs. Based on Figure 4.1.2, the critical curing temperature of 220 ^{0}C obtained lowest bulk resistivity for system 6 which is similar to system 1. This shows that the bulk resistivity for ICAs is strongly influenced by the volume fraction of filler material added to the polymer resin in ICAs. The lower bulk resistivity obtained in system 6 could be due to the present of MWCNTs.

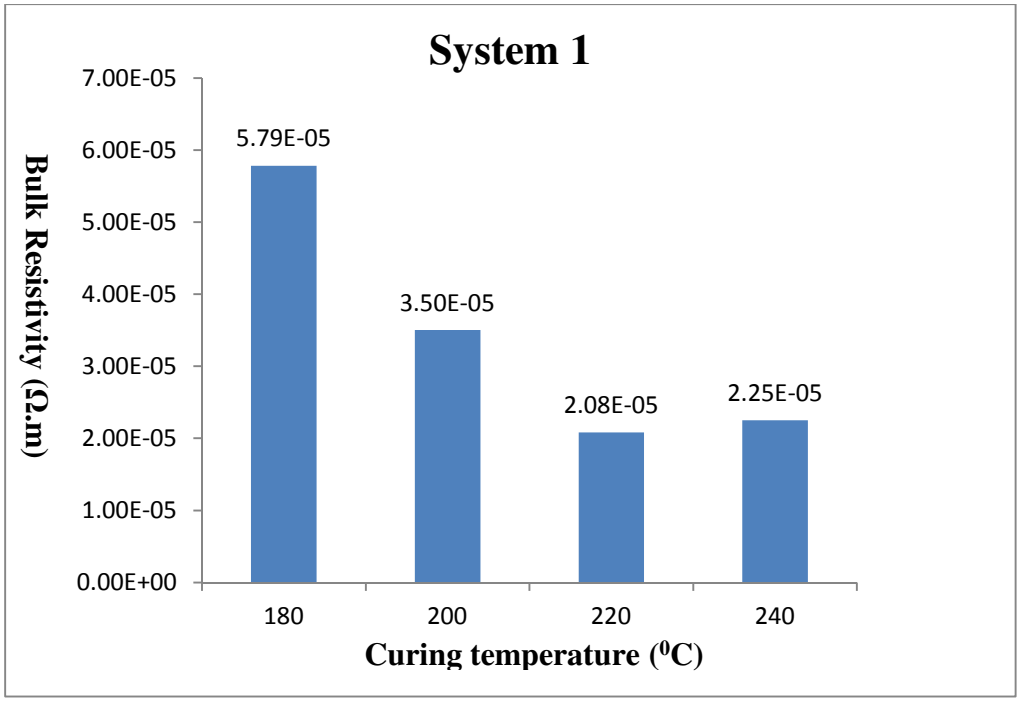

Figure 4.1 System 1 cured under curing temperature of 180 ^{0}C, 200 ^{0}C, 220 ^{0}C, and 240 ^{0}C.

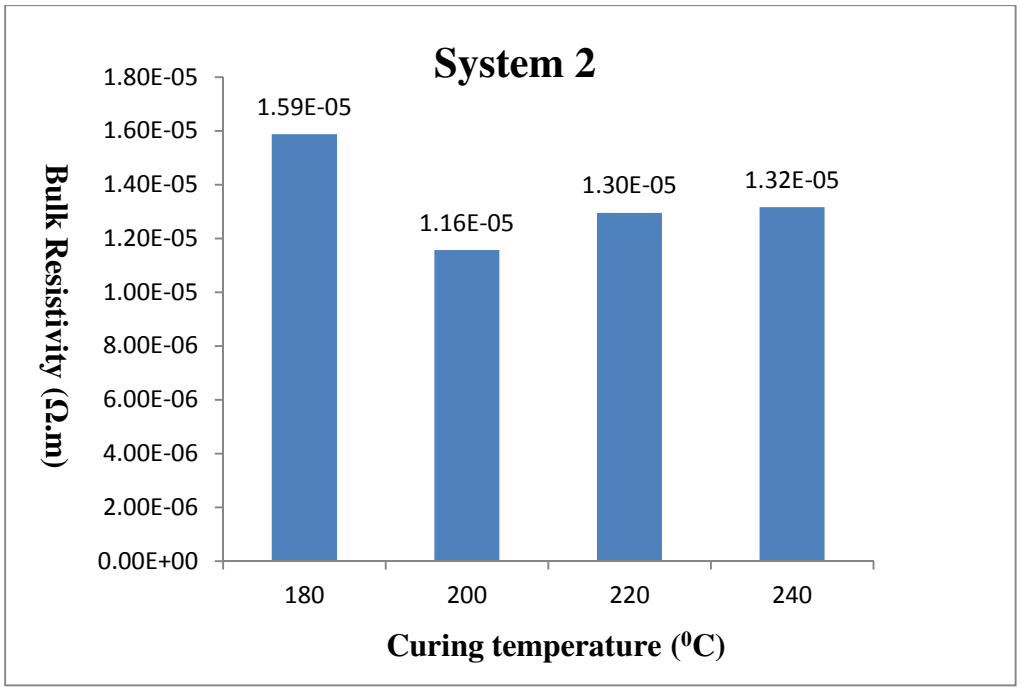

Figure 4.1.1 System 2 cured under curing temperature 180 ^{0}C, 200 ^{0}C, 220 ^{0}C, and 240 ^{0}C.

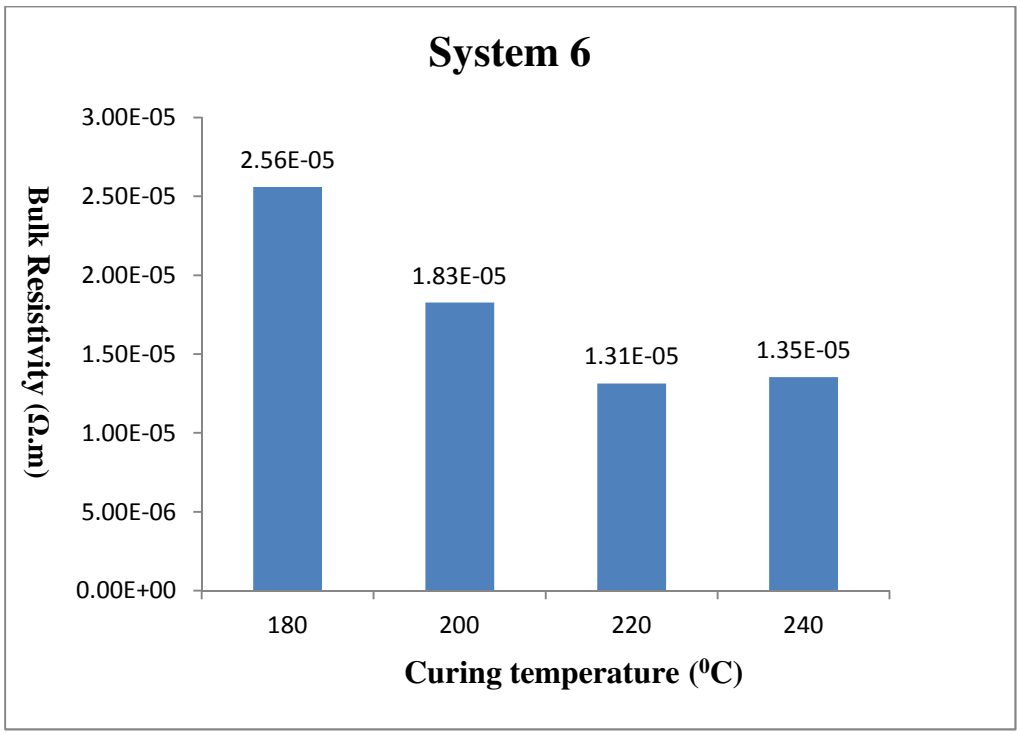

Figure 4.1.2 System 6 cured under curing temperature 180 ^{0}C, 200 ^{0}C, 220 ^{0}C, and 240 ^{0}C.

4.1.2 Effect of reinforcing silver flakes with nano-sized silver particles on bulk resistivity in ICAs

In this study, small percentages of main conductive filler (silver flakes) were replaced by the secondary conductive filler (silver nano-particles). This was done to investigate the effect of silver nano-particles on the bulk resistivity of ICAs. By refer to Table 3.4 in section 3.3. System 3, 4 and 5 were formulated by replaced silver flakes with silver nano-particle at different size of nano-particles, system 3 was replaced silver flakes by 6wt% of silver dispersion nano-particles with size 10 nm. System 4 was replace silver flakes by 6wt% of silver dispersion nano-particles with size 20 nm while system 5 was formulated by replaced silver flakes by 6wt% of synthesised silver nano-particles with size of 10~20 nm.

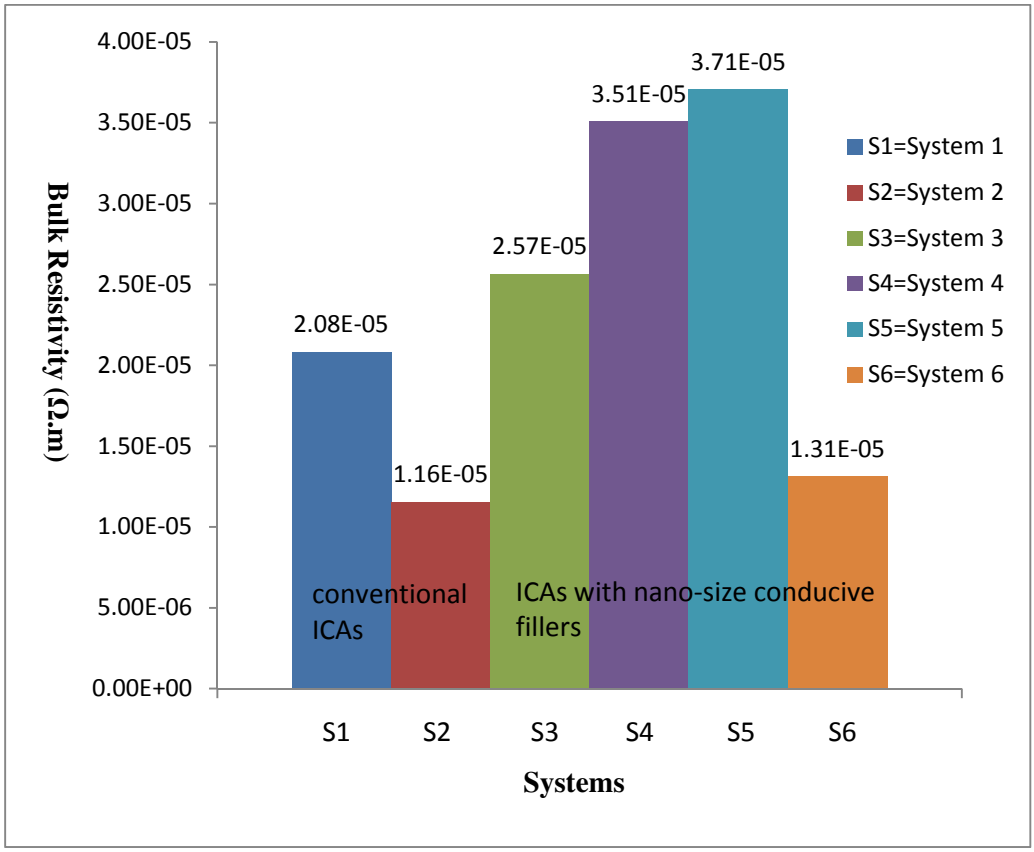

Figure 4.1.3 Comparisons of bulk resistivity with different systems.

Based on Figure 4.1.3, system 1 and system 2 were conventional ICAs which the bulk resistivity was benchmarked against to system 3, system 4, system 5, system 6, and system 7a to system 7j. System 1 which is a conventional ICAs shows higher bulk resistivity if compared to system 2, the reason is the volume fraction of silver flakes in system 1 is 60wt% meanwhile the volume fraction of system 2 is 80wt% .

System 2 (conventional ICAs) shows the lowest bulk resistivity compared to others system, because the volume fraction of conductive filler in this system is 80wt%. The conductivity of the ICA depends on the volume fraction of the conductive filler. High volume fraction of conductive filler (silver flakes) could lead to high concentration of conductive filler in ICAs which displacement of silver flakes very close to each other's thus, conductive path in ICAs was easily formed and lower the bulk resistivity.

System 3 consist 54% silver flakes and 6% silver nano-particles. Based on Figure 4.1.3, system 3, 4 and 5 showed a higher resistivity compare to the conventional ICAs system 1. It should be noted that system 3, 4 and 5 were compared with system 1, because the total conductive filler is 60wt% of conductive filler whereas system 2 contained 80wt% of conductive filler. It was found that silver nano-particles increased the bulk resistivity of ICAs significantly by contributed the contact resistance between the particles in ICAs. The addition of nano-particles may help to fill the voids between the silver flakes but it could also increase the contact points between the silver

nano-sized particles/particles and particles/silver flakes contributing to an increase in the resistivity.

Based on Figure 4.1.3, bulk resistivity showed an increasing trend for system 3, 4, and 5. This phenomenon could be due the size of silver nano-particles were increasing. 10 nm for system 3, 20 nm for system 4 and system 5 with 10~20nm. This shows that bulk the resistivity of the systems strong influence by the particle size. For system 5 which formulated with synthesized silver nano-particles, it show higher bulk resistivity if compared to system 1 and system 2. Possible reason is silver nano-particles for system 1 and 2 is commercial used silver nano-particles while silver nano-particles in system 5 are chemical synthesized in the lab with different processing conditions. In addition, the presence of wide range of particle size distribution could have also contributed to the higher resistivity.

System 3 which showed the lowest bulk resistivity within the three systems, the possible reason is silver nano sized-particles surfaces are diffused into another during the curing process. The diffusion of the particles ultimately reduces the contact point thus creating network of diffused silver nano-sized particles throughout the whole conductive adhesives. In a study by Jiang et al. (2006) found that the surface diffusion or sintering could be achieved for the silver nanoparticles during the curing process. This will however depend on the size of the silver nanoparticles. As a result, the particle to particle contact point

which contributes to the increase in bulk resistivity as previously reported could be reduced as illustrated in Figure 4.1.4 (a)-(c).

For system 4 and 5, the sintering process of silver nano-particles might not occur as much as in system 3 thus showing a higher bulk resistivity. In this study, it was noticed that when the size of the silver nano-particles increased, the bulk resistivity of ICAs increase slightly. Based on the finding above, it is believed that the sintering behavior of silver nano-particle is strongly influence by the size of the silver-nano-particle which will reduce the contact resistance in ICAs.

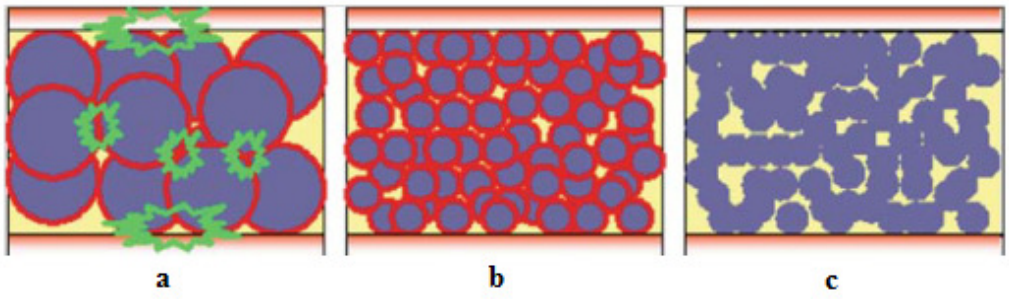

Figure 4.1.4 Schematic illustrations of particles between the metal pads (Jiang et al 2006).

System 6 was formulated by replacing silver flakes with 3 wt% of MWCNTs. It was found that system 6 showed a lower bulk resistivity if compare to system 1. System 1 showed 2.08 x 10^{-5} Ω·m in bulk resistivity reading and system 6 showed 1.31 x 10^{-5} Ω·m in bulk resistivity reading, this is 37% lower in bulk resistivity after replace 3wt% of silver flakes with MWCNTs. This is totally different to the silver nano-particle which increases the bulk resistivity of ICAs. Figure 4.1.5 showed an electron micrograph image of MWCNTs. The

MWCNTs looks similar to a polymer entangled chain, which could enhance the overall connectivity of the silver flakes in the ICAs.

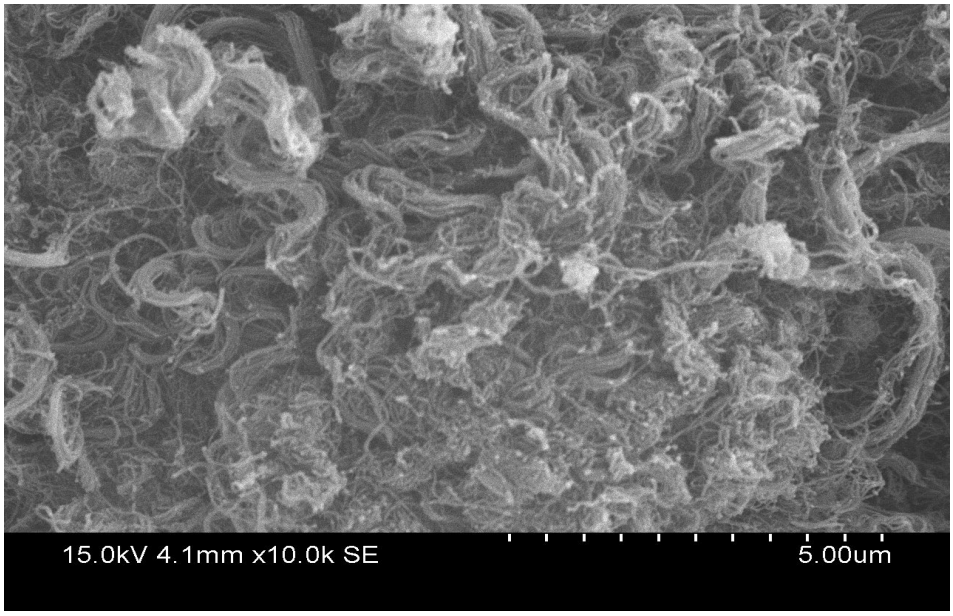

Figure 4.1.5 SEM image of MWCNTs.

4.1.3 Effect of different volume fraction of MWCNTs to bulk resistivity of ICAs

Different volume fraction of MWCNTs from 0.3wt% until 3.0wt% was added to replace silver flakes in order to study the effect on electrical properties of ICAs. The detail about the composition of system 7 was listed in Table 3.5 in chapter 3. In overall, there were ten systems labelled from 7a to 7j. The measured bulk resistivity reading from system 7a to system 7j were presented in Figure 4.1.6. Based on Figure 4.1.6, the bulk resistivity reading showed a decreasing stage from system 7a to system 7b and then start showed an increase from system 7b to system 7e, and followed by a decrease from system

7e to system 7j. Based on the data collected, it was found that, system 7e which contained 1.5wt% of MWCNTs showed highest bulk resistivity. While system 7j contained 3.0wt% of MWCNTs showed the lowest bulk resistivity in these studies. A study by Wu et al. (2009) stated that when CNT included, ECA sample attains a better electrical conductivity around 1wt%. After 1wt%, the resistivity increases with an increase of CNT concentration.

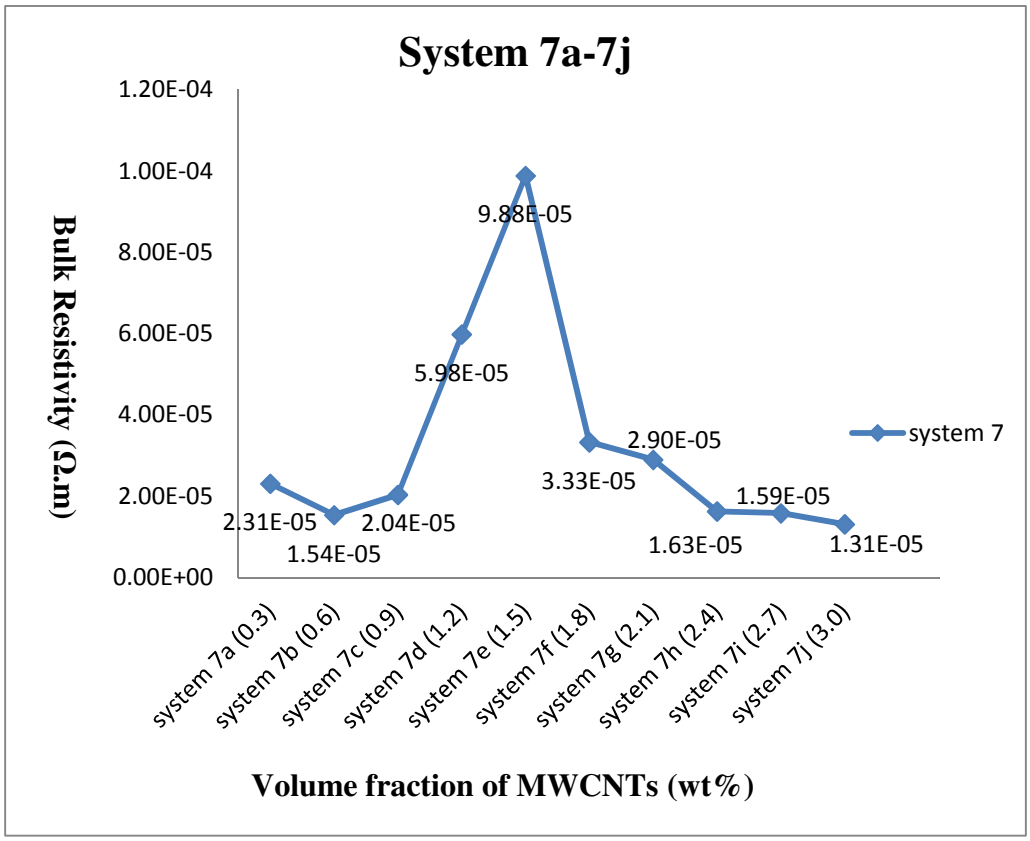

Figure 4.1.6 Bulk resistivity versus different volume fraction of MWCNTs.

When MWCNTs are included in ICAs, concentration is within 0.3 wt% to 0.6wt % (system 7a to system 7b), MWCNTs can provide a connection complementary to the silver flakes, thus decease the bulk resistivity in ICAs as

showed in Figure 4.1.7 (a). But negative effect showed with high MWCNTs concentration 0.9wt % - 1.5wt % (system 7c to system 7e), agglomeration of MWCNTs may occur in ICAs, which leads to a disconnected channel and cause the increase in bulk resistivity.

Possible reason for the phenomenon above is the amount of MWCNTs agglomeration could affect the bulk resistivity in ICAs, for system 7c to system 7e, the agglomerated of MWCNTs just started occur within this level, so it can be said that agglomerations of MWCNTs might be few at this level of concentration. The agglomerated MWCNTs particles broke the conductive path in ICAs thus increase the bulk resistivity as showed in Figure 4.1.7 (b). On the contrary, when large amount of agglomeration of MWCNTs for system 7f to system 7j, the agglomerated MWCNTs particles could form another conductive path in ICAs and help to decrease in bulk resistivity. From the finding above, it was found that, only within a certain percentage of MWCNTs volume fraction in ICAs could help in reduce the bulk resistivity. Bulk resistivity was decreasing after reached highest bulk resistivity at system 7e (1.5wt % MWCNTs). As showed in Figure 4.1.7 (c), when MWCNTs concentration from 1.8wt%- 3.0wt % (system 7f to system 7j), an decreasing stage in bulk resistivity reading was obtained, the possible reason is the agglomerated MWCNTs in ICAs get connected to each other's and decreased bulk resistivity .

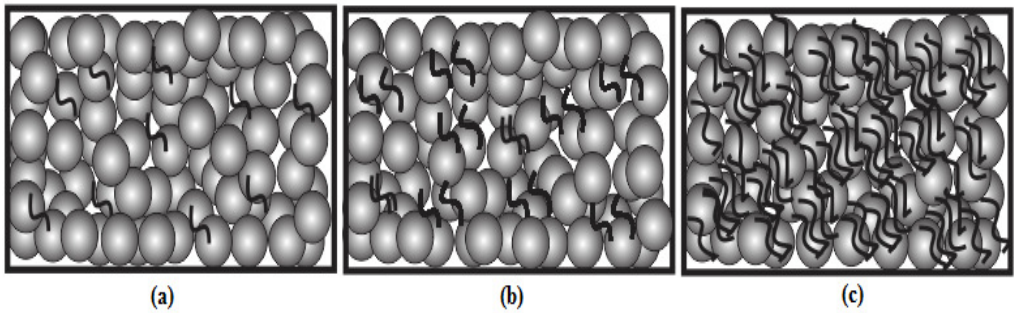

Figure 4.1.7 Schematic illustrations of MWCNTs and silver particles in ICAs. The black string represent to MWCNTs and the grad color solid ball represent to silver flake in ICAs.

4.2 Results and discussion (Mechanical properties of conventional ICAs and MWCNTs based ICAs.)

4.2.1 Vickers micro-hardness study on formulated ICAs

All the formulated ICAs were tested by Vickers micro hardness tester in these studies. For more details about the system formulation please refers to Chapter 3, Table 3.3, Table 3.4 and Table 3.5. The data collected was reported in units *(HV) Vickers Pyramid Number* and showed in Figure 4.2 for comparisons purpose.

Hardness tests of the formulated ICAs in this study were investigated by an instrument called Vickers micro hardness tester. Hardness has defined as "Resistance of metal to plastic deformation", usually by indentation. However, the term may also refer to stiffness or to resistance to scratching, abrasion, or cutting. It is the property of a metal, which gives it the ability to resist being permanently, deformed (bent, broken, or have its shape changed), when a load is applied. The greater the hardness of the composites, the greater resistance it has to deformation.

Based on Figure 4.2, Vickers micro hardness reading of system 1 and system 2 (conventional ICAs) were benchmark against to system 3, 4, 5, and 6 which contained nano-sized silver particle and MWCNTs.

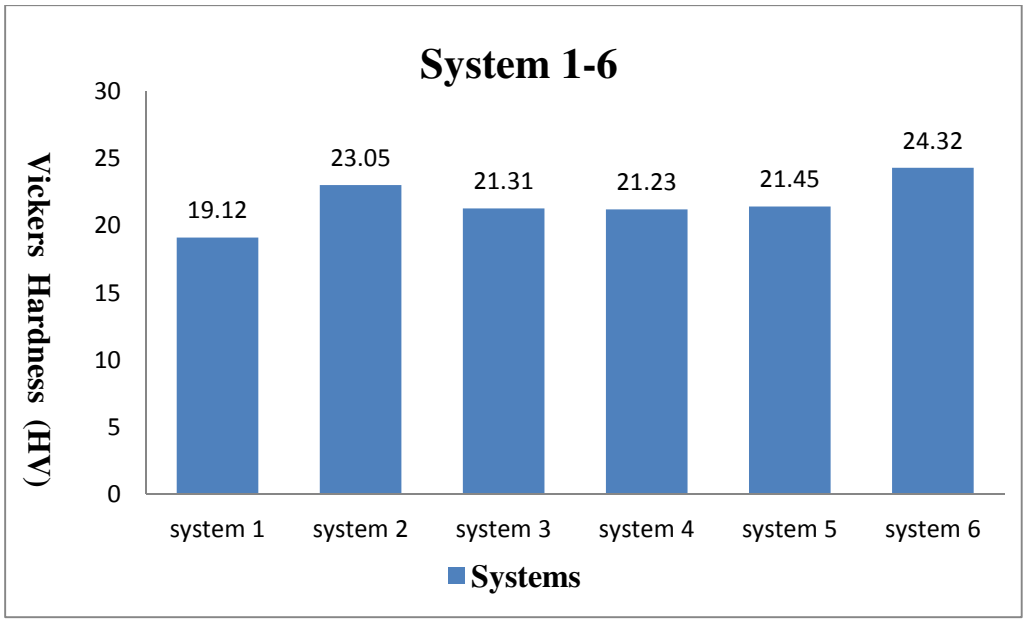

Figure 4.2 Vickers micro hardness results for different systems.

Hardness reading was related to the metal particles displacement in specimen, Figure 4.2 shows that the conventional ICAs system 2 (23.05HV) having higher reading than system 1 (19.12HV), because system 1 only contained of 60wt% of metal filler as shows in schematic illustrations, Figure 4.2.1 (a). System 2 consists of 80 wt% metal filler as shows in schematic illustrations Figure 4.2.1 (b). Lower filler concentration produced the lower hardness reading due to the majority area on specimen tested consists of polymer resin (DGEBA). The presence of polymer chain in system 1 (due to lower filler concentration) provided a better resistance to plastic deformation.

For system contained nano-sized silver particles, system 3, system 4 and system 5, hardness reading showed almost the same in this studies. System that contained nano-sized silver particles show slightly higher hardness reading if compare to the conventional ICAs system 1. The possible reason regarding to

this phenomena is the nano-sized particles had disintegrated well into interstitial of large particles (silver flake) as shows in Figure 4.2.1 (c). It was found that system that contained nano-sized silver particles performed better hardness reading in these studies.

Besides, it was also noticed that, the sized of the nano-size silver particles in the tested ICAs doesn't really affect the hardness reading of ICAs. For system 3, 6 wt% of silver flakes was replaced by 10 nm silver particles, system 4 which are 6wt% silver flakes replaced by 20 nm silver particles, and system 5 are 6wt% of silver flakes replaced by 10-20 nm silver particles, These three systems did not showed big changes in hardness reading. Based on Figure 4.2, hardness reading of system 3, 4 and 5 was almost the same, from the finding above; it can be conclude that the size of the silver particles in nano range did not bring huge effect to the hardness reading of ICAs.

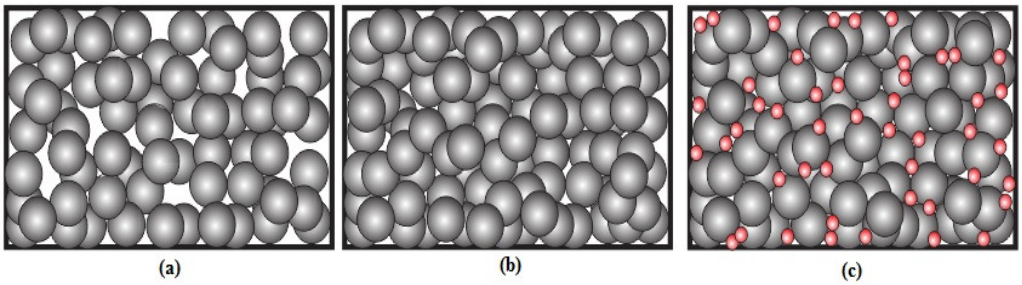

Figure 4.2.1 Schematic illustrations of silver flakes and nano-sized silver particles in ICAs.

Schematic illustrations, Figure 4.2.1 (a) and (b) showed, the gray in color solid ball represent to silver flakes and small sized solid ball in Figure 4.2.1(c) represent to nano-sized silver particles in ICAs.

For system 6 which contained of 3wt % of MWCNTs and 57wt% of silver flakes, showed the higher hardness reading among all the system tested. The hardness reading of system 6 was comparable with system 2 which contained of 80wt% of metal filler. Furthermore, compared system 1 which contained of 60wt% of silver flakes with system 6, it was found that 27.2% increased in hardness reading after replaced only 3wt% silver flakes by MWCNTs in ICAs. It is strongly believed that the MWCNTs function like a web in ICAs to grab the silver flakes around to closer the particles displacement, thus showed higher hardness reading. Based on the results in Figure 4.2, it can be conclude that system 6 having the higher ability to resist plastic deformation.

4.2.2 Effect of different volume fraction of MWCNTs in ICAs to Vickers micro hardness results

Formulated ICAs that contained MWCNTs were tested in these studies. The volume fraction of MWCNTs was increased from 0.3wt% to 3.0wt% and 0.3 wt% per increment in order to investigate the effect of different volume fraction of MWCNTs in term of hardness reading. For more detail about the system formulation in this section please refer to Chapter 3, Table 3.5. Totally ten system (system 7a-system 7j) was tested by Vickers micro hardness tester in these studies. The data collected was reported in units *(HV) Vickers Pyramid Number* and plot into chart in Figure 4.2.2.

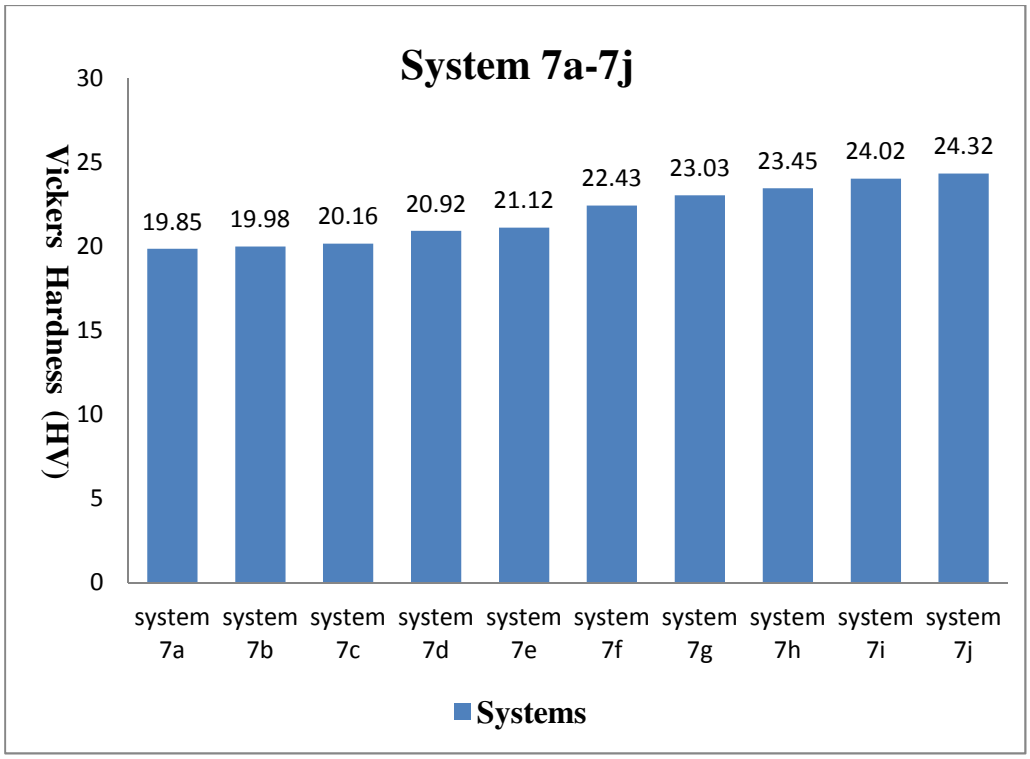

Figure 4.2.2 Vickers micro hardness results for different volume fraction of MWCNTs.

Based on Figure 4.2.2, it was found that hardness reading for system 7a to system 7j increased when loading/volume fraction of MWCNTs increased. As the volume fraction of MWCNTs is increased the hardness reading of formulated ICAs increased gradually.

Based on Figure 4.2.2, it was found that when concentration MWCNTs in ICAs reached 2.1wt% (system7g), the hardness reading (23.03HV) was already compatible with system 2 (23.05HV) which formulated by 80wt% metal filler and 20wt% epoxy resin. Furthermore, when MWCNTs concentration reached 3.0wt% (system 7j), it showed 5% exceed in hardness value compared to system 2. Base on the explanation above, it can be conclude that ability to resist plastic deformation increased when the loading of MWCNTs increased.

4.2.3 Drop test study on formulated ICAs

The impact performance of cured conductive adhesives was tested by using drop test. The results of drop test was converted in percentage of failure and reported in this section. As mentioned in chapter 3, Section 3.5.4, eight specimen of each system was prepared for drop test experiment, and the formula to calculate the percentage of failure is given by:

$$\text{Percentage of failure} = \frac{\text{Number of specimen fail}}{\text{Total specimen}} \times 100\%.$$

Where *number of specimen fail* represent to total number of failure out of eight specimens. Results of drop test were calculated and list in Table 4.1. For more detail regarding to system composition please refer to Chapter 3, Table 3.4, Table 3.4 and Table 3.5.

Table 4.1 Drop test results in table form for formulated ICAs.

Number of test	System 1	System 2	System 3	System 4	System 5	System 6
1st test	/	x	/	/	/	/
2nd test	/	/	/	x	/	/
3rd test	/	/	/	/	/	/
4th test	x	x	x	/	/	/
5th test	/	/	/	/	/	/
6th test	/	/	/	/	/	/
7th test	x	x	/	/	x	/
8th test	/	x	/	/	/	/
Percentage of failure	25.0%	50.0%	12.5%	12.5%	12.5%	0 %

The symbol represent pass and fail condition in drop test was given by following:

Table 4.2 Pass and fail symbol.

Pass and fail symbol	
x	Split (fail)
/	Attach (pass)

For more detail about condition of pass and fail please refer to Chapter 3, Table 3.6. Table 3.6 clearly stated the condition of pass and fail in drop test experiment.

Based on Table 4.1, system 2 which formulated by 80wt% metal filler and 20 wt% of epoxy resin showed the highest in percentage of failure based on drop test experiment. Based on the results above, weight percentage of epoxy resin (DGEBA) plays an importance role to increase the impact performance of ICAs. This is because characteristic of polymer resin (DGEBA) could contribute to adhesion between ICAs and PCB and avoid cracking in ICAs. Referring to previous study from Kotthaus et al. (1997) mentioned the approach of reducing the filler loading in order to improve the impact strength.

Based on the observation during the drop test experiment, most of the failure case in tested specimens was cracking between ICAs. Figure 4.2.3 shows the image of specimen which failed the drop test experiment.

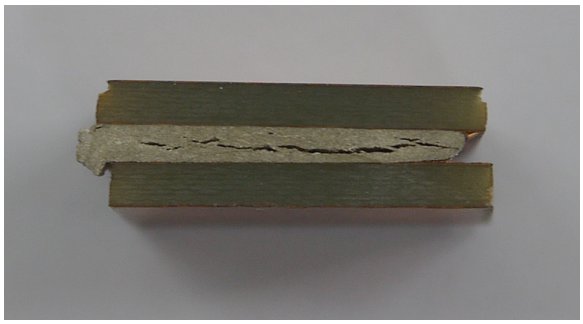

Figure 4.2.3 Image of unqualified specimen.

For system 1, which formulated by 40wt% of epoxy resin (DGEBA) and 60wt% of silver flakes, showed lower percentage of failure compared to system 2. This reasonable result obtained because the weight percentage of epoxy resin (DGEBA) in system is 60wt% while system 2 only contained of only 20wt% of epoxy resin (DGEBA).

Based on the drop test results, it was noticed that when nano-sized silver particle included in ICAs (system 3, system 4 and system 5), percentage of failure was lower compared to conventional ICAs (system 1). From the results, it can conclude that system that contained nano-sized silver particles showed a better impact strength compared to conventional ICAs. Previous study by Kotthaus et al. (1997) stated that nano-sized metal particles used in ICAs were improved the mechanical (impact) strength.

On the other hand, for the system 6 that contained 3wt% MWCNTs, the drop test results showed zero percentage of failure in drop test experiment. The results showed that MWCNTs able to improve the impact performance of ICAs. The possible reason is the addition of MWCNTs form a stronger network with epoxy resin and could absorb energy when ICAs drop on floor. Besides it is also strongly believed that MWCNTs could stop the movement of silver flakes (chain) during the drop test, thus showed better impact performance.

Figure 4.2.4 Image of qualified specimen.

With respect to system 6, based on the observation during the drop test experiment, image in Figure 4.2.4 was taken, there is no crack or split between the ICAs and PCB for the entire specimen tested. The drop test results for system 6 indicated that the fixed amount, 3wt% MWCNTs able improved the impact strength to zero percentages of failure, the following section will investigate about effect of different volume fraction of MWCNTs to impact strength .

4.2.4 Drop test study on different volume fraction of MWCNTs in ICAs

In previous section, MWCNTs were proven able to improve the impact performance to zero percentage of failure. This section will study about effect of different volume fraction of MWCNTs to drop test results. Volume fractions of MWCNTs were increased from 0.3 wt% to 3 wt% and 0.3 wt% per increment in order to investigate impact performance with different volume fraction of MWCNTs. The same formula in Section 4.2.3 was used to calculate the percentage of failure for formulated ICAs. Drop test results from system 7a to system 7j were listed in Table 4.3. For more detail regarding to system composition please refer to Chapter 3, Table 3.5.

Table 4.3 Drop test results in table form for system 7a to system 7j.

Drop test results										
Number of test	**System 7a**	**System 7b**	**System 7c**	**System 7d**	**System 7e**	**System 7f**	**System 7g**	**System 7h**	**System 7i**	**System 7j**
1st test	/	/	x	/	/	x	/	/	/	/
2nd test	/	/	/	x	x	/	x	/	/	/
3rd test	x	/	/	/	/	/	x	/	x	/
4th test	/	/	x	x	/	/	/	/	/	/
5th test	x	/	/	/	x	x	/	x	/	/
6th test	/	x	/	x	/	/	/	/	/	/
7th test	/	/	x	/	/	/	/	/	/	/
8th test	/	x	/	/	x	/	/	/	/	/
Percentage of failure	25.0%	25.0%	37.5%	37.5%	37.5%	25.0%	25.0%	12.5%	12.5%	0%

Based on Table 4.3, for system 7a and system 7b, the percentage of failure is similar with system 1, which is about 25 %. It can concluded that 0.3 wt% to 0.6 wt% MWCNTs does not affect the impact performance of ICAs. The low concentration of MWCNT does not alter the microstructural properties of the ICAs.

When volume fraction of MWCNTs increased to 0.9 wt% (system 7c), percentage of failure increased to 37.5%, similar results obtained when volume fraction of MWCNTs reached 1.2 wt% (system 7d) and 1.5 wt% (system 7e). Percentage of failure increased from 25% to 37.5% when MWCNTs volume fraction reached 0.9 wt% (system 7c), 1.2 wt % (system 7d) and 1.5 wt% (system 7e). This illustrate that within certain level volume fraction of

MWCNTs brings a negative effect to the impact performance of ICAs. This could be attributed the poor dispersion of MWCNT within the overall system. The low concentration of MWCNT is not sufficient to prevent localised movement between the silver flakes. Thus showed higher percentage of failure on drop test results when MWCNTs volume fraction 0.9 wt % - 1.5 wt % (system 7c - system 7e).

Based on Table 4.3, percentage of failure showed a decreased when MWCNTs volume fraction reached 1.8 wt% (system 7f) and above, and finally showed zero percentage of failure when volume fraction of MWCNTs reached 3.0wt%. Results above indicated that, with 1.8wt% or more volume fraction of MWCNTs, within this amount of MWCNTs, MWCNTs were able to prevent localised movement between the silver flakes hence reducing the percentage of failure.

4.3 Results and discussion (Thermal aging studies of ICAs)

As a solder replacement conductive adhesives must have stable properties between non-noble finished components during aging elevated temperature and humidity aging (Bailey and Stoyanov, 2004). The national center of manufacturing sciences (NCMS) set specifications for solder replacement adhesives, contact resistance shift should be less than 20% after 500 h 85°C/ 85% RH aging (Zwolinski et al., 1996).

Besides, in order to pro-long the service life of the ICAs in electronics devices, thermal aging process of ICAs under specific condition were studies, formulated ICAs was stored in a curing furnace under condition 85°C/85% RH for 600 hour in this project in order to study the effect of thermal aging process to mechanical and electrical properties of ICAs, for every 100 hours, the mechanical and electrical properties of ICAs was measured.

Only selected system will experience the thermal aging process in this study. System 1, system 2 and system 6 were chosen to proceed on thermal aging studies because those systems perform the lower bulk resistivity among all the system. System 1 and system 2 which is conventional ICAs and system 6 is ICAs reinforce by 3wt% MWCNTs. System 1 was formulated by 40 wt% of epoxy resin (DGEBA) and 60wt% of silver flakes, system 2 was formulated by 20wt% of epoxy resin (DGEBA) and 80wt% of silver flakes. For system 6, it was formulated by 40wt% epoxy resin (DGEBA), 57wt% of silver flakes and 3 wt% of MWCNTs as replacement for silver flakes.

4.3.1 Thermal aging studies on bulk resistivity of ICAs

Bulk resistivity of ICAs (system 1, 2 and 6) that experienced thermal aging process was measured by four point probes. This section will study about the effect of thermal aging to the bulk resistivity of ICAs. Measurements were taken for every 100 hours by four point probes, bulk resistivity reading of thermal aged specimens were plot into a graph (Figure 4.3, 4.3.1 and 4.3.2) for every 100 hours and study the changes of bulk resistivity during the thermal aging process. The smaller changes in bulk resistivity during the thermal aging process bring a good impression in electronics packaging process, electronics assembly process, reliability and modelling. It might also enhanced the lifetimes and prolong the shelf life of electronic devices in consumers side.

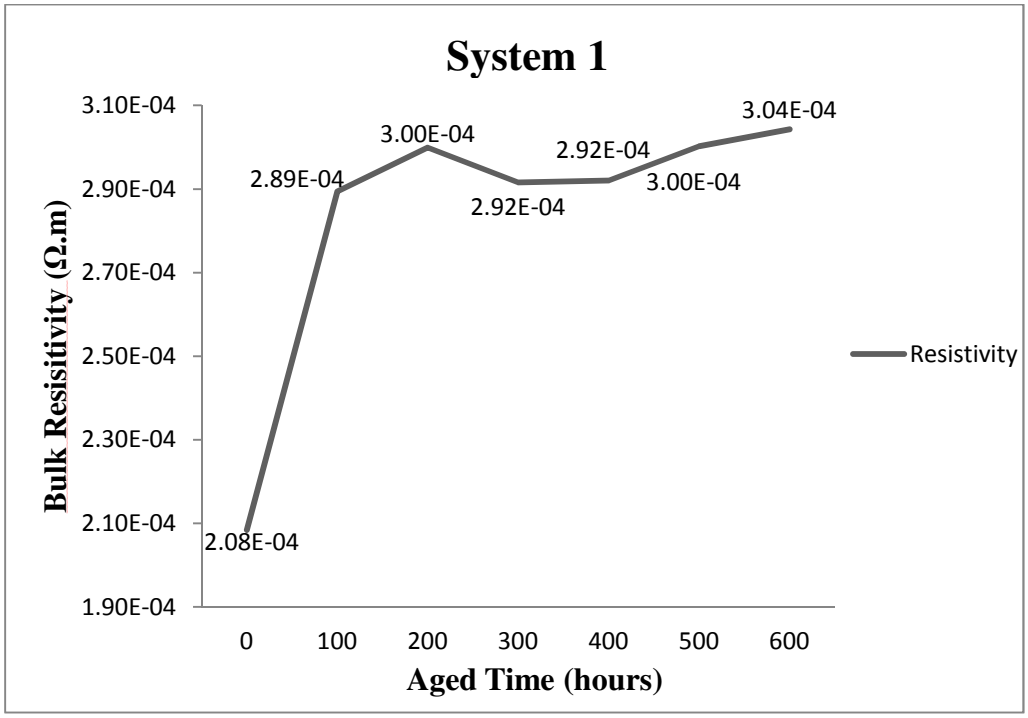

Figure 4.3 Bulk resistivity reading for system 1 during thermal aging process.

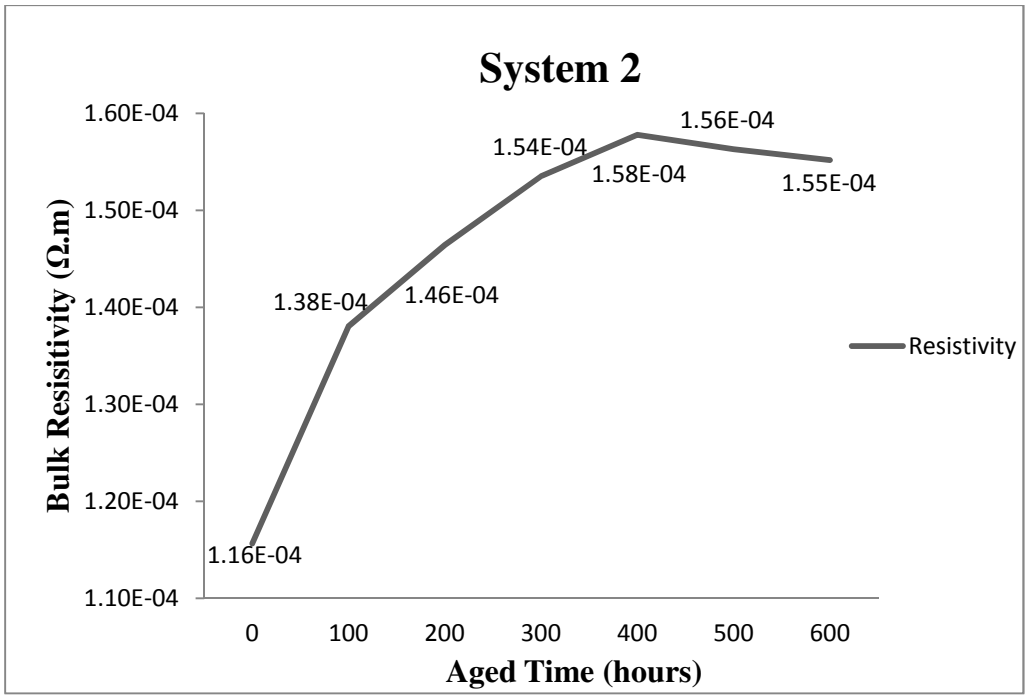

Figure 4.3.1 Bulk resistivity reading for system 2 during thermal aging process.

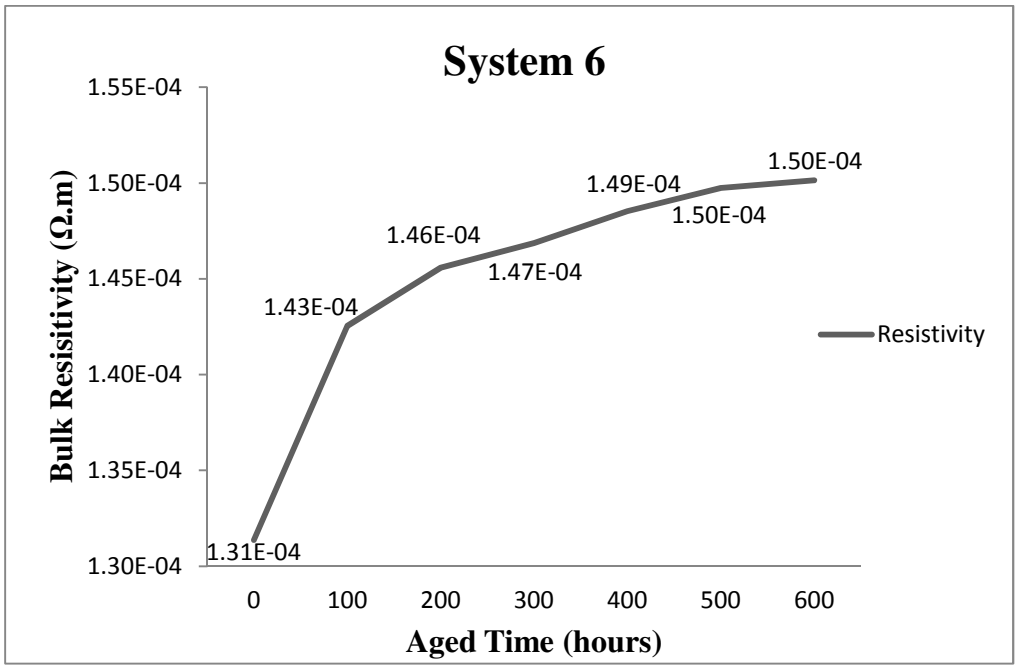

Figure 4.3.2 Bulk resistivity reading for system 6 during thermal aging process.

Based on observation from Figure 4.3, 4.3.1 and 4.3.2, from aged time 100 to 600 (hours), bulk resistivity for system 1, system 2 and system 6 doesn't showed big changes. It was noticed that changes in bulk resistivity are mainly occurred at aged time 0-100 (hours). From Figure 4.3, it was found that bulk resistivity for system 1 increased from 2.08 x 10^{-4} Ω.m (non- aging) to 2.89 x 10^{-4} Ω.m (100 hour aged), this is 38.94% shift in bulk resistivity after thermal aging the specimen for 100 hour.

For system 2 (Figure 4.3.1), it is increased in bulk resistivity from 1.16 x 10^{-4} Ω·m (non-aging) to 1.38 x 10^{-4} Ω·m (100 hour), this is 18.96 % shift in bulk resistivity after 100 hour aging.

For system 6, which contained 3wt% of MWCNTs, it's showed increased in bulk resistivity from 1.31 x 10^{-4} Ω·m (non-aging) to 1.43 x 10^{-4} Ω·m (100 hour aged), this is 9.16 % shift in bulk resistivity after 100 hour of thermal aged. By comparing the results in beginning stage (0 hour to 100 hour) of thermal aging for system 1, 2 and 6, system 6 showed smaller changes in bulk resistivity among three systems.

Table 4.4 showed shift in bulk resistivity during the thermal aging process for system 1, system 2, and system 6. Based on Table 4.4, the average percentage shift in bulk resistivity was calculated by dividing the total percentage shift in bulk resistivity by the aging stage, which is six (6). It was found that shifting in bulk resistivity mostly happened on beginning stage (0 – 100 hours) of thermal aging process.

Table 4.4 Percentage shift in bulk resistivity during thermal aging process.

Percentage Shift in bulk resistivity during thermal aging process			
Aged time (hours)	**System 1**	**System 2**	**System 6**
0-100	38.94%	18.96%	9.16%
100-200	3.80%	5.78%	2.10%
200-300	2.66%	5.48%	0.68%
300-400	0.00%	2.60%	1.36%
400-500	2.74%	1.27%	0.67%
500-600	1.33%	0.64%	0.00%
Average percentage shift in bulk resistivity.	8.25%	5.79%	2.33%

Based on Table 4.4, system 1 which contained of 40wt% of epoxy resin and 60 wt% of silver flakes showed 8.25% in average bulk resistivity shift, system 2 which formulated by 20wt% epoxy resin and 80wt% of silver flakes showed 5.79% in average bulk resistivity shift. System 6 which formulated by 40 wt% of epoxy resin and 57wt% of silver flakes and 3wt% of MWCNTs as replacement for silver flakes showed only 2.33% in average bulk resistivity shift. Results indicated that system 6 which contained 3wt% of MWCNTs had

better conductivity reliability if compared to conventional ICAs, system 1 and system 2.

For system 6 which contained 3wt% of MWCNTs, result obtained showed lowest average percentage shift in bulk resistivity. It was strongly believed that MWCNTs had stronger the network between silver to silver connection in ICAs, besides also reinforced the bonding between silver to epoxy resin connection.

Based on Table 4.4, system 1, 2 and 6 were showed shift in bulk resistivity accordingly, one of the reasons is moistures absorption that occurred in ICAs during the thermal aging process which will degrade the conductivity. Previous study by Zhao et al. (2007) stated that polymers absorb moisture and not impermeable to moisture. Moisture diffusing through the polymer can transport ions to the die surface and other interfaces and possibly cause electrical current leakage or corrosion.

During aging time from 0-100 hours, there is a high chance of polymers will absorb surrounding moistures during the thermal aging process. Due to very high rate of moistures absorption during this aging time (0-100 hour), hence there is a change in bulk resistivity were obtained. Moistures absorption that occurred on formulated ICAs during the thermal aging process could cause to

current leakage or corrosion on the metal filler (silver flakes/carbon nano-tubes) which will degrade the overall bulk resistivity of ICAs.

On the other hand, when moistures absorption process in ICAs reached certain level that cannot further absorb surrounding moistures, current leakage or corrosion process was slowed down or stopped due to very low moistures absorption rate. Based on Table 4.4, this phenomenon happened on aged times from 100 to 600 (hour) during the thermal aging process, thus only small percentage shift in bulk resistivity within aged times from 100 to 600 (hour).

Besides, silver migration in ICAs might also an issue that affect the stability and reliability of bulk resistivity of ICAs. Furthermore, galvanic corrosion that occurred between the metal filler (silver flakes/carbon nano-tubes) and the PCB causing the unstable bulk resistivity on formulated ICAs. Another issue that need to consider is the adhesion degradation (epoxy resin) in ICAs might also an issue that cause to shift in bulk resistivity. A previous study by Lu et al. (1999) reported that poor stability in the measured contact resistance between the conductive adhesive and component metal finish due the effect of humidity, which affects the reliability of the ICAs joints. Exposure to higher temperature and humidity environment, the main contributing mechanism for poor contact resistance was found to be galvanic corrosion rather than oxidation.

Based on Table 4.4, it can conclude that, in term of electrical reliability, system 6 which contained of 3wt% of MWCNTs had the higher electrical reliability because showed the lowest average percentage shift in bulk resistivity. Besides, system 2 had better electrical reliability if compared to system 1.

4.3.2 Thermal aging studies on Vickers micro hardness of ICAs

Hardness tests were conducted on the thermally aged system 1, 2 and 6. Hardness measurements were taken for each 100 hours. Table 4.5 presents the data pertaining to hardness measurement. Table 4.6 shows the average percentage shift in Vickers micro hardness. This data was calculated to study the hardness stability during thermal aging process. System that obtained lower average percentage shift in Vickers micro hardness indicates to better hardness stability under the thermal aging process. This is very important issue to electronic interconnects material and electronic devices reliability in real life. Furthermore, unstable ICA hardness under thermal aging attack will also lead to failure in mechanical site. Huge changes in hardness indicate that shrink and dense process in ICAs during thermal aging process is occurring rapidly. Cracking between adhesion PCB and ICAs may occur which lead to connection failure.

Table 4.5 Vickers micro hardness reading during thermal aging process

VICKERS MICROHARDNESS RESULTS (AGED)			
Time (hours)	**System 1**	**System 2**	**System 6**
Non-aging	19.12HV	23.05HV	24.32HV
100	20.65HV	23.78HV	24.71HV
200	21.25HV	24.42HV	24.98HV
300	21.72HV	24.98HV	25.21HV
400	22.26HV	25.32HV	25.34HV
500	22.46HV	25.58HV	25.44HV
600	22.58HV	25.79HV	25.53HV

Table 4.5 was converted into graph like Figure 4.3.3 for comparison purpose. Based on Figure 4.3.3, it can be concluded that hardness reading for system 1, 2 and 6 were increased gradually under thermal aging process. The hardness reading increasing during thermal aging process, due to the densification of epoxy resins. As results, there is higher degree of compaction of the silver flakes. Thus higher hardness reading obtained when aged time increased.

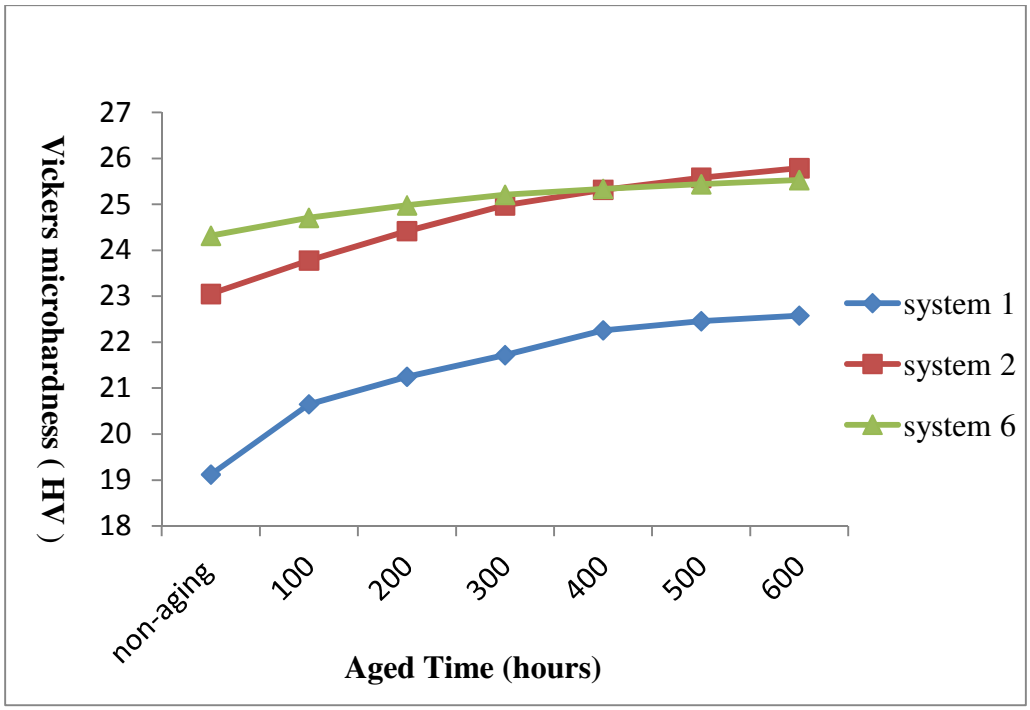

Figure 4.3.3 Vickers micro hardness reading during thermal aging process for system 1, 2 and 6.

Based on Table 4.6, system 1 showed high percentage shift from aged time 0-400 (hours), hardness increased in big step for this aged time. The possible reason for this phenomenon is percentage of metal filler for system 1 is 60wt% which still consist of space between metal filler (silver flakes) in epoxy resin, when system 1 under thermal aging environment, epoxy resin get dense and shrink and silver flakes easily get close to each other and closer displacement between them. In other word, metal filler easily get closer to each other under thermal aging environment when low percentage of filler loading. From aged time 400-600 (hours), system 1 showed lower percentage shift because epoxy resin and metal filler was reached maximum level that cannot be further shrink and dense. Overall, system 1 showed the higher average percentage shift in Vickers micro hardness during the thermal aging process if compared to system 2 and system 6.

Table 4.6 Percentage shift in Vickers micro hardness during thermal aging process.

Percentage Shift in Vickers micro hardness during thermal aging process			
Aged time (hours)	**System 1**	**System 2**	**System 6**
0-100	8.00%	3.16%	1.60%
100-200	2.91%	2.69%	1.10%
200-300	2.21%	2.29%	0.92%
300-400	2.49%	1.36%	0.52%
400-500	0.90%	1.03%	0.39%
500-600	0.53%	0.82%	0.35%
Average percentage shift in Vickers micro hardness.	2.84%	1.89%	0.81%

For system 2, which formulated by 80wt% of metal filler and 20wt% of epoxy resin, hardness reading was increased rapidly in aged time 0-300 hours. The similar theory on system 1 was applies for this phenomenon, on beginning stage in thermal aging process, system 2 still consist of space between metal filler (silver flakes) in epoxy resin, when under thermal aging environment, epoxy resin getting shrink and dense cause to metal filler get closer to each other, thus showed increasing in hardness reading due to silver flakes getting closer to each other in system 2. Hardness reading showed small changes on aged time from 300-600 hours, this is because epoxy resin and metal filler in system 2 was reached maximum level that cannot be further shrink and dense.

Based on Table 4.6, compared the average percentage shift in Vickers micro hardness for system 1 and system 2. System 2 showed lower average percentage shift in Vickers micro hardness. This is not surprisingly because the weight percentage of metal filler for system 1 and system 2 was different. System 2 which consists of 80wt% metal filler and system 1 only consists of 60wt% metal filler. When higher weight percentage of metal filler in ICA, specimen (system 2) tested by Vickers micro hardness tester are mostly occupied by metal filler. Furthermore, when higher weight percentage of metal filler in ICA, metal fillers were very close to each other which had stronger bonding between the metal filler in ICA. Thus hardness reading is quite stable because shrink and dense process occurred rarely under thermal aging environment for system 2.

On the contrary, for system 1 which consists of 60wt% metal fillers, when lower weight percentage of metal filler in ICA, metal fillers were not very close to each other which provided opportunity to shrink and dense under thermal aging environment, thus showed higher average percentage shift in Vickers micro hardness.

For system 6 which formulated by 57wt% silver flakes, 3 wt% MWCNTs as replacement for silver flakes and 40wt% of epoxy resin, it showed a better hardness stability under thermal aging environment. Based on Table 4.6, hardness reading was increased slightly form aged time 0-300 hours, and then hardness reading are quite stable for aged time 300-600 hours. It shows almost

no different in hardness reading in aged time 500-600 hours. System 6 brings a good impression in hardness reading during thermal aged process. The possible reason for this phenomenon is MWCNTs was created a very strong network with epoxy resin and metal filler (silver flakes) in system 6. This network was able to resist certain forces which apply through the indenter by Vickers micro hardness tester, thus, showed stable hardness reading during thermal aging process. Besides, MWCNTs also function like webs in ICA to graps the surrounding metal filler (silver flakes) become a stronger network which result to well performance in hardness and impact.

Overall, system 6 which contained of 3wt% of MWCNTs had showed the lower average percentage shift in Vickers micro hardness, this indicated that 3wt% of MWCNTs as replacement to silver flakes was able to obtained better hardness stability under thermal aging environment. On the other hand, system 2 had better hardness stability during thermal aging process if compared with system 1 due to the different weight percentage metal filler in the system.

CHAPTER 5

5.0 CONCLUSION AND FURTHER WORK

5.1 Conclusion

A number of conclusions can be drawn from the results of the work presented in this research:

1) The MWCNTs was able to decrease the bulk resistivity by replacing certain amount of metal filler (silver flakes) in ICAs. It was found that 37% improvement in bulk resistivity after replaced silver flakes with 3wt% of MWCNTs in system 6 when compared to system 1, which is a conventional ICA.

2) The results showed that 27.2% increase in hardness value after replaced silver flakes by 3wt% MWCNTs (system 6) in ICAs when compared to system 1.

3) When volume fraction MWCNTs in ICAs reached 2.1wt% (system 7g), the hardness reading was comparable to system 2 (conventional ICA). It shows 5% improvement in hardness reading when volume fraction of MWCNTs reached 3.0wt% (system 6) in ICAs when compared to system 2.

4) The study showed that incorporating MWCNTs was able to improve the impact performance of ICAs. For system that contained 3wt% MWCNTs (system 6), the drop test results showed zero percentage of failure.

5) Based on thermal aging study, system 6 which contained 3wt% of MWCNTs, showed the lowest average percentage shift in bulk resistivity if compared to conventional ICAs. In addition, system 6 that contained 3wt% of MWCNTs, showed better hardness stability under thermal aging process if compared to conventional ICAs.

6) As a conclusion, system 6 (3wt% of MWCNTs) provided satisfactory electrical conductivity and desirable mechanical strength in this study. In thermal aging study, system 6 showed higher stability in term of bulk resistivity and hardness reading if compared with conventional ICAs (system 1 and system 2). Although system 7b showed a comparable bulk resistivity to system 6, but the impact performance and hardness value was poor.

5.2 Suggestion for future work

In order to optimize the electrical properties, strength, long-term stability, impact performance, and reliability of MWCNTs based ICAs, the following are suggestions for possible further work in this area:

1) High temperature may contribute to the oxidization of metal fillers in ICAs, thus reducing the conductivity of ICAs. Further work is recommended, to cure the adhesives with the combination of temperature and pressure. The presence of pressure will increase the shrinkage of polymer resin, thus possibly enhancing conductivity of ICAs.

2) Further research work to understand the dispersability of the MWCNTs in polymer matrix is required. Further work is recommended to implement melt mixing, bulk polymerization and sonication method during the MWCNTs dispersion process to encounter MWCNTs aggregation problem which will affect the conductivity of ICA.

3) Curing of the adhesive, both thermosetting and thermoplastic, results in a slight decrease in the weight of the adhesive. This weight loss is caused by the evaporation of solvent, or reactive solvents. It is desirable to understand the effect of the solvents on the electrical and mechanical properties of ICAs.

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