ACCELERATED AGING OF MWCNT FILLED ELECTRICALLY CONDUCTIVE ADHESIVES

Ashwanth Reddy Vangala

University of Kentucky, VASHWANTREDDY@UKY.EDU

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ABSTRACT OF THESIS

ACCELERATED AGING OF MWCNT FILLED ELECTRICALLY CONDUCTIVE ADHESIVES

Electrically conductive adhesives (ECA) are discussed and studied with ever-increasing interest as an environmentally friendly alternative to solder interconnection in microelectronics circuit packaging. They are used to attach surface mount devices (SMD), Integrated Circuits (IC) and Flip chips in electronic assembly. The use of ECAs brings some benefits like flexibility, mild processing conditions and process simplicity. Multi walled carbon nanotubes (MWCNT) are used instead of metal fillers because of their novel properties such as light weight, high aspect ratio, corrosion resistant, reduced processing temperature, lead free, good electrical conduction and mechanical strength.

The purpose of the present work is to investigate the aging behavior of MWCNT filled adhesives based on anhydride cured epoxy systems and their dependence on loading. Composites with different loadings of MWNT in epoxy and epoxy: heloxy are prepared and then stencil printed onto different surface finished boards like gold, silver and tin to prepare contact resistance samples and onto aluminum oxide boards to prepare volume resistivity samples. These samples are kept at room temperature for about 90 days and then placed in a temperature chamber to observe the behavior of these samples after accelerated aging. The readings are taken for as prepared samples, after 45 days, after 90 days and after accelerated aging. The results are summarized and different trends are observed for different loadings of MWNT, different combinations of epoxy: heloxy and for different surface finished boards.

KEYWORDS: solder, electrically conductive adhesives (ECAs), multi walled carbon nanotubes (MWCNTs), aging, temperature chamber.

Ashwanth Reddy Vangala
01/11/2010
ACCELERATED AGING OF MWCNT FILLED ELECTRICALLY CONDUCTIVE ADHESIVES

By
Ashwanth Reddy Vangala

Dr. Janet K Lumpp
Director for Thesis

Dr. Stephen Gedney
Director of Graduate Studies

(01/11/2010)
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THESIS

Ashwanth Reddy Vangala

The Graduate School
University Of Kentucky
2010
ACCELERATED AGING OF MWCNT FILLED ELECTRICALLY CONDUCTIVE ADHESIVES.

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Electrical Engineering in the College of Engineering at the University of Kentucky

By

Ashwanth Reddy Vangala

Lexington, Kentucky

Director: Dr. Janet K Lumpp, Professor

Electrical and Computer Engineering

Lexington, Kentucky

2010

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DEDICATION

To My Parents and Family
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Chapter 1 Introduction:

Tin-lead solders are widely used in the electronic industry. They serve as interconnect that provide the conductive path between different circuit elements. Solder be used as bump interconnect in flip chip assembly, die attach material in wire bond assembly or interconnect material for through-hole and surface mount technologies in printed circuit board assembly. Solder is applied as solder paste by screen printing, stencil printing or pressure dispensing. Then a reflow oven activates the flux and melts the solder. However, there are increasing concerns with the use of tin-lead alloy solders in recognition of hazards of using lead. In manufacturing facilities worldwide, the traditional tin-lead solders are being replaced by lead-free solders in response to the international restriction on the use of hazardous substances legislation (RoHS).

Lead free solders and electrically conductive adhesives (ECAs) have been considered as the best alternatives to tin-lead solder. ECAs consist of a polymeric resin (such as epoxy, silicone, or polymide) that provides physical and mechanical properties such as mechanical strength, adhesion, impact strength and it has metal filler such as, silver, gold, nickel or copper that conducts electricity. ECAs have many advantages, such as mild processing conditions (enabling the use of heat-sensitive and low-cost components and substrates), environmental friendliness, less number of processing steps (reducing processing cost), low stress on the substrates, and fine pitch interconnect capability (enabling the miniaturization of electronic devices). Therefore, conductive adhesives have been used as an interconnect material in liquid crystal display (LCD) and smart card applications and it is used in flip-chip assembly, chip scale package (CSP) and ball grid array (BGA) applications, instead of solder. However, ECAs still cannot replace tin-lead metal solders in all applications due to some issues such as lower electrical conductivity, conductivity fatigue (decreased conductivity at elevated temperature and humidity aging or normal use condition) in reliability testing, limited current-carrying capability, and poor impact strength[1].

Considerable research has been conducted recently to study and optimize the performance of ECAs, such as electrical, mechanical and thermal behaviors improvement as well as reliability enhancement under various conditions. High aspect ratio (length to diameter), large surface area multiwall carbon nanotubes (MWCNTs) have the potential to replace the metal filler particles to reach the percolation threshold with small volume fraction loading. There are many other advantages with MWCNTs such as light weight, corrosion resistant, lead free, high
Strength, good mechanical strength and electrical conductivity. The MWNTs used in the present study have aspect ratio around 2500(50µm/20nm).

In this study, we mainly focused on change in the electrical properties of carbon nanotube adhesives such as contact resistance and volume resistivity after accelerated aging. We prepared samples of different loadings of MWNTs on different commercially available surface finishes like gold, silver and tin. Later on, we also added different percentages of heloxy (a viscosity modifier) to the adhesive to make it more processable. All these samples are kept in a temperature chamber and then tested for change in the electrical properties.
Chapter 2  Background:

2.1 Electronic Packaging Technologies:

Usually, every micro electronic device has at least two levels of packaging. They are IC packaging or first level packaging and board level packaging or second level packaging.

2.1.1 IC Packaging:

The functions of IC packaging are to protect, power, and cool microelectronic device and provide electrical and mechanical interconnections for the devices [2]. These ICs are electrically connected to a substrate by using three primary techniques: wire bonding, tape automated bonding and flip chip bonding.

2.1.1.1 Wire Bonding:

Wire bonding is the primary method of making interconnections between an integrated circuit (IC) and either the printed circuit board (PCB) or package lead frame during semiconductor device fabrication. It is generally considered as the most cost effective and flexible interconnect technology. These wires are usually made of copper, gold, and aluminum. Junction size, bond strength and conductivity requirements typically determine the most suitable wire size for a specific wire bonding application. Ball bonding and wedge bonding are considered to be the main classes of wire bonding. Ball bonding is usually restricted to gold and copper wire and requires heat where as wedge bonding can use either gold or aluminum with only the gold wire requiring heat.

Copper is used for fine wire ball bonding in sizes up to 0.003 inch. Generally it is used at smaller diameters. Copper wire up to .010 inch can be successfully wedge bonded with the proper set-up parameters. Even though, copper is easy to use and cost effective, it does pose some challenges. It is harder than both gold and aluminum, so bonding parameters must be kept under tight control. There is a high probability of forming oxides with this material, so storage and shelf life are issues that must be considered [3].

If a gold wire is to be used for ball bonding, it has to be doped with beryllium and other elements using heat, pressure and ultrasonic energy. The most common approach in thermosonic bonding is to ball-bond to the chip, then stitch-bond to the substrate [4].
Aluminum is suitable for ultrasonic bonding. In all the low current devices, alloyed aluminum wires are generally preferred to pure aluminum but in high current devices, pure aluminum is preferred because of greater drawing ease to fine sizes. Pure aluminum and 0.5% magnesium-aluminum are most commonly used in sizes larger than 0.004 inches. All aluminum systems in semiconductor fabrication eliminate the “purple plague” (brittle gold-aluminum intermetallic compound) sometimes associated with pure gold bonding wire [5].

2.1.1.2 Tape Automated Bonding (TAB):

Tape automate bonding is an interconnect technology between IC and substrate, using a prefabricated carrier with copper leads adapted to the IC pads instead of single wires. The tape used in tape automated bonding is usually single-sided, although two-metal tapes are also available. Copper, a commonly-used metal, in tapes, can be electrodeposited on the tape or simply attached to the tape using adhesives. The metal patterns of the circuit are imaged onto the tape by photolithography. The TAB bonds connecting the die and the tape are known as inner lead bonds (ILB), while those that connect the tape to the package or to external circuits are known as outer lead bonds (OLB).

Tap Automated Bonding (TAB) offers lot of advantages. Some of them are shorter production cycle time, flexibility, less amount of gold needed for bonding and use of finer bonding pitch. Tape automated bonding is a better alternative to conventional wire bonding, if very fine bond pitch, reduced die size, and higher chip density are desired. Tab is generally most cost effective for use in high-volume production [6].

2.1.1.3 Flip Chip Bonding:

Flip chip microelectronic assembly is the direct electrical connection of face-down (hence, “flipped”) electronic component onto substrates, circuit boards, or carriers, by means of conductive bumps on the chip bond pads. The boom in flip chip packaging results both from flip chip’s advantages in size, performance, flexibility, reliability, and cost over other packaging methods and from the widening availability of flip chip materials, equipment, and services.

There are three stages in making flip chip assemblies: bumping the die or wafer, attaching the bumped die to the board or substrate, and in most cases, filling the remaining space under the die with an electrically non-conductive material. The conductive bump, the attachment materials, and the processes used differentiate the various kinds of flip chip assemblies [7].
2.1.2 Board Assembly:

A printed wiring board (PWB), or printed circuit board (PCB) assembly integrate different electrical components into functional systems. It is a composite of organic and inorganic materials with external and internal wiring, allowing electronic components to be electrically interconnected and mechanically supported. In addition, a PWB must provide power to the components and conduct away heat when necessary. The boards are also called as mother boards or system level boards, because they carry all of the components required for the system or the sub system.

There are two major PWB assembly technologies: through-hole assembly and surface mount assembly. The fundamental difference between them is through-hole assembly is achieved by inserting the leads of the components into plated holes in the board. While the surface mount assembly is done by stencil-printing solder paste to a board placing the component on the board and then heating the entire assembly, so that the solder melts and forms solder joints. The flux is already mixed in with the solder paste, and apart from reducing metal oxides, it provides necessary stickiness to hold the components in their correct positions until the solder joints are created. Both methods are still widely used but the use of surface mount assembly has grown rapidly in the past decade. The main reason for this change is size reduction. Both the size reduction of the component and real estate used on and inside the board, are greatly reduced. A hole used for through-hole assembly goes all the way through the PWB, using valuable board area in every layer of the board. All electrical traces have to be routed around the holes at a safe distance. Another important factor is that automated assembly has become simplified with surface mount assembly [8].

2.2 Lead Free Trend in Electronic Packaging:

As public environmental awareness increases, the toxicity of lead has become increasingly important, and the pressure to eliminate or reduce the industrial use of lead is growing. Legislation and policies have been proposed in Europe to ban or limit the use of lead in solders, and the United States is very likely to follow this trend. Following this tendency, great efforts have been made in the industry to develop lead-free and environmentally friendly soldering materials to replace lead-based solders in response to the international restriction on the use of hazardous substances legislation (RoHS). One alternative to lead-bearing solders is lead-free, low melting temperature metals and metal alloys. Some applications have been found in this
area. However, some limitations still exist in lead-free solder technology, including the relatively high cost or limited availability of some candidate metals, and the requirement for relatively high soldering temperature for some metal and metal alloys. Moreover, compared with lead-bearing solders, joint embrittlement and fatigue are also serious concerns in lead-free solder applications as embrittlement of solder joints after reflow and fatigue cracks induced by temperature cycling are among the major causes of lead-free solder joint failure [8].

The other alternative for lead-bearing solders is electrically conductive adhesives (ECAs). ECAs consist of a polymer binder that provides mechanical strength, and conductive fillers, which offer electrical conduction. Electrically conductive adhesives provide an environmentally friendly solution for interconnections in electronic applications. Moreover, ECAs also offer several potential advantages over conventional solder interconnection technology including finer pitch printing, lower temperature processing, and more flexible and simpler processing. In addition, compared with lead-free solders, conductive adhesive systems exhibit greater flexibility, creep resistance, and energy damping, which can reduce the possibility of failures that occur in lead-free solder interconnections. Therefore, electrically conductive adhesives are perceived as the next generation interconnection material for electronic packaging. As a relatively new interconnection technology, however, conductive adhesive technology does have some limitations and drawbacks. Some reliability issues including limited impact resistance, increased contact resistance, and weakened mechanical strength in various climatic environmental conditions are several major obstacles currently preventing ECAs from becoming a general replacement for solders in electronic applications [9]. Therefore, fundamental studies are necessary to develop a better understanding of the mechanisms underlying these problems, and to improve the performance of conductive adhesives for electronic applications, before ECAs are widely used for solder replacement.

2.3 Electrically Conductive adhesives:

Electrically conductive adhesives are of three types: isotropic conductive adhesives (ICA), anisotropic conductive adhesives (ACA) and conductive silicones. Although the concepts of these materials are different, both ICA and ACA materials are composite materials consisting of a polymer matrix containing conductive fillers. Since there is no flux involved in the assembly process, the use of ECAs is a no-clean process. The ECAs also work well with all types of board finishes. Conductive silicone materials allow device manufacturers to shield EMI/RMI emissions
and seal electronic enclosures, protecting them from environmental hazards. They are also used to provide ground paths for electronic devices that require high flexibility. They can be applied directly to the areas that require environmental shielding, and cured-in-place.

2.3.1 Anisotropic Conductive Adhesives:

Anisotropic conductive adhesives can be used to provide structural strength without an electrical interconnection on other areas of device. They are available in two forms-single component, heat curable liquids and pastes and heat curable thermosetting or thermoplastic adhesive films. They are pastes or films of thermoplastics or b-stage epoxies filled with metal particles or metal-coated polymer spheres. In ACAs, the volume fractions of conductive fillers are normally between 5 and 10 vol.% and the electrical conduction path is generally built only in the pressurization direction during curing. ACA technology is very suitable for fine pitch technology and is principally used for flat panel display applications, flip chips and fine pitch surface mount devices [9].

2.3.2 Isotropic Conductive Adhesives:

Isotropic conductive adhesives, as an alternative to solder reflow processing, are widely used for die attach and surface mount assemblies. Isotropic conductive adhesives generally consist of a polymer matrix such as epoxy and conductive filler particles such as silver flakes or spheres. Most of ICAs are epoxy-based thermosetting adhesives and cured by heat. Isotropic Conductive adhesives (ICA) conduct electricity among all the axes and are able to solder on thermally sensitive components and on devices that require a ground path. They can be used as electrical interconnect on non-solderable substrates such as glass, ceramics or to replace solder on thermally sensitive components that cannot withstand the 200°C processing temperatures of typical solders. Isotropically conductive epoxies offer non-directional or all directional, conductivity by incorporating conductive particles such as silver into the adhesive formulation. Both electrically and thermally conductive, these epoxies provide strong, durable bonds on many different substrates [9].
2.3.2.1 Polymer Binders:

Electrically conductive adhesives consist of a polymer binder that provides mechanical strength and conductive fillers, which offer electrical conduction. Polymers are commonly classified as either thermosets (such as epoxies, polyimides, silicones and acrylic adhesives) or thermoplastics. Thermoplastics are also referred to as remeltables and hot melts. This class of polymers typically has a long linear molecular structure, which allows these materials to melt and flow when heated to a specific melting point without significantly altering their intrinsic properties. Thermosets are cross linked polymers and generally have an extensive three-dimensional molecular network structure. Thermoset epoxies filled with silver particles are by far the most common adhesive binders for isotropic conductive adhesives used for component assembly. They have been used for decades due to their many superior properties, such as low shrinkage, good adhesion, and good resistance to moisture and chemical attacks. With different applications of ECAs, polymer binders can be of either type. For conductive fillers, metallic materials such as gold, silver, copper, and nickel or nonmetallic materials such as carbon have found application in ECA technology. Epoxy resin is considered one of the best adhesives due to its good adhesion to metal, low cost and relative safety of use. The filler particles vary in shape and size as well as in material composition. Heloxy is used as a viscosity modifier in the adhesive used in this research. Heloxy modifier offers:

1. improved cured system flexibility
2. increased peel and impact strength
3. increased levels of filler loading
4. improved resin wetting action
5. reduced viscosity and surface tension

Heloxy modifiers are epoxy functionalized alcohols, diols, polyols and acids. There are three classes of Heloxy modifiers: monofunctional glycidyl ethers, polyfunctional glycidyl ethers and flexibilizers [10]. The polyfunctional Heloxy products are aliphatics which provide an increase in the chemical resistance and mechanical performance of the system. The cycloaliphatic modifier offers improved UV resistance when compared to aromatic modifiers, and our trifunctional modifier increases the crosslink density of a system.
2.3.2.2 Conductive Fillers:

The most frequently used material for conductive fillers are silver, gold, copper and nickel. Silver has high electrical conductivity and the silver oxide layer, unlike many other metal oxides layers, has good electrical conductivity too. Due to this special characteristic, the aging of the silver fillers will not result in significantly reduced conductivity in a composition including silver fillers. The disadvantages of silver are its tendency to migrate and the relatively expensive price. Silver is found to be the most frequently used filler particle material in electrically conductive adhesives for surface mount technology. Gold has lower conductivity than silver and is much more expensive, but it has a very low ability to migrate and the oxide layer (formed by Ni coating) of gold is also conductive. Thus gold is often chosen for use in military and space electronics to avoid the risk of silver migration. Copper has good conductivity and is not very expensive but in the presence of oxygen it will form a continually growing insulating oxide layer, which reduces the electrical conductivity of the composition. This means that copper cannot offer stable electrical conductivity when exposed to oxygen. Nickel has relatively low electrical conductivity. Work with nickel can cause allergies and nickel dust is found to be carcinogenic. Both copper and nickel are limited to the low cost applications. In addition to the pure metals, composites such as copper and glass plated with silver or gold are also developed as filler material [11]. Traditional metal filled ICAs require 25% to 30% volume fraction (up to 80 wt %) to ensure electrical conductivity. Such a high volume fraction degrades the mechanical properties of the polymer matrices. With conventional metal filled only a small portion of shear strength of polymer matrix can be retained. The volume fraction loading of conductive filler particles in ICA must be higher than the percolation threshold to ensure the electrical conductivity. MWCNTs have very high aspect ratio, and it is possible to reach the percolation threshold with small volume fraction. Even, MWCNTs have extremely high strength to weight ratio. Hence, replacing the metal fillers with MWCNTs has the potential benefits of being lead free, low process temperature, corrosion resistant, high electrical conductivity, high mechanical strength and lightweight. In recent years, electrical and mechanical properties have been investigated for the MWCNT/polymer composites. While consumer electronics represent a large potential market for nanotube filled conductive adhesives, the benefits are also applicable to military and aerospace applications. Weight limitations and reliability in harsh environments are two priorities where the non-metallic conductor may provide improved performance over soldered assemblies. The potential weight savings of MWCNT ICA over solder is 83% for the same volume. By eliminating tin and silver from the contact area, MWCNT ICA bonded
components should exhibit no degradation by silver migration and tin whisker formation. Other metallic corrosion and fatigue mechanisms are also reduced by using polymer adhesives to separate component metal leads from the metal interconnect on the circuit board. Thermal conductivity and mechanical properties need to be evaluated at higher loadings to determine the usefulness of MWCNT filled adhesives for thermal management and structural elements.

2.3.3 Conduction Mechanisms in Isotropic Conductive Adhesives:

In general, there are two conductive pathways for isotropic conductive adhesives as shown in figure (1). One is direct conduction, caused by particle-to-particle contact within the polymer matrix [12]. The other is percolation, which involves electron transport brought about by quantum-mechanical electron tunneling between particles close enough to allow dielectric breakdown of the matrix. For isotropic conductive adhesives, as the conductive filler loading is progressively increased, the electrical resistance does not decrease significantly until the filler loading reaches a critical value, \( P_c \). This point, where the electrical resistance decreases abruptly, is called the percolation threshold. Practical isotropic electrically conductive adhesives are typically manufactured with filler loading \( P \) sufficiently greater than the threshold value \( P_c \) to guarantee low electrical resistance. The percolation threshold may vary with filler particle sizes and shapes, and their orientation in the polymer matrix.

![Conduction mechanisms in conductive adhesives](image)

1(a) Particle-to-particle  
1(b) electron tunneling

Figure 1: Conduction mechanisms in conductive adhesives.

2.3.3.1 Conductivity:
Pristine polymers have intrinsically large energy band gaps, thus are good insulators. Typical conductivity of an epoxy is less than 10-14 S/cm. In commercially available metal filled conductive adhesives, highly conductive metal particles are mixed with insulating polymer matrix to form electrically conductive composites. At low filler loading levels, the conductivity of the filler/polymer composite is very low (close to the intrinsic conductivity of the polymer) and does not change with increasing filler loading. When the volume fraction of conductive filler in the polymer system exceeds the critical volume fraction (percolation threshold), a three-dimensional network is established by the conductive filler particles and the conductivity of the composite increases dramatically by several orders of magnitude. This is called the critical range. In conductive adhesives, there are three major factors affecting the conductivity of the composite: intrinsic conductivity of the filler particles, dimension (aspect ratio) of the filler particles and the contact resistance between the particles. MWCNTs with small size and high aspect ratio can form more contacts than large metal particles with the same weight percent loading. MWCNTs therefore form conductive networks in the composite more readily than the spheres or flakes used in commercial silver filled conductive adhesives. The percolation threshold of MWCNTs/epoxy composite has been observed to be extremely low as 0.0025 wt% [13].

2.4 Carbon Nanotubes:

Carbon nanotubes were discovered in 1991 by S.Iijima, Japan. They are allotropes of carbon with a nano structure that can have a length-to-diameter ratio greater than 1,000,000:1[14]. They have novel properties useful in a wide variety of applications in sensors, electronics, optics and other field of materials science. They exhibit extraordinary strength and unique electrical properties and are efficient conductors of heat. Inorganic nanotubes have also been synthesized.

Nanotubes are members of the fullerene structural family. Nanotubes are cylindrical, with at least one end typically capped with a hemisphere of the buckyball structure. Their name is derived from their size, since the diameter of a nanotube is on the order of a few nanometers (approximately 50,000 times smaller than the width of a human hair), while they can be up to several millimeters of length.

Manufacturing a nanotube is dependent on applied quantum chemistry, specifically, orbital hybridization. Similar to graphite, nanotubes are composed of sp² bonds, which is stronger than sp³ (found in diamond). This bonding structure provides the molecules with their unique
strength. Nanotubes naturally align themselves into “ropes” held together by Vander Waals forces. Nanotubes can merge together under high pressure, trading some sp² bonds for sp³ bonds, giving great possibility for producing strong, unlimited-length wires through high pressure nanotube linking.

2.4.1 Types of Carbon Nanotubes:

They exist in various shapes—cylinders, spheres, cones, tubes and also complicated shapes. But, there are two main types of carbon nanotubes, Single walled carbon nanotubes (SWNT) and Multi walled carbon nanotubes (MWCNT).

![SWNT and MWNT](image)

Figure 2: Molecular structures of Single walled carbon nanotubes (SWNT) and Multi walled carbon nanotubes (MWNT) [15].

2.4.1.1 Single walled nanotubes (SWNT):

Single walled carbon nanotubes consists of a seamless cylinder of graphitic sheet capped by hemi spherical ends composed of pentagons and hexagons. Nanotubes generally have a length to diameter ration of 1000 so they can be approximated as one dimensional structure. They exhibit different properties depending on chirality. All armchair tubes are metallic. Chiral and Zigzag tubes are either metallic or semiconducting depending on the chiral vector integers n and
m. When the chiral vector n-m=3q, where q is an integer, the carbon nanotube is expected to be metallic, while all others are semiconducting. It is estimated that 1/3 of all carbon nanotubes are metallic.

SWCNT exhibit important electric and physical properties that are not exhibited by the other variants. Single walled nanotubes are still very expensive to produce, and the development of more affordable synthesis techniques is vital to the future of carbon nanotube technology. If cheaper means of synthesis cannot be discovered, it would make it financially impossible to apply this technology to commercial scale applications such as ECAs [16].

2.4.1.2 Multi walled nanotubes (MWNTs):

These can be considered as a collection of concentric SWNTs with different diameters, lengths and properties. The inter layer distance of MWNTs is 0.34 nm which is slightly larger than graphite sheets. These layers are coupled together by Vander waals forces. MWNTs are conductive irrespective of the synthesis method and offer high strength to weight ratio. The MWNs used in the present study have an aspect ratio of 2500:1. The wide range of electrical and mechanical properties of MWNTs is attracting many researchers to work in this field.

CHAPTER 3: MWCNT/Epoxy and Epoxy: Heloxy Composite Preparation

3.1 Materials:

The composite consists of epoxy resin, viscosity modifier, curing agent, catalyst and MWCNT’s. The materials used as resin, viscosity modifier, curing agent and catalyst are diglycidyl ether bisphenol-F (Epon 862, Shell Chemical, USA), neopentyl glycol diglycidyl ether (Miller-Stephenson Chemical, USA), hexahydro phthalic anhydride (MHHPA, Miller-Stephenson Chemical, USA) and Cyanoethyl-2-ethyl-4 methylimidazole (2E4MZ-CN, Shikoku Chemical, Japan) respectively. The length and diameter of the multiwalled carbon nano tubes, which are used in this experiment, are 50 µm and 20 nm respectively. MWCNTs, which are grown by Chemical Vapor Deposition Method, are obtained from University of Kentucky Center for Applied Energy (CAER) [17].Different surface finished printed circuit boards are purchased from Imagineering Inc., and 1206 zero ohm thick film surface mount resistors are purchased from DigiKey.
3.2 MWCNT-Epoxy Composite Preparation:

Polyethylene containers are used to prepare and store this mixture. Epoxy resin, curing agent and catalyst are added to the polyethylene container in 100:85:0.5 weight ratio. The total weight of this mixture is calculated there by calculating the weight of MWCNTs for desired percentages that are to be added to this mixture. A ThinkyAR250 planetary mixer is used to disperse the MWCNTs into epoxy. This mixer generates a centripetal force (up to 400G) by compound motion of the centrifuge and the counter rotation of the material container. There is a provision in this mixer to equate the weight of the centrifuge to the weight of the material container to ensure proper mixing. Each mixing cycle consists of a mixing stage and deforming stage. Mixing cycle is about five minutes at 800 rpm rotation and 2000 rpm revolution rates followed by a deforming cycle for three minutes at 60 rpm rotation and 2200 rpm revolution rates. By using this preparation method, different weight percentage MWCNT (2%-8%) mixtures are prepared. These mixtures are stored in a refrigerator at 40°C. The average pot life of these mixtures at room temperature is approximately 72hrs and it is approximately 1month at 40°C.

3.3 MWCNT-Epoxy/Heloxy Composite Preparation:

This composite is prepared in a similar way as MWCNT-Epoxy composite is prepared. Heloxy is used as a viscosity modifier which decreases the viscosity of epoxy. Heloxy is included in the resin portion to prepare 1:1, 2:3, 3:2, 7:3, 3:7 epoxy/heloxy mixtures. Curing agent and catalyst are added in the same proportions as earlier. The total weight of these mixtures is calculated and then the corresponding weight of MWCNT’s for the desired %wt is calculated and added to this mixture. Then, the container is placed in the thinky mixer to disperse the MWCNT’s into the resin and followed the same steps as before. In this way, 8wt%, 12wt% and 14wt% are prepared with different percentage combinations of epoxy and heloxy. The mixtures are stored in a refrigerator and remixed before use.
CHAPTER 4: Experimental Procedure

4.1 Contact Resistance Measurement:

Initially the adhesive is taken out of the refrigerator and allowed to come to room temperature. It is remixed for about three minutes of mixing cycle and two minutes of deforming cycle. Then, it is stencil printed on to a surface finished printed circuit board using a stencil printer (figure 3). Later, a pick and place machine (figure 4) which has a vacuum tip to hold the resistors, is used to place 1206 size zero ohm resistors on the pads of the circuit board. In this way, four daisy chains are formed as shown in the (figure 5), which has 10 resistors in each row. This circuit board is placed in a heat chamber at $85^\circ$C for 4 hours and then at $150^\circ$C for 40 minutes and then removed from the chamber. During this curing process, a flat sheet of certain amount of weight is placed on the circuit board to increase the area of contact between the pads and MWCNTs thereby decreasing the contact resistance.

Figure 3: Screen Printer.
The resistance of a daisy chain pattern is measured with a digital multimeter RSA MAS830 and it is divided by 20 to get the average resistance of each pad. Likewise, the resistance of all the daisy chains is measured to calculate the average resistance of pads in a daisy chain. By taking the average of these four values, the average contact resistance of corresponding mixture on corresponding surface finish board is calculated. Like this, the contact resistance is calculated for samples of different percentage MWCNTs with different weight percentages of resins and combination of resins (epoxy/helixy) on different surface finished circuit boards.
4.2 Volume Resistivity Measurement:

To measure the volume resistivity, the MWCNT-epoxy/MWCNT-epoxy/helox mixture is stencil printed on an aluminum oxide substrate (4 inches x 4 inches, CoorsTek, USA). This pattern has six 1cm x 1cm squares as shown in the figure. Two such substrates are stencil printed and the volume resistivity is average of all twelve values. The samples are kept in a temperature chamber for 4 hours at 85°C and then cured at 150°C for 45 minutes.

![Pattern of squares](image)

**Figure 6: The Volume Resistivity sample.**

The resistivity (ρ) is a measure of the potential electrical resistance of a conductive material. It is determined experimentally using the equation ρ=RA/l, where R is the measured resistance of some length of the material, A is its cross-sectional area (which must be uniform), and l is its length. It is measured in ohm-cm.

A Signatone four point probe tester is used to measure the voltage drop for an injected current. The sheet resistance (R_s) is proportional to the ratio of voltage, V to current, I. The schematic of four point probe is as shown in figure (7).

\[
R_s = \frac{C \cdot V}{I} \quad \text{------------------------4.2.1}
\]

\[
C = 4.53 \text{ for an infinite film.}
\]
The sheet resistance is multiplied by the thickness of the sheet to get the volume resistivity according to the formula

$$R_v = 4.53 \times \frac{V}{I} \times t$$

A Stylus profilometer (Alpha-Step 500, Tencor, USA) is used to scan each square in four directions to measure the average thickness, t. Thus, the volume resistivity of each of the twelve squares is calculated and average of all these values is recorded as the volume resistivity of that material.
4.3 Aging Experiments:

Aging experiments are done on both contact resistance and volume resistivity samples. After taking the as prepared sample readings, they are kept at room temperature and readings are taken for every 30 days to measure the effect of temperature and time on volume resistivity. After 90 days, all the samples are kept in a temperature chamber (Model SD-302, Associated Environmental Systems, USA) and readings are taken after 10, 20 and 40 cycles.

The model SD-302 is a low temperature/high temperature test chamber which has 2 cubic feet of working volume. The SD-302 is designed to generate and control low and high temperature environments in the range of -65°C to +200°C (-85°F to +392°F).

For temperature control, it incorporates an all solid state microprocessor programmer which features +/- 1/4°C ( +/- 1/2°F) temperature control stability at the sensor. Fast response nichrome type heaters on ceramic cores are used to raise the temperature and a two stage cascade mechanical refrigeration system lowers the temperature. The chamber has a high temperature failsafe to prevent the temperature from exceeding a present limit. The power requirements are 120V 1PH 60HZ.
This temperature chamber uses Walton’s series F4 ¾ DIN industrial ramping controller. The test is programmed as a ramping profile of 27 steps. The temperature is varied from -55°C to +165°C in steps of 20°C for every 5 minutes. To make sure the equipment is at the ambient chamber temperature, a wait condition is put on step 6 and step 18 (soak time is 15 minutes). A Jump step (26th step-jump to step 2 and repeat steps 2 to 26) is created to make sure the cycle is repeating and End step (27th step) is created to stop the profile. It takes approximately 140 minutes to complete a full cycle.
Figure 10: Walton series F4 ¼ DIN industrial ramping controller.

Figure 11: One Complete Temperature Cycle.
### Table 1. Steps in One Complete Cycle.

<table>
<thead>
<tr>
<th>Step Number</th>
<th>Step Type</th>
<th>Time</th>
<th>Set Point (in °C)</th>
<th>Step</th>
<th>Repeat</th>
<th>End Step</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ramp Time</td>
<td>1 sec.</td>
<td>25°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>5°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>-15°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>-35°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>-55°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Soak</td>
<td>15 min.</td>
<td>-55°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>-35°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>-15°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>5°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>25°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>45°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>65°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>85°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>105°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>105°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>125°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>145°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Soak</td>
<td>15 min.</td>
<td>165°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>165°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>145°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>125°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>105°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>85°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>65°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>Ramp Time</td>
<td>5 min.</td>
<td>45°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>Jump</td>
<td></td>
<td>25°</td>
<td>2</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>End</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>All Off</td>
</tr>
</tbody>
</table>
CHAPTER 5: Results and Discussion

5.1 Contact Resistance Results and Discussion:

5.1.1 MWCNT-Epoxy Composite:

All the contact resistance experiments are carried out as described in the earlier chapter. Table 2 shows the values of contact resistance for different percentages of MWCNT on three different surface finishes. In general, the contact resistance of silver surface finished boards is less than gold surface finished boards in the order $R_{Ag} < R_{Sn} < R_{Au}$. The graph is not showing the general trend in all the cases, this is due to the fact that the results are often dominated by high resistance joints as we can see the standard deviation is much more than expected. It is observed that by applying a pressure on the zero ohms resistors while curing, the conductivity is dramatically increased. The average resistances of individual samples with 2-6 wt% MWCNT are very high so, they are not suitable as solder replacement as of now.

Table 2: Contact resistance measurement corresponding to various MWCNT % loadings on different surface finishes for epoxy adhesives.

<table>
<thead>
<tr>
<th>Loading (Wt %)</th>
<th>Silver</th>
<th></th>
<th>Tin</th>
<th></th>
<th>Gold</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average Resistance(Ω)</td>
<td>Standard Deviation</td>
<td>Average Resistance(Ω)</td>
<td>Standard Deviation</td>
<td>Average Resistance(Ω)</td>
<td>Standard Deviation</td>
</tr>
<tr>
<td>2%</td>
<td>127.5</td>
<td>73.6</td>
<td>239.6</td>
<td>73.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3%</td>
<td>361.1</td>
<td>77.9</td>
<td>387.5</td>
<td>381.5</td>
<td>906.6</td>
<td>100.5</td>
</tr>
<tr>
<td>4%</td>
<td>216</td>
<td>102.9</td>
<td>665</td>
<td>325.1</td>
<td>550</td>
<td>317.4</td>
</tr>
<tr>
<td>5%</td>
<td>258.2</td>
<td>137.1</td>
<td>487.7</td>
<td>192.6</td>
<td>488.7</td>
<td>99.53</td>
</tr>
<tr>
<td>6%</td>
<td>211.2</td>
<td>88.4</td>
<td>353.7</td>
<td>32.1</td>
<td>812.5</td>
<td>238.5</td>
</tr>
</tbody>
</table>

Figure (12) shows the contact resistance behavior of as prepared samples.
Table 3 shows the values of contact resistance of same samples after 60 days storage at room temperature and humidity. It is evident from the table that there is a significant increment in the contact resistance after aging. A similar trend was observed by Lu and Wong with same type of epoxy and surface metals [18]. They suggest that, when the sample is exposed to air, the moisture in the air is absorbed by the polymer matrix and it is condensed at the interface of surface finish and adhesive. The moisture then forms an electrolyte solution at the interface which causes galvanic corrosion and forms a metal oxide. Since there is no fluxing agent to clean this metal oxide, it increases the resistance with increase in aging time. The absence of fluxing agent is advantageous in one way because there is no need to clean the residue and reduce long term corrosion of printed circuit assemblies.
Table 3: Contact resistance measurement corresponding to various MWCNT %loadings on Different surface finishes for epoxy adhesives after room temperature storage for 60 days.

<table>
<thead>
<tr>
<th>Loading (Wt %)</th>
<th>Silver Average Resistance (Ω)</th>
<th>Silver Standard Deviation</th>
<th>Tin Average Resistance (Ω)</th>
<th>Tin Standard Deviation</th>
<th>Gold Average Resistance (Ω)</th>
<th>Gold Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%</td>
<td>1107.5</td>
<td>433.8</td>
<td>561.2</td>
<td>157.5</td>
<td>1795</td>
<td>189.33</td>
</tr>
<tr>
<td>3%</td>
<td>307.5</td>
<td>208.1</td>
<td>860</td>
<td>375.6</td>
<td>523.7</td>
<td>575.8</td>
</tr>
<tr>
<td>4%</td>
<td>841.7</td>
<td>253.3</td>
<td>959.2</td>
<td>442.3</td>
<td>1000</td>
<td>434.2</td>
</tr>
<tr>
<td>5%</td>
<td>480</td>
<td>198.7</td>
<td>1287.5</td>
<td>560.1</td>
<td>785</td>
<td>184.7</td>
</tr>
<tr>
<td>6%</td>
<td>1013.7</td>
<td>1209.9</td>
<td>487.5</td>
<td>52.5</td>
<td>707.5</td>
<td>335.1</td>
</tr>
</tbody>
</table>

Figure (13) shows the contact resistance behavior after 60 days.
Figure 13: Graphical representation of contact resistance of epoxy adhesives on different surface finished PCBs with Different wt% of MWCNT loading taken after certain amount of time under room temperature and humidity.

Table 4 shows the behavior of contact resistance when the samples are kept in a temperature chamber and subjected to varying temperatures for different number of cycles. In general, the contact resistance decreases slightly in the beginning and then increases thereafter. The slight decrease in the early stage of aging was probably due to the fluxing action of the organic acid which was formed after the residual anhydride was hydrolyzed by moisture [18]. A similar trend was observed in the experiments carried out in reference 19 where the contact resistance increase after the initial decrease was probably due to the metal oxide formation caused by galvanic corrosion of metal surface after moisture penetrated into cured polymeric matrix and condensed at the interface between the ECA and metal surface [18]. In MWCNT experiment, the graph is not showing the initial decrement because the decrement is in the initial 1 or 2 cycles whereas the first reading is taken readings after 10 cycles.
Table 4: Contact resistance measurement corresponding to various MWCNT %loadings on Different surface finishes for epoxy adhesives after placing in a Thermal chamber.

<table>
<thead>
<tr>
<th></th>
<th>2%</th>
<th>3%</th>
<th>4%</th>
<th>5%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ag</td>
<td>Sn</td>
<td>Au</td>
<td>Ag</td>
</tr>
<tr>
<td>Res(KΩ) before placing the samples in chamber</td>
<td>5.3</td>
<td>4.3</td>
<td>2.4</td>
<td>1.9</td>
</tr>
<tr>
<td>Res after 10 cycles</td>
<td>8.1</td>
<td>5.2</td>
<td>4.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Resistance after 20 cycles</td>
<td>8.3</td>
<td>6.5</td>
<td>5.9</td>
<td>4.1</td>
</tr>
<tr>
<td>Resistance after 40 cycles</td>
<td>8.8</td>
<td>7.9</td>
<td>6.4</td>
<td>4.9</td>
</tr>
</tbody>
</table>
Figure 14: Graphical representation of contact resistance of epoxy adhesives on different surface finished PCBs with Different wt% of MWCNT loadings after 10, 20 and 40 cycles in Temperature chamber.

5.1.2 MWCNT-Epoxy/Heloxy Composite:

As the contact resistances of MWCNT-Epoxy composites are very high, a viscosity modifier is added to the epoxy composite to reduce the contact resistance. The contact resistance of samples of tin, silver, gold surface finished PCB’s for each % loading, say 8%, 12% and 14% loading of MWCNT and at each % loading, for various epoxy-Heloxy compositions, 3:7, 2:3, 1:1, 3:2, 7:3 ratios are measured and tabulated as below. The following tables show the average contact resistance and standard deviation for the three surface finished boards for all epoxy-Heloxy ratios for 8wt %, 12 wt%, 14wt% MWCNT loading in the mixture respectively.
Table 5: Contact Resistance and standard deviation values for 8 wt% loading of MWCNT in Mixture with varying epoxy-Helox ratios (all the resistance values are in Ohms) on different Surface finished PCBs.

<table>
<thead>
<tr>
<th>E: H</th>
<th>3:7</th>
<th>2:3</th>
<th>1:1</th>
<th>3:2</th>
<th>7:3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>143</td>
<td>43</td>
<td>866</td>
<td>43</td>
<td>8</td>
</tr>
<tr>
<td>Ag</td>
<td>43</td>
<td>1</td>
<td>5</td>
<td>314</td>
<td>187</td>
</tr>
<tr>
<td>Au</td>
<td>5</td>
<td>8</td>
<td>187</td>
<td>151</td>
<td>285.0</td>
</tr>
<tr>
<td>S. D</td>
<td>86.5</td>
<td>22</td>
<td>560</td>
<td>80</td>
<td>.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>201</td>
<td>202</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>45.9</td>
<td>91.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>203.9</td>
<td>137</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>33.7</td>
</tr>
</tbody>
</table>

The graphical representation of these values is as below:
Figure 15: Graphical representation of Contact resistance of epoxy: heloxy adhesive on different surface finished PCBs with 8wt% MWCNT loading and varying epoxy-helox ratios.

Table 6: Contact Resistance and standard deviation values for 12 wt% loading of MWCNT in Mixture with varying epoxy-helox ratios (all the resistance values are in Ohms) on different Surface finished PCBs.

<table>
<thead>
<tr>
<th>E:H</th>
<th>3:7</th>
<th>2:3</th>
<th>1:1</th>
<th>3:2</th>
<th>7:3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>53.8</td>
<td>12.5</td>
<td>5.8</td>
<td>8.5</td>
<td>283</td>
</tr>
<tr>
<td>Ag</td>
<td>331</td>
<td>52</td>
<td>94.2</td>
<td>19</td>
<td>251</td>
</tr>
<tr>
<td>Au</td>
<td>651</td>
<td>133</td>
<td>95</td>
<td>5.6</td>
<td>503</td>
</tr>
<tr>
<td>S.D</td>
<td>49.4</td>
<td>2.4</td>
<td>1.6</td>
<td>8.6</td>
<td>154</td>
</tr>
<tr>
<td></td>
<td>146</td>
<td>62</td>
<td>14.1</td>
<td>17</td>
<td>346</td>
</tr>
<tr>
<td></td>
<td>157</td>
<td>105</td>
<td>41</td>
<td>2.7</td>
<td>305</td>
</tr>
</tbody>
</table>

The graphical representation of these values is as below:
Figure 16: Graphical representation of Contact resistance of epoxy: heloxy adhesives on different surface finished PCBs with 12wt% MWCNT loading and varying epoxy-helox ratios.

Table 7: Contact Resistance and standard deviation values for 14 wt% loading of MWCNT in Mixture with varying epoxy-helox ratios (all the resistance values are in Ohms) on different Surface finished PCBs.

<table>
<thead>
<tr>
<th>14 wt% Loading of MWCNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>E:H</td>
</tr>
<tr>
<td>Sn</td>
</tr>
<tr>
<td>Ag</td>
</tr>
<tr>
<td>Au</td>
</tr>
<tr>
<td>Sn</td>
</tr>
<tr>
<td>Ag</td>
</tr>
<tr>
<td>Au</td>
</tr>
<tr>
<td>S.D</td>
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<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

The graphical representation of these values is as below:
Figure 17: Graphical representation of Contact resistance of epoxy: heoxy adhesives on different surface finished PCBs with 14wt% MWCNT loading and varying epoxy-heloxy ratios.

Consider the following set of graphs, drawn for each metal and its contact resistance behavior for each % loading with varying epoxy-heloxy composition.

Figure 18: Graphical representation of contact resistance behavior of Tin for various % loading of MWCNT with varying epoxy-heloxy ratio.
Figure 19: Graphical representation of contact resistance behavior of Silver for various % loading of MWCNT with varying epoxy-helox ratio.
Figure 20: Graphical representation of contact resistance behavior of gold for various %
loading of MWCNT with varying epoxy-heloxy ratio.

It is observed that silver has least contact resistance among all the three metals
while gold has highest contact resistance in the order $R_{Ag} < R_{Sn} < R_{Au}$. From the above tables
and graphs, it is evident that the contact resistance is decreased considerably (1/10
approximately) when heloxy is added. By adding heloxy, the loading limit is increased to
14% while it is just 8% in the previous case. This is because heloxy acts as a viscosity
modifier which disperses the MWNT’s well in the adhesive.

The minimum contact resistance with least variability for all the metals for
8% loading is observed at 2:3 ration of epoxy-heloxy while it is observed at 3:2 for 12% and
14% as well. Tin has shown some consistency at 12% and gold has shown consistency at
14% wt loading. The values obtained are still not consistent because of the fact that one bad
contact can change the resistance considerably.
All these samples are stored at room temperature and humidity conditions and readings are taken once again after 60 days. The following graphs show the contact resistance behavior with aging.

**Figure 21:** Graphical representation of behavior of Contact resistance of epoxy: heloxy adhesives with 60 days aging on different surface finished PCBs with 8wt% MWCNT loading and varying epoxy-heloxy ratios.
Figure 22: Graphical representation of behavior of Contact resistance of epoxy: heloxy adhesives with 60 days aging on different surface finished PCBs with 12wt% MWCNT loading and varying epoxy-heloxy ratios.

Figure 23: Graphical representation of behavior of Contact resistance of epoxy: heloxy adhesives with 60 days aging on different surface finished PCBs with 14wt% MWCNT loading and varying epoxy-heloxy ratios.
From the above graphs, it is observed that silver has the least contact resistance and gold has the highest resistance. It is also observed that contact resistance increases with aging time the same as the epoxy composite samples.

All the samples are placed in a temperature chamber and exposed to varying temperature cycles to observe the contact resistance behavior. In general, the contact resistance should decrease in the beginning and then increase later. It is because of the same reason mentioned in case of MWCNT-epoxy composites. All these graphs are following a general trend (increasing continuously) same as MWCNT-epoxy composites.

![Graphical representation of behavior of Contact resistance of epoxy: heloxy adhesives with aging on different surface finished PCBs with 8wt% MWCNT loading and varying epoxy-helox ratios after 10, 20 and 40 cycles in a temperature chamber.](image)

**Figure 24:** Graphical representation of behavior of Contact resistance of epoxy: heloxy adhesives with aging on different surface finished PCBs with 8wt% MWCNT loading and varying epoxy-helox ratios after 10, 20 and 40 cycles in a temperature chamber.
Figure 25: Graphical representation of behavior of Contact resistance of epoxy: heloxy adhesives with aging on different surface finished PCBs with 12wt% MWCNT loading and varying epoxy-heloxy ratios after 10, 20 and 40 cycles in a temperature chamber.

Figure 26: Graphical representation of behavior of Contact resistance of epoxy: heloxy adhesives with aging on different surface finished PCBs with 14wt% MWCNT loading and varying epoxy-hel oxy ratios after 10, 20 and 40 cycles in a temperature chamber.
5.2. Volume Resistivity Results and Discussion:

5.2.1 MWCNT-Epoxy Composite:

The loading of MWCNT is varied from 2 to 8 wt% in MWCNT-epoxy composite and corresponding readings of volume resistivity are taken. A graph is drawn between loading of MWCNT and corresponding volume resistivity as shown in the figure (28).

In general, the volume resistivity decreases with increase in loading of MWCNT because of increase in number of conductive paths, however we could not increase the weight % of MWCNT beyond 8% because the composite is too viscous to process for wt % above 8%. The general trend is observed in the below figure. It can also be observed from the figure that 8% MWCNT-epoxy composite has least volume resistivity among all the readings taken.

![Vol. Resistivity(ρ) vs %MWNT](image)

**Figure 27:** Plot between Volume Resistivity $\rho$ (Ω-cm) of epoxy adhesives and Weight percentage of MWCNT loading.
The below graph shows the behavior of volume resistivity when the samples are kept in a temperature chamber and exposed to varying temperatures from -55°C to +165°C same as contact resistance experiments. The Blue line graph is the original plot before environmental testing was done. Red, Green, and Purple line graphs show their proximity to the original value. This graph is statistically supported by the bar graph in the figure (30).

Figure 28: Plot showing the accelerated aging behavior of Volume Resistivity $\rho$ (Ω-cm) of epoxy adhesives.
5.2.2 MWCNT-Epoxy/Heloxy Composite:

As mentioned earlier, we could not increase the wt % of MWCNT beyond 8% because it is too viscous to process. Therefore, a viscosity modifier is added to the MWCNT-epoxy composite to make the composite less viscous to process. By adding heloxy, the wt% of MWCNT that can be added to the composite is increased to 14%. The volume resistivity is recorded for samples with 8%, 12% and 14% wt% of MWCNT for different ratios of epoxy and heloxy (say 3:7, 3:2, 1:1, 2:3, 7:3).

A graph is drawn between volume resistivity and wt% of MWCNT with different ratios of epoxy and heloxy as shown in the figure (31). From the graph, it is evident that the volume resistivity is less for 12% wt for all the ratios of epoxy and heloxy. It is also observed that the average resistance of each sample is decreased by adding heloxy.

![Vol. Resistivity(ρ) vs %MWNT](image)

Figure 29: Plot showing the accelerated aging behavior of Volume Resistivity ρ (Ω-cm) of epoxy adhesives.
For aging experiments, the resistivity was measured only for 12 percent of MWCNT contained samples, assuming the behavior would be similar for the other percentages and because 12% is the highest loading across all epoxy:helox compositions. The readings are taken after 10, 20 and 40 cycles same as in contact resistance experiments. This graph is statistically supported by the bar graph in the figure (33).
Figure 31: Plot showing the accelerated aging behavior of Volume Resistivity $\rho$ (\(\Omega\text{-cm}\)) of epoxy: heloxy adhesives for 12% loading of MWCNT.

Figure 32: Plot showing the accelerated aging behavior of Volume Resistivity $\rho$ (\(\Omega\text{-cm}\)) of epoxy: heloxy adhesives for 12% loading of MWCNT.
CHAPTER 6: Conclusion and Future Work

This research mainly focused on replacing metal filler particles in electrically conductive adhesives with MWCNTs, to make a conductive adhesive with improved electrical properties and testing the conductive adhesives on different surface finished boards like gold, silver and tin. Electrical properties of MWNT/epoxy and MWNT/epoxy: heloxy composites before and after aging were analyzed.

The results obtained so far for contact resistance are encouraging and also draw more attention towards the investigation of contact resistance behavior of different surface finishes to MWCNT filled ECAs. Though the contact resistance is observed to decrease by adding heloxy to the composite, there is certainly a need to decrease it further. The results show that silver has least contact resistance and gold has highest contact resistance for MWNT/epoxy composite and tin has shown least contact resistance for MWNT/epoxy: heloxy composite. It is also observed from the aging experiments that the contact resistance is increasing with increase in number of cycles.

The results obtained for volume resistivity shows that it decreases with increase in percentage loading of MWNTs but the epoxy composite is not processable above 12%. The volume resistivity is decreased further by the addition of heloxy (a viscosity modifier). The aging experiment results shows that, even though there is a decrease in the volume resistivity with increase in number of cycles, the variation is very less when compared with contact resistance.

Even though, we are able to reduce the contact resistance and volume resistivity by some means (adding heloxy), they are still not comparable with the commercially available metal filled ICAs. The contact resistance and volume resistivity are more consistent for 2:3, 3:2 and 1:1 so, it is advisable to omit 3:7 and 7:3 samples in further research.

The preparation of the composite involved the usage of epoxy, heloxy, curing agent and a catalyst. The pot life of the composite was observed to be 72 hrs. The composite was able to be reused when refrigerated. The MWCNT filled adhesives were compatible with oven curing, pressure dispensing and stencil printing.

Based on current results, there are a number of possible directions to extend this research. These directions include:

- A detailed study of chemical reactions involved between the surface finishes and composites used
- Investigate the compatibility for MWNT filled conductive adhesives with different PCB pad surface finishes
- The same experiments can be repeated with different set of resins, viscosity modifiers, curing agents and different curing methods. This may enable the % increase in loading of MWNTs in the adhesive
- The same experiments can be carried out by adding silver flakes to the MWNTs
- The rework of conductive adhesive which is analogous to desoldering of solder paste
- The aging experiments can be carried out in an environmental chamber (in which, temperature and humidity can be controlled) instead of temperature chamber
REFERENCES


9. K.Gilleo, Assembly with Conductive Adhesives, Soldering and Surface Mount Technology, No 19, 12-17, 1995


11. J.Liu, Conductive Adhesives for Electronics Packaging, Electrochemical Publications LTD, Port Erin, Isle of Man, British Isles, 1999


17. http://www.caer.uky.edu/

18. Daoqiang Lu, Member, IEEE, and C. P. Wong, Fellow, IEEE. “A Study of Contact Resistance of Conductive Adhesives Based on Anhydride-Cured Epoxy Systems”
VITA

Ashwanth Reddy Vangala was born on February 28, 1985 in Hyderabad, Andhra Pradesh, India. He received the Bachelors of Engineering degree in Electronics and Communications Engineering from Osmania University, Hyderabad, India, in 2007. His research is extending the carbon nanotube filled conductive adhesive work to evaluate lead free surface finishes. In 2007 he began to study in department of Electrical Engineering at University of Kentucky.