PROPERTIES OF SILVER FILLED EPOXY COMPOSITES FOR ELECTRICAL CONDUCTIVE ADHESIVE APPLICATIONS

KHAIRUL ANUAR BIN SHARIFF

UNIVERSITI SAINS MALAYSIA

2011

PROPERTIES OF SILVER FILLED EPOXY COMPOSITES FOR ELECTRICAL CONDUCTIVE ADHESIVE APPLICATIONS

by

KHAIRUL ANUAR BIN SHARIFF

Thesis submitted in fulfillment of the requirements

for the degree of

Master of Science

June 2011

ACKNOWLEDGEMENTS

TABLES OF CONTENTS

CHAPTER 1 - INTRODUCTION

CHAPTER 2 - LITERATURE SURVEY

CHAPTER 3 - MATERIALS AND METHOD

CHAPTER 4 - RESULTS AND DISCUSSION

CHAPTER 5- CONCLUSIONS AND RECOMMENDATIONS

LIST OF FIGURES

LIST OF ABBREVIATIONS

Argentum	Ag
Tin/Lead	Sn/Pb
Electrical Conductive Adhesive	ECA
Ball Grid Arrays	BGA
Printed Circuit Board	PCB
Integrated Circuit	IC
Surface Mount Device	SMD
Anisotropic Conductive Adhesive	ACA
Isotropic Conductive Adhesive	ICA
Electromagnetic Interference	EMI
Coefficient of Thermal Expansion	CTE
Field Emission Scanning Electron Microscopy	FESEM
Thermal Exfoliated Graphite	TEG
Electrical Conductive Polymer Composite	ECPC
Electromagnetic	EM
Radio Frequency	RF
Energy Dispersive Spectroscopy	EDS
Dynamic Mechanical Analysis	DMA
Thermogravimetry Analysis	TGA
Printed Wiring Board	PWB
Diglycidyl ether of bisphenol F	DGEBF
Jeffamine D230	JEA D230
American Standard Testing of Materials	ASTM

Diglycidyl ether of bisphenol A	DGEBA
Amine Adduct Powder	AAP
Personal Electronic Device	PED
Shielding Effectiveness	SE
Variable Pressure	VP
Carbon nanotube	CNT
Transmission Electron Microscope	TEM
Per Hundred Resin	Phr
Part by weight	Pbw
Epoxide Equivalent Weight	EEW
Amine Hydrogen Equivalent Weight	AHEW
Rotation per minute	Rpm
American Standard Testing Method	ASTM
Differential Scanning Calorimetry	DSC
Tape Automated Bonding	TAB

LIST OF SYMBOLS

R_v	Volume resistance
ρ_v	Volume resistivity
V_f	Volume fraction of filler
V_c	Critical volume fraction
I_v	Resultant Current
V_v	Voltage potential
S_f	Flexural strength
E_B	Flexural modulus
ε_f	Flexural strain
Ω	Ohm
$\Omega.cm$	Ohm.cm
T_g	Transition glass temperature
ε_b	Strain at break

LIST OF APPENDICES

SIFAT-SIFAT KOMPOSIT EPOKSI TERISI PARTIKEL PERAK BAGI APLIKASI PEREKAT KONDUKTIF ELEKTRIK

ABSTRAK

Matlamat kajian adalah untuk meningkatkan sifat konduktiviti elektrik, terma dan lentur komposit epoksi terisi partikel perak bagi aplikasi perekat konduktif elektrik. Bagi mencapai matlamat utama ini, analisa ke atas kesan kandungan agen pematang, perbandingan diantara dua jenis pengisi perak dan kesan komposit epoksi terisi partikel hibrid perak dijalankan. Kajian mendapati kandungan 21 per seratus resin dan 18 per seratus resin agen pematang di dalam epoksi masing-masing memberikan modulus lentur dan kekuatan lentur yang tinggi. Analisis CTE dan DMA menunjukkan bahawa 15 per seratus resin agen pematang memberikan nilai CTE terendah, modulus dan suhu peralihan kaca (T_g) yang tinggi. Bahagian kedua dari kajian ini melibatkan penghasilan perekat konduktif elektrik. Perekat konduktif elektrik sistem satu bahagian dihasilkan dengan menggunakan dua jenis pengisi perak iaitu pengisi perak SF 135 dan SF 499. Hasil pemerhatian menunjukkan bahawa sistem perekat terisi perak SF 135 menghasilkan nilai konduktiviti elektrik yang tinggi dengan ambang perkolasi yang rendah, modulus lentur yang tinggi, dan pekali pengembangan terma (CTE) yang rendah berbanding sistem perekat terisi perak SF 499. Seterusnya, aplikasi pengisi perak SF 135 di dalam sistem epoksi satu bahagian dan dua bahagian telah dijalankan. Sistem epoksi satu bahagian menunjukkan konduktiviti elektrik dan pengembangan terma yang lebih baik berbanding sistem epoksi dua bahagian. Bahagian ketiga kajian ini merangkumi penghasilan komposit epoksi terisi partikel hibrid perak. Keputusan menunjukkan penambahan 0.4% isipadu pengisi perak bersaiz nano dengan 30% isipadu pengisi perak SF 135 di dalam epoksi memberikan 11% peningkatan nilai konduktiviti

elektrik berbanding dengan penambahan 1.5% isipadu pengisi perak bersaiz nano. Secara ringkasnya, berdasarkan sifat elektrik, CTE dan T_g yang baik, sistem epoksi satu bahagian, pengisi perak SF 135 dan penghibridan antara partikel perak bersaiz nano dan mikron adalah dicadangkan dalam penghasilan perekat konduktif elektrik.

PROPERTIES OF SILVER FILLED EPOXY COMPOSITES FOR ELECTRICAL CONDUCTIVE ADHESIVE APPLICATIONS

ABSTRACT

The study aims to improve the electrical conductivity, thermal and flexural properties of silver filled epoxy composites for electrical conductive adhesive applications. In order to achieve the main aim, few parameters such as effect of hardener content, comparison on two types of silver filler and hybrid silver filled epoxy composites were investigated. It is found that 21 phr and 18 phr of hardener content in the epoxy give an optimum flexural modulus and flexural strength, respectively. CTE and DMA analysis shows that the 15 phr of hardener content give the lowest CTE value, highest storage modulus and high T_g. Second part of the research involves the production of electrical conductive adhesives. One-part electrical conductive adhesives are prepared by using two types of silver (silver SF 135 and silver SF 499). It is observed that the silver SF 135 adhesives systems exhibits higher electrical conductivity with lower percolation thresholds, higher flexural modulus, and lower coefficient of thermal expansion (CTE) compared with silver SF 499 adhesive system. Furthermore application of Silver SF 135 in one-part and two-part epoxy systems was carried out. One-part epoxy system exhibits better electrical conductivity and thermal expansion properties compared with two-part epoxy system. The third part of the study covers on the hybrid silver filled epoxy composites. Results indicate that addition of 0.4 vol.% of nanosilver with constant 30 vol.% silver SF 135 in epoxy resin give 11% increased of electrical conductivity value compared with 1.5 vol.% of nanosilver addition. In short, due to the higher electrical conductivity, CTE and T_g, one-part epoxy system, silver SF

135 and hybridization between micron-size and nano-size of silver is recommended for the production of electrical conductive adhesives.

CHAPTER 1

INTRODUCTION

1.1 Overview of conductive polymer composites

Conductive polymer composites consist of a polymer/conductive polymer and conductive fillers that provides mechanical strength and conduct electricity, typically through the addition of conductive fillers such as gold, silver, nickel, copper and aluminum or carbon nanotubes (CNTs) (Zhao et al., 2007). This material has gained much attention in the past decade owing to their environmental and technical profit. In general, they consist of metal powder fillers usually silver that conducts electricity inside a polymeric resin. For electronic applications, silver are widely used since this material are easy to precipitate into wide range of controllable size and shapes. Different percolation threshold of the conductive polymer composites can be achieved using different size and shapes of silver fillers (Lin et al., 2009). Additionally, this silver shows high electrical conductivity when it is oxides compared with other metal oxides such as copper or aluminum oxides (Lin et al, 2009).

Resins such as an epoxy, silicon or polyimide have been widely used in electronic applications due to superior properties such as thermal resistance, adhesion, mechanical strength and impact strength (Toon, 2005). Epoxy is normally preferred due to many beneficial properties, i.e. low shrinkage, good adhesion and resistance to thermal and mechanical shocks. They also have good resistance to moisture, solvents and chemical attacks. The primary reason for adding conductive fillers to a polymer is to enhance the electrical and/or thermal conductivity characteristics of the polymer.

Electrical conductivity can be explained by the established percolation theory (Gojny et al., 2006). Percolation can be defined as a phase transition at which dramatic change occurs at one sharply defined parametric value, as this parameter is continuously changed (Tee et al., 2007). The concentration of filler that marks the insulator-conductor transition is often referred to as the percolation threshold. This sudden jump conductivity is attributed to the formation of the first infinite agglomeration pathway that allows electrons to travel a macroscopic distance through the composites

Conductive polymer composites posses the capability to have tailored resistivity ranging from 10^{10} to as low as 10^{-3} Ω.cm, depending on variables such as conductive filler type, aspect ratio, concentration and processing method (Strong, 1996). One of the applications of conductive polymer composite is electrical conductive adhesives (ECA). There are two types of ECAs, isotropic conductive adhesives (ICA) and anisotropic conductive adhesives (ACA) (Shimada et al., 2000). Although the concepts of these materials are different, both materials are composed from insulating polymers and conductive particle fillers.

The use of ECAs as solder replacement has recently become important, not only because of environmental issues such as reduction in use of lead and fluxes, but also because of requirements on fine pitch interconnections and short curing time at lower curing temperatures. ECAs are perceived as the next generation interconnection material for printed wiring boards (PWBs) and electronic packaging (Wong et al., 1997; Wong et al., 1998; Liu et al., 1995). ECAs technology can offer numerous advantages, such as fewer processing steps that eliminate the fluxing and cleaning of the components which reduce processing cost (Li and Wong, 2004a ; Li and Wong 2004b ; Li et al., 2004a).

1.2 Problem statement

Electrical conductive adhesives (ECA) have been explored as an environment friendly interconnection technique (Fan et al., 2004). Typical ECA materials have some reliability issues including conductivity fatigue, limited current- carrying capability and silver migration (Kang et al., 1998). There are a number of factors need to be considered in the conductive polymer composites system such as filler concentration, filler shape and size, filler composition, curing time and temperature and the presence of additive or solvent in the composite system (Tee et al., 2007). The desirable properties may further be improved with a suitable choice of solvents, fillers, colorants, flame retardants, flexibilizers and cure accelerators (Tan, 2003). The application of conductive nanoparticles to an isolating polymer matrix is expected to induce an electrical conductivity and also enhance the thermal properties at very low filler contents.

The good electrical and mechanical properties of conductive polymer composites can be achieved when a homogeneous dispersion of conductive fillers, a good impregnation of matrix resin and a strong adhesion of conductive fillers to the matrix are fulfilled (Zhu et al., 2004; Gojny et al., 2004; Gojny et al., 2005). As known, curing agent and type of resin greatly influences the properties of electrical conductive adhesives (Li et al., 2004). Previous work done by Li et al. (2004) reported that types of curing agents greatly influence the electrical conductivity of isotropic conductive adhesives (ICA).

Nowadays, two-part system conductive adhesive is widely used in electronic applications. However there are some issues in two-part system such as the requirement to pre-mix before used hence results in the two stage of mixing during manufacturing

3

process and filler settling problem. To solve this problem, one-part system electrical conductive adhesives are applied. In one-part system, amine adducts powder is preferred to be used in epoxy resins compared with other amine curing agents due to outstanding adhesion to a wider range of substrates and very high bond strength between two surfaces (Minford,1993).

In an attempt to understand and improve the properties of ECA materials, silver nanoparticles were introduced into the conventional ECA compositions that contains silver micron flakes as conductive fillers. Silver micron flakes are existing conductive filler used in ECA applications. Properties of mixture between silver flakes and silver nanoparticles as fillers in ECA materials were investigated and analyzed.

1.3 Objectives and scope of thesis

This study aims at improving the electrical, mechanical as well as thermal properties of conductive epoxy composites. The present work is conducted based on the following objectives:

i.   To investigate the optimum hardener content (phr) in producing a cured sample with higher mechanical and thermal properties.

ii. To study the effect of different type of silver fillers (SF 135 and SF 499) and epoxy system (one-part and two-part) on the properties of conductive epoxy composites.

iii. To study the effect of hybrid silver (nanoparticles and micron particles) composition on the properties of conductive epoxy composites.

CHAPTER 2

LITERATURE REVIEW

2.1 Conductive polymer composites

2.1.1 Introduction

During the past decades, conductive polymer composites have found use in a variety of applications. Incorporating the conductive fillers into polymer matrix creates a material that is tough, flexible and electrically conductive. The ability of polymers when used as matrix can enhance the adhesion properties, corrosion resistance, processing characteristic and strength to weight ratio of composites while maintaining excellent electrical and thermal insulations. The electrical and thermal conductivity properties of polymers can be increased by adding conductive fillers such as metals (silver, aluminum, copper and nickel), carbon black and graphite (Zhao et al., 2007). By adding conductive fillers to polymers, composites can be designed with specific properties tailored to each application.

2.1.2 Theory of conductive polymer composites

The primary reason for adding conductive fillers to a polymer is to enhance the electrical and thermal properties of the polymer. The change of a polymer from insulator to electrically conductive is important to be focused and discussed. The addition of conductive materials to insulating polymer materials affects the electrical properties of the composites according to the degree of filling and proximity of conductive particles to other conductive particles. There are three situations that are

possible to occur after the addition of conductive materials to polymer; no contact between conductive particles, close proximity and physical contact.

In general, there are two conductive pathways for conductive polymer composites as shown in Figure 2.1. One is genuine condition, caused by particle- to-particle contact within the polymer matrix. Electron can jump the gap between the particles and creating current flow when the conductive particles are in close proximity. The ability of an electron to jump a gap under given voltage increases exponentially with decreasing gap size. According to Bhattacharya (1998), electrons are able to jump gaps as large as 10 nm.
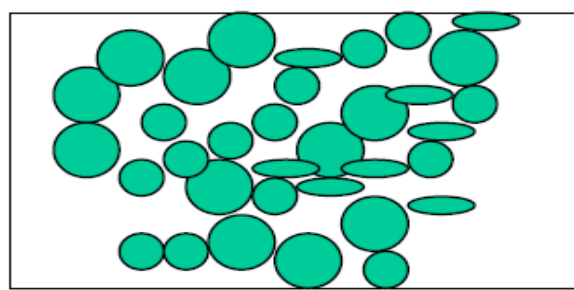
(a)
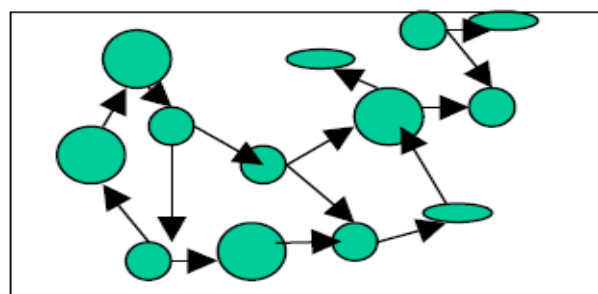
(b)

Figure 2.1: Conduction mechanisms in conductive adhesives (a) Particle-to particle (b) Electron tunneling (Ritter, 1999).

The most general approach to descript the electron transportation in conductive polymer composites in relation to the contact of conductive particles is provided by the percolation theory. In conductive polymer composites, as the conductive filler loading is progressively increased, the electrical resistance does not decrease significantly until the filler loading reach a critical volume fraction, V_c. The critical volume fraction meaning a minimal fraction of conductive filler at which continuous conducting chain of macroscopic length appears in the conductive polymer composites system (Vilcakova et al., 2002). At this point, where the electrical resistance decreases abruptly, is called percolation threshold. Trends in properties of metal-filled polymer composites with volume loading (Bhattacharya, 1998) as shown in Table 2.1:

Table 2.1: Trends in properties of metal-filled polymer composites with filler volume (V_f) and critical volume (V_c) (Bhattacharya, 1998).

Properties	Effect of increasing concentration of metallic particles
Mechanical Flexural modulus	For filler volume (V_f) < critical volume (V_c) flexural modulus increase; However if $V_f > V_c$ flexural modulus increase or decrease
Flexural strength	For filler volume (V_f) < critical volume (V_c), flexural strength increase or decrease; However if $V_f > V_c$ flexural strength decrease
Compressive strength	Increase
Elongation at break	Large decrease
Physical Density	Usually increase
Shrinkage during cure	Decrease

Table 2.1. Continued

Thermal	
Thermal expansion coefficient	Usually decrease
Thermal conductivity	Increase
Glass transition temperature	Little or no change
Electrical	
Volume resistivity and dielectric strength	Decrease
Dielectric constant	Increase
Dissipation factor	Increase
Shielding effectiveness	Increase

The percolation theory describes in general the electrical conductivity of cured conductive adhesives (Wu et al., 2007), depending on the filler fraction of composites. Wu et al. (2005) showed that the isotropic conductive adhesives (ICA) with spherical particles posses the percolation threshold near 15-30% based on volume fraction. Also, Wu et al. (2005) reported that the percolation threshold is lower for filler with higher aspect ratio (e.g flake, wire or rod geometry) or a mixture of micro and nanoparticles.

2.1.3 Raw materials

2.1.3.1 Polymeric resin

Thermosetting polymer resins are widely used as matrix material for electronic packaging applications such as electrical conductive adhesives (ECA) and electromagnetic interference (EMI). Owing to their densely cross-linked structure, they exhibit a number of superior qualities such as high glass transition temperature, high modulus, high creep resistance, low shrinkage at elevated temperature and good resistance to chemicals. These unique properties have been employed to develop reinforced composites that exhibit high specific strength, corrosion resistance to most

chemicals and good dimensional stability at elevated temperatures. Thermosetting polymers required the chemical reactions for curing; therefore the process of thermoset polymers is reactive processing (Du, 2003). Thermoset polymers are typically insoluble and cannot be re-melted or reformed into another shape after curing process (Du, 2003).

Liquid thermosets resin allow for easy mixing of colorants, fillers, reinforcements and processing aids, usually with just simple stirring or mechanical mixing. The low viscosity of thermosets polymers in the beginning of the process has advantages in being molded into very complex shapes and capable of wetting the reinforcement fillers in the composite. Among the several available thermosetting polymers, epoxy resins are a popular choice due to their ability to adhere to a wide variety of fillers and to form a densely cross-linked molecular structure during curing, which provide excellent stiffness, dimensional stability and resistance to chemicals.

However, due to its highly cross-linked structure, epoxy exhibits poor resistance to crack initiation and propagation. Besides, epoxy adhesives adhere to a large number of materials including metals and glasses. Epoxy adhesives are widely used in aerospace, automotive, building, and electrical and woodworking applications (Tan, 2003). Advantages over other reaction-setting adhesives are that no volatile products are released on cure and shrinkage is low. Thermoset epoxies filled with silver particles so far the most common adhesive binders for isotropic conductive adhesives (ICA) used for component assembly.

Epoxy resin has been used for decades due to their many superior properties, such as low shrinkage, good adhesion, and good resistance to moisture and chemical attacks (Matthews and Rawlings, 1999). Table 2.2 shows the general properties between thermoset and thermoplastic material.

Table 2.2: General properties between thermoset and thermoplastic material (Matthews and Rawlings ,1999).

Properties	Thermoset	Thermoplastic
Young modulus (GPa)	1.3-6.0	1.4-4.8
Tensile strength (MPa)	20-180	40-190
Fracture toughness		
K_{IC} (MPa.m$^{1/2}$)	0.5-1.0	1.5-6.0
G_{IC} (KJ/m^2)	0.02-0.2	0.7-6.5
Maximum service temperature (^{0}C)	50-450	25-230

Hardener is used especially for epoxy adhesives. These hardeners are necessary to produce a cross-linked epoxy polymer by chemical reactions. There are two main types of hardener/curing agents for epoxies; amines and acid anhydrides. Amine hardeners are mixed with resin in such quantities that there is approximately one amine-hydrogen for each epoxide ring; a primary amine and epoxide will react in a condensation polymerization, as shown in Figure 2.2:

$$\text{-NH}_2\text{+ CH}_2 - \overset{\displaystyle O}{\overset{\displaystyle /\backslash}{\text{CH- CH}_2\text{–O-}}} \longrightarrow \text{-NH}_2\text{+ CH}_2 - \overset{\displaystyle OH}{\underset{|}{\text{CH- CH}_2\text{–O-}}}$$
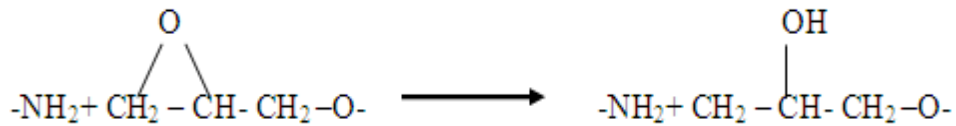
Reaction for first amine-hydrogen

$$\text{-NH- CH}_2 - \overset{\displaystyle OH}{\underset{|}{\text{CH- CH}_2\text{–O-}}} \quad + \quad \text{-NH}_2\text{+ CH}_2 - \overset{\displaystyle O}{\overset{\displaystyle /\backslash}{\text{CH- CH}_2\text{–O-}}}$$

$$\longrightarrow \quad \begin{array}{c} \overset{\displaystyle OH}{\underset{|}{\text{CH}_2 - \text{CH- CH}_2\text{–O-}}} \\ \text{CH}_2 - \text{CH- CH}_2\text{–O-} \\ | \\ OH \end{array}$$
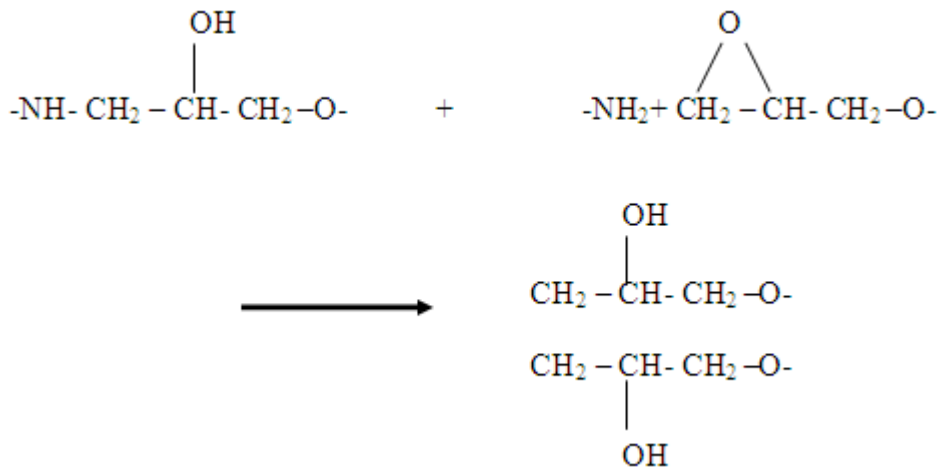
Reaction of second amine-hydrogen

Figure 2.2: Reaction of condensation polymerization (Tan, 2003)

The amine group breaks the epoxy ring, allowing the nitrogen to connect to the epoxy. This leaves hydrogen on the nitrogen available to react with another epoxy. Thus cross-linking is propagated as these multi-ended molecules react. Amines are subdivided into two main classes: (1) aliphatic and their derivatives (which react at room temperature), and (2) aromatic, which require heat to cure. Aliphatic amines are low viscosity, almost colorless liquids. They exhibit a transient ammonia odor as the container is opened and a permanent, slightly 'fishy' odor. They are used where a room temperature curing system is necessary and where the operating temperature of the device will not exceed $130\,^{0}$C.

However, aliphatic amines inherent some disadvantages. It can cause allergenic responses in some people due to its high vapor pressure. Thus, modification has been made and the product is called aliphatic amine adducts (Tan, 2003). The general formula and description for aliphatic amine adducts are shown in Figure 2.3:
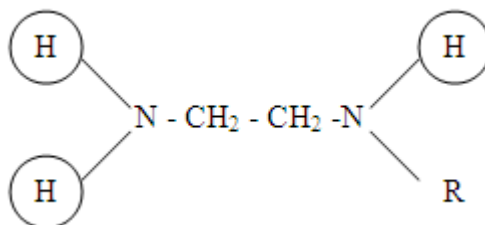
Figure 2.3: General formula and description for aliphatic amine adducts (Tan, 2003).

R can be an epoxy molecule or one of several of other chemicals reactive toward amines. The circle "H's" are still reactive and will react with any other available epoxy groups. The amine is pre-treated with a small amount of epoxy or other chemical that is reactive toward the amine. There is still a large excess of untreated amine left. However, the ratios are significantly increased and it has lower vapor pressure, which means fewer and less severe allergenic responses. Aromatic amines differ markedly from aliphatic amines; it is also a member of the amine family. Aromatic amines offer significantly higher heat deflection temperature and retention of electrical properties to higher temperatures than their aliphatic counterpart. Some typical examples of aromatic amines are shown in Figure 2.4:
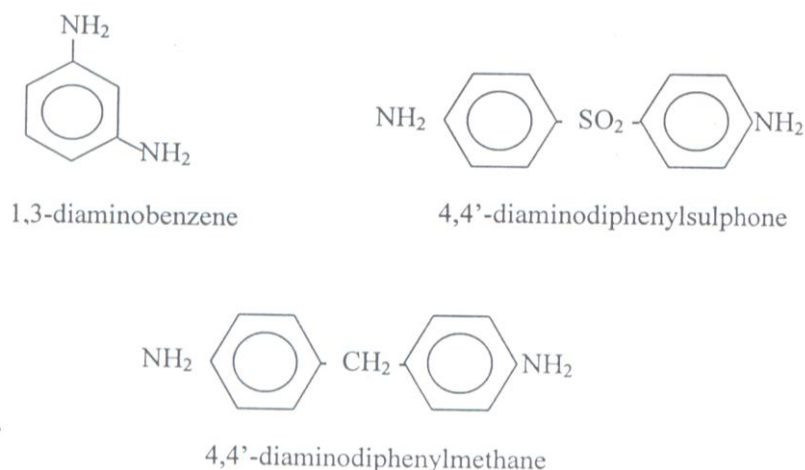
Figure 2.4: Types of aromatic amine (Tan, 2003).

The mechanism of cure is the same as that for aliphatic amines. The only difference is that it occurs so slowly at room temperature that is impractical, so heat from 50°C to 60°C is necessary. Most aromatic amine curing agents will crystallize upon standing. This is a physical phenomenon and is reversible with heat. These curing agents are a eutectic blend of two solid aromatic amines, metaphenylene diamine and methylene dianiline. When blended in the right ratio and melted, they become a liquid at room temperature. Crystallization occurs slowly and reheating to 140°C to $150\,^{o}$C is necessary to completely reliquefy. Vapors coming off during heating cause brown stains on everything with which they come in contact, including people, so heating ovens should be vented to the outside.

Acid anhydrides are a non-amine class of epoxy curing agents. Epoxy cured with acid anhydrides by condensation polymerization and it requires an elevated temperature (Tan, 2003). Examples of some acid anhydrides hardeners are shown in Figure 2.5:
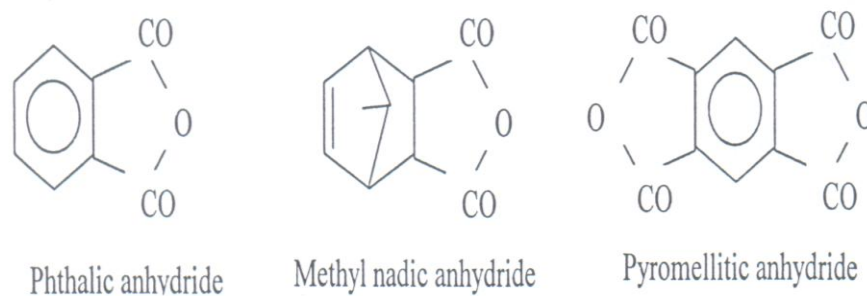
Figure 2.5: Examples of some acid anhydride hardeners (Tan, 2003).

The anhydride most commonly used are very low viscosity liquids, with high combining ratios, making measurement easier and fitting well into meter-mix-disperse equipment. They offer superior high temperatures (above 150°C), insulation resistance and dielectric strength, give a very long pot life (measured in days) and require high temperatures for several hours for a complete cure (Tan, 2003). The cure mechanism of anhydrides is radically different from that of amines. The amine curing agent reacts on the basis of one amine hydrogen to one epoxy group. However, anhydrides group causes the epoxy group to become bifunctional, where the epoxy molecule with a group at each end reacts as though there were two groups at each end. This results in a high cross-link density and improves high temperatures properties.

2.1.3.2 Metal fillers

Fillers are an important class of materials employed for the modification of conductive polymer composites properties. They typically represent the second highest percentage ingredient by weight in the formulated conductive polymer composites, after the base matrix resin. Fillers are used for economic as well as performance reasons. Silver is the most commonly used conductive filler for conductive polymer composites because of its high electrical conductivity, chemical stability, and lower cost compared

to gold (Tan et al., 2005). Unlike many other metals such as copper, that become non-conductive after being oxidized due to exposure to heat and humidity, silver oxides show high conductivity. The other important attribute is that silver can be easily precipitated into a wide range of controllable sizes and shapes (Wang et al., 2005).

Silver flakes are widely used as fillers in electrical conductive adhesives (ECA). Silver flakes can provide conductivity by allowing the flake particles to overlap one another. On the other hand, the voids caused by the overlapping can be filled with the small particles such as silver nanoparticles. Silver is slightly more ductile, excellent electrical conductivity and similar thermal conductivity compared with copper. Besides that, silver has a higher density than copper. Further, the cost of silver is approximately four times of copper (Renee et al., 2006).

2.1.4 Factors that influence the electrical properties of conductive polymer composites.

Several factors that influence the electrical properties of conductive polymer composites include the type, concentration and conductivity of the additive, as well as polymers materials selected. In most cases, these factors are all interrelated and therefore must be addressed collectively to yield the most cost effective material selection (Jia et al., 2001). Basically, an increase in conductive fillers concentration in polymer decreases the resistivity (increase the conductivity) of the composite materials. Generally, resistivity is not increased with increasing conductive fillers concentration until the critical threshold level is reached. At this level, the resistivity of the polymer composites decreases sharply with every small increase in conductive filler

concentration which pass the critical threshold level continue to lower resistivity but at a substantially lower rate.

Therefore, the conductive filler concentration influences the resulting resistivity values. The actual concentration of a particular conductive filler requires in a specific applications is directly related to all of the factors previously mentioned, that is, filler type, aspect ratio, material, and processing method (Mcqueen et al., 2004). The conductive filler size can affect the degree of connection and distribution between conductive fillers in the composites. Theoretically, continuity of conductive fillers will decrease the electrical resistivity (increase electrical conductivity) for the conductive polymer composites materials. The differences in conductive filler size distributions significantly affect the critical concentration at which the polymer composites become conductive (Tee, 2006). Fillers electrical conductivity is a major factor in determine the electrical properties of conductive polymer composites. It also controls the critical concentration level. All other factors being equal, the higher the conductivity of the filler, the lower the concentration required to achieve a particular level of conductivity.

The electrical resistivity of conductive polymer composites is strongly dependent on the shape of the conductive filler. Conductive polymer composites filled with silver flake-shape particles shows slightly higher electrical conductivity than the cured conductive polymer composites that consists of spherically shaped silver particles (Tee, 2006). Silver particles with flake shape provide a greater contact area for the filler particles in conductive polymer composites compared with spherical shape, resulting in a better electrically conductive path (Tee et al., 2007). Figure 2.6 shows a schematic

diagram of the contact area involved silver particles and silver spheres in polymer matrix resin.
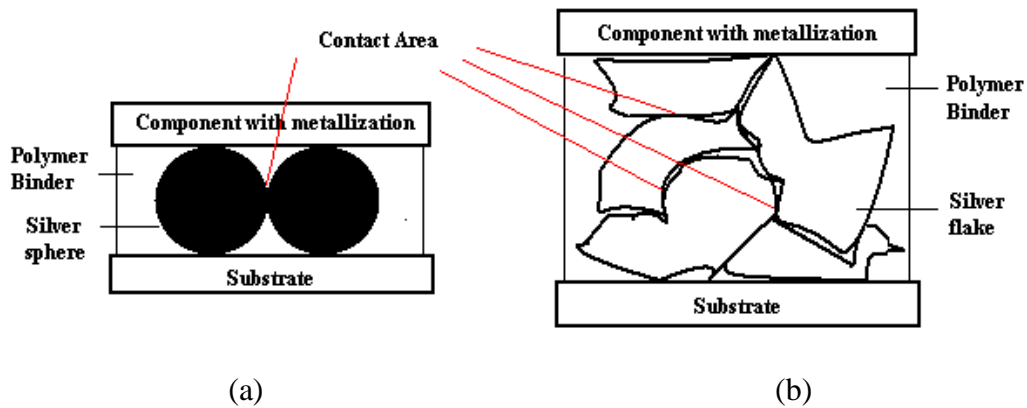
Figure 2.6: Contact area accounted for when (a) silver spheres in contact with lower area and (b) silver flakes with irregular shape in contact with each other in greater area (Tee, 2006).

2.2 Types of conductive epoxy composites

2.2.1 Metal filler filled epoxy composites

2.2.1.1 Silver filled epoxy composites

Silver-filled thermosetting polymers were first patented as electrically conductive adhesives (ECA) in the 1950s (Fan, et al., 2004; Lu and Wong, 2000). ECA nanocomposites are typically formulated with conductive nanoparticles, usually spherical silver particles, and an insulating polymer matrix, usually a thermosetting epoxy resin, as the binder (Fan et al., 2004). The establishment of electrical conductivity would result primarily from more intimate contact between the silver particles, caused by the curing shrinkage of the polymer matrix (Fan et al., 2004). When nanoparticles are present in the ECA systems, electron tunneling (Muraviev, 2005; Fan et al., 2004; Li et al., 2004a) and thermionic emission may also be effective conduction mechanisms (Fan et al., 2004). There are a number of advantages and limitations of silver nanoparticles/epoxy adhesives over existing solder technology (Tee, 2006).

The advantages are lower processing temperatures (80°C to 140°C) in comparison to that of solder (220°C), reducing problems associated with solder joint fatigue and stress induced cracking, decreasing stress on heat sensitive components, nano-sized filler facilitate finer line resolution, closely-matched CTE than solders to that of epoxy based substrate, offers a compliant attachment, minimizing failures with high flexibility, higher creep resistance and stress dampening. On the other hand, the limitations are found in areas such as moisture absorption, silver migration, rework is not as convenient as for solder, possible production problem such as air entrapment, and increase in contact resistance during thermal exposure and low joint strength. The electrical conductivity of the silver epoxies is compared to the values of pure metals and epoxy as shown in Table 2.3.

Table 2.3: Bulk electrical conductivity values for selected metals, polymers and composites (Fan et al., 2004).

Material	Electrical conductivity (S/cm)
Silver	2.7×10^6
Copper	1.7×10^6
Aluminum	1.6×10^6
Carbon Nanotubes (CNT)	300×10^6
Epoxy resin	1.0×10^{-15}
Conductive adhesive	1.0×10^6

2.2.1.2 Copper filled epoxy composites

Ductile material such as copper have a large plastic work potential which can contribute to composite toughness if properly utilized (Robert and Pradipta, 2007). The addition of copper fibers to a thermoset matrix creates multifunctional composites with high stiffness, toughness, strength and electromagnetic interference (EMI) shielding

18

(Renee et al., 2006). Applications of these composite materials include non-destructive measurement of damage within the composite by monitoring variation in conductivity and applications in machine brake materials since copper fiber exhibit good friction and elevated temperature fade resistance (Robert and Pradipta, 2007).

These composites are also extensively used in microelectronics applications and printed circuit board (PCB) technology where copper lead frames are embedded in an epoxy matrix. Copper was chosen because of its high ductility, formability, strength and electrical properties. There are other metal fiber materials that could be considered besides copper to create a multifunctional material, but most of these have inherent problems (Renee et al., 2006). Previous work by Mamunya et al. (2004) reported that the conductivity of copper powder increases exponentially with increasing particle size.

2.2.1.3 Aluminum filled epoxy composites

Aluminum is one third the density of copper and is half the cost weight (Renee et al., 2006). However aluminum is approximately half a ductile as copper, has lower thermal conductivity, lower electrical conductivity, lower Young's modulus and strength versus density than copper (Martin et al., 2007). Therefore, we would expect that a composite with aluminum fibers would have lower fracture and impact toughness to a composite with copper fibers at the same volume fraction (Renee et al., 2006). Previous works by Martin et al. (2007) reported that the nano Aluminum containing composites exhibited a higher elastic modulus due to cross-link density, as revealed by dynamic mechanical analysis measurement.

2.2.2 Carbon filler filled epoxy composites

2.2.2.1 Carbon nanotubes filled epoxy composites

Carbon nanotubes (CNTs) are new materials, which have many interesting application in different fields such as nanoelectronic devices, aeronautic and aerospace industries (Broza et al., 2007). Most researchers agree that CNTs can exhibit a large variety of thermo physical properties depending on the structure and diameter of nanotubes (Mamunya et al., 2008). A combination of CNTs with an insulating polymer matrix is expected to enhance the thermal conductivity and results in obtaining electrical conductive composites at very low filler concentrations (Moisala et al., 2006). Improvement of the polymer/CNT properties strongly depends on several factors, such as orientation and distribution of CNTs in the polymer matrix, the manufacturing process, the surface contacts and adhesion between both components (Young et al., 2005).

The use of CNT in polymer /CNT composites has attracted wide attention in terms of particular mechanical and electrical properties (Breuer and Sundaraj, 2004). The main problems and challenging tasks are in creating a good dispersion, well alignment and strong interface bonding of CNTs in the polymer matrix, forming a structural frame and electrical conducting path, attaining good load transfer from the matrix to the CNTs during loading and increasing the electrical conductivity (Breuer and Sundaraj, 2004).

CNTs can improve the mechanical properties and electrical conductivity of composites because of their high aspect ratio and excellent electrical, mechanical, thermal and magnetic properties (Siu et al., 2007). These properties, in combination with an aspect ratio up to several thousands, enables the developments of electrically

conductive polymers using only very low filler contents, such that the composites retain or even improve on mechanical performance of the matrix (Gojny et al., 2006).

2.2.2.2 Graphite filled epoxy composites

The graphite-epoxy composite materials consist of a reinforcement made of successive graphite layers and an epoxy resin matrix. The reinforcement is meant to assure the imposed mechanical properties, while the matrix role is to assure a relatively uniform distribution of the mechanical stresses, to protect the reinforcement against the external aggressive agents and to give the parts a wanted shape (Grimberg et al., 2001). The advantages of the graphite-epoxy composites are well known, for example high breaking strain, low density and low coefficient of expansion, as well as the lack of fatigue behavior. Among their disadvantages we should mention a low resistance to delaminations both between the reinforcement fibers and matrix (Grimberg et al., 2001).

Therefore, graphite platelets are a potential alternative to carbon nanotubes with regards to cost and desired properties. Polymers reinforced with such particles have many potential applications such as fuel cells, electromagnetic interference shielding of electronic enclosures, radar absorbent coatings and thermo mechanically enhanced materials (Asma and Isaac, 2004). The use of thermal exfoliated graphite (TEG) as a filler gives an opportunity to obtain the composite materials with a wide range of electrical and thermal characteristics. A form of polymer/graphite oxide composites can be obtained by mixing graphite oxide with the polymer precursors and subsequently heating the mixture for polymerization. Graphite nanoplatelet/ polymer composites have been a focus of recent development (Pan et al., 2000; Chen et al., 2001; Fukushima and Drzal, 2002; Thongruang et al., 2002; Yalcin et al., 2003; Zheng et al., 2004) for use as

low cost, lightweight materials with mechanical properties potentially superior to those of pure polymers without the penalty of increased weight.

2.3 Application of electrical conductive polymer composites (ECPC)

2.3.1 Resistors and Transducers

The electrical conductive polymer composites (ECPCs) most often applied for the preparation of resistors, which form solid composites with a low value of coefficient thermal expansion (CTE) (Mohd Anuar, 2008). Stability to changes in humidity, high wearing qualities in comparison with ceramic and core potentiometers and high corrosion resistance provide high exploitation time of potentiometers prepared from ECPCs. Pressure transducers from ECPCs are of great importance for robot production. Transducers for robots are constructed with a large number of outlets possessing alternating electrically conductive and insulating elements (Mohd Anuar, 2008).

2.3.2 Die attach adhesives

Metal-filled conductive adhesives have been established as an adhesive material used for die attachment (Tadashi et al., 2003). Die attach is an assembly process of wire bonding in electronic industry where the silicon die or chip is placed on the substrate, die pad or cavity before the implementing first interconnection. The main purpose of die attaching is to hold the die in exact position before wire bonding or first interconnection. For this purpose, a die attach adhesive with strong adhesion property is needed. Figure 2.7 shows the placement of die attach adhesive in a wire bond ball grid array package. This adhesive provides thermal and/or electrical conductivity between the die and the package, essentially affecting the performance of the device while operating in the field. Higher thermal conductivity is preferable for the die attaching material, since it results

in better heat dissipation from die (Tadashi et al., 2003). Therefore, proper selections of the most suitable die attach materials for a product and application is very important.
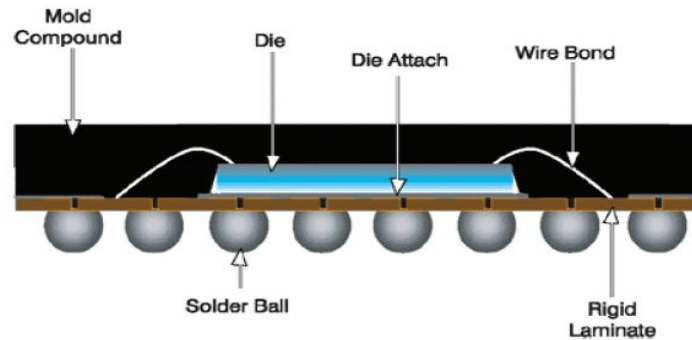
The base material for the adhesive is commonly thermosetting polymers that consist of long chains molecules, contain large percentage of silver fillers for electrical conductivity (Tadashi et al., 2003). The most common polymer matrix for die attach adhesive is epoxy due to their low temperature cure and high strength properties that allow a one-step, quick cure. However, epoxy has relatively higher ionic content. The metal-filled conductive adhesive must be able to address the requirements of higher-temperature processes such as lead-free manufacturing, suited for attachment of integrated circuits (ICs) and components to metallic lead frames.

Silver-filled adhesive is able to offer hydrophobic properties and temperature stability for production of void-free bond lines. The adhesive is designed to provide high thermal conductivity and therefore it can deliver excellent electrical conductivity for attachment of ICs and components to metallic lead frames. The material's hydrophobic and high temperature stability characteristics produce void-free bond lines with excellent adhesive strength, enabling adhesion to a wide variety of metals and ceramic surfaces, including copper, silver-plated copper and pre-plated lead frames.

2.4 Current research on electrical conductive adhesives (ECA)

Electrical conductive adhesives (ECA) are adhesives, which are made electrically conductive in one way or another. Most often this is done by incorporation electrically conductive particles (metal) into the polymer structure. Electrically conductive adhesives (ECAs) are gaining great interest as potential solder replacements in microelectronics assemblies. Basically, there are two types of ECAs, isotropic conductive adhesive (ICA) and anisotropic conductive adhesive (ACA) (Tee, 2006). Electrically Conductive adhesives (ECAs) are typically formulated with conductive particles, usually silver flakes, and a polymer matrix, usually a thermosetting epoxy resin, as the binder (Fan et al., 2004).

Conductive particles in the adhesives are responsible for the electrical interconnection, while the polymer matrix mainly provides the mechanical interconnection (Fan et al., 2004; Li et al., 2004a). Particles in flake form usually used to produce Isotropic Conductive Adhesive (ICA) (Figure 2.8), whereas Anisotropic Conductive Adhesive (ACA) is being fabricated by incorporating the spherical form particles into polymer resin (Figure 2.9).
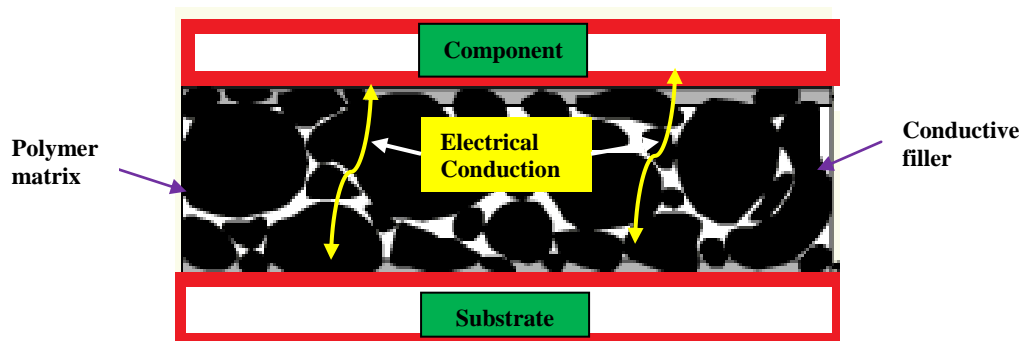

Figure 2.8: A cross section of an isotropic conductive adhesive (ICA) junction between silver flakes.(Li et al., 2004a).
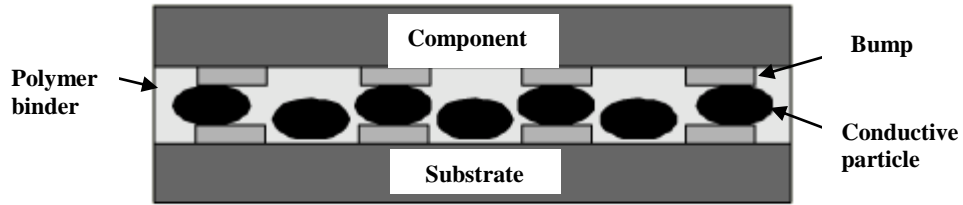
Figure 2.9: A cross section of anisotropic conductive adhesive ACA) junction between spherical silver particles (Li and Wong, 2004b).

ICA which conducts electricity along all axes, is able to replace solder on thermally sensitive components, and can also be used on devices that require a ground path. On the contrary, an ACA allows electrical current to flow only along a single axis, provide electrical connectivity and strain relief for flip chip devices. The difference between the two types of ECAs based on the percolation theory is shown in Figure 2.10:
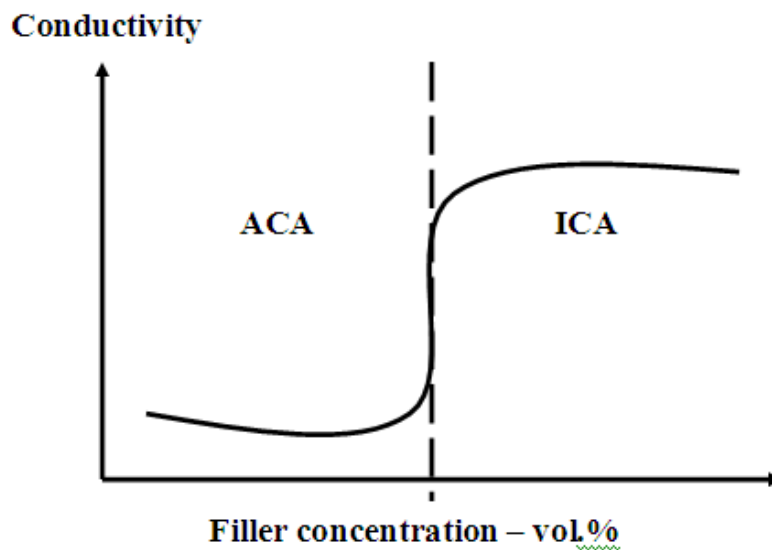

Figure 2.10: Percolation phenomenon of ECAs (Li and Wong, 2004b).

Although the concepts of these materials are different, both materials are composites materials consisting of a polymer matrix containing conductive fillers. Typically, ICAs contain conductive filler concentrations between 20 and 35 vol.% and the adhesives in