PROPERTIES OF SILVER-FILLED EPOXY COMPOSITES FOR ELECTRONIC APPLICATION USING SYNTHESIZED AND COMMERCIAL SILVER NANOPARTICLES

by

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LIST OF ABBREVIATIONS

Pb/Sn	Lead/Tin
ECA	Electrically Conductive Adhesives
ACA	Anisotropic Conductive Adhesives
ICA	Isotropic Conductive Adhesives
CTE	Coefficient of Thermal Expansion
DMA	Dynamic Mechanical Analysis
FESEM	Field-Emission Scanning Electron Microscope
TEM	Transmission Electron Microscope
MPa	Mega Pascal
XRD	X-ray Diffraction
TGA	Thermogravimetry Analysis
FTIR	Fourier-Transmission Infrared
ASTM	American Standard Testing Material
PEA D230	Polyetheramine D230
3AMPTES	3-aminopropyl triethoxysilane
SMT	Surface-Mount Technology
Ag	Argentum
LM	Light Microscope
EDX	Energy Dispersive X-ray
NP	Nanoparticles
SPR	Surface Plasmon Resonance

LIST OF SYMBOLS

$AgNO_3$	Silver nitrate
$Na_3C_6H_5O_7.2H_2O$	Tri-sodium citrate dihydrate
$C_6H_8O_6$	Ascorbic acid
ρ_v	Volume resistivity
R	Resistance
t	Thickness of samples
A	Area of conductor
σ	Conductivity
Ω	Ohm
α	Coefficient of thermal expansion
δ	Tan delta
λ	Wavelength
Δ	Delta
°	Degree Celcius
θ	Theta
V_f	Volume fraction
E'	Storage modulus
T_g	Glass transition

SIFAT-SIFAT KOMPOSIT EPOKSI TERISI-PERAK UNTUK APLIKASI ELEKTRONIK MENGGUNAKAN PARTIKEL NANO PERAK YANG DISINTESIS DAN KOMERSIL

ABSTRAK

Dalam kajian ini, partikel nano perak (SAgNPs) telah disintesis melalui kaedah kimia reduksi dengan menggunakan *trisodium citrate* dan askorbik asid sebagai agen penurunan dan juga agen penstabil. Kesan kepekatan silver nitrat, agen penurunan dan juga agen penstabil diuji melalui TEM, SEM, EDX, XRD dan UV-vis. Oleh kerana partikel nano perak yang diperolehi melalui proses sintesis terlalu rendah, sampel komposit disediakan dalam bentuk filem nipis dan dibandingkan dengan partikel perak komersil, e.g. nano perak (CAgNPs) dan kepingan perak (CAgFs). Tujuan kajian ini dijalankan untuk mengkaji kesan teknik pemprosesan, saiz dan bentuk pengisi, pengisi campuran di antara partikel Ag bersaiz nano dan mikron, dan rawatan kimia terhadap pengisi ke atas sifat-sifat elektrik, mekanikal, terma dan juga morfologi permukaan patah komposit yang terhasil untuk aplikasi elektronik. Kajian awal terhadap sifat-sifat komposit diperbuat melalui teknik pemprosesan berbeza, iaitu pengadukan menggunakan tangan dan juga penghomogen dilakukan dengan kesan kandungan pengisi (0 hingga 8 % isipadu). Berdasarkan peningkatan sifat-sifat lentur dan elektrik yang ditunjukkan oleh komposit yang terhasil dengan menggunakan penghomogen, teknik ini dipilih dalam penyediaan komposit dengan pengisi berbeza saiz dan bentuk, iaitu kepingan perak (dalam saiz) mikron-meter dan partikel nano perak (dalam saiz nano-meter). Sifat lentur untuk komposit terisi kepingan perak menunjukkan penurunan terhadap kandungan pengisi sementara komposit terisi partikel nano menunjukkan sifat lentur

maksimum pada 4 % isipadu pengisi sebelum menurun dengan pertambahan isipadu pengisi. Kekonduksian elektrik untuk kedua-dua komposit terisi kepingan perak dan partikel nano perak menunjukkan bahawa peralihan penebat-pengalir berlaku pada kandungan 6 % isipadu pengisi. Oleh itu, komposit dengan pengisi campuran (100F:0NP, 75F:25NP, 50F:50NP: 25F:7NP, 0F:100NP) disediakan pada kandungan pengisi tetap, 6 % isipadu. Kajian lanjut kesan rawatan kimia menggunakan agen pengganding *3-aminopropyl triethoxysilane* (3AMPTES) dijalankan pada komposit terisi 50F:50NP dengan pelbagai peratusan 3AMPTES iaitu 5%, 10% dan 30%. Jika dibandingkan dengan komposit tidak terawat, komposit terawat Ag/epoksi menunjukkan peningkatan sebanyak ~ 8 % dalam kekonduksian elektrik, ~ 13 % dalam kekuatan lentur dan ~ 42 % dalam modulus penyimpanan menerusi kehadiran ikatan –Si-O-C-, N-H dan C-H yang ditunjukkan dalam analisis FTIR. Namun, tiada peningkatan yang jelas dapat dilihat dalam kekonduksian elektrik, sifat lentur dan sifat terma apabila kandungan 3AMPTES ditingkatkan.

PROPERTIES OF SILVER-FILLED EPOXY COMPOSITES FOR ELECTRONIC APPLICATION USING SYNTHESIZED AND COMMERCIAL SILVER NANOPARTICLES

ABSTRACT

In this research, silver nanoparticles (SAgNPs) were synthesized by chemical reduction method while trisodium citrate and ascorbic acid were used as reducing agent and stabilizing agent, respectively. The effect of silver salt, reducing agent and stabilizing agent's concentration were analyzed by TEM, SEM, EDX, XRD and UV-vis. Due to very low yield in obtaining SAgNP through synthesis route, composite sample was prepared in thin film form and compared with commercial silver; e.g. silver nanoparticles (CAgNPs) and silver flakes (CAgFs). The aims of this research are to study the effect of processing techniques, sizes and shapes of filler, hybrid between nano and micron size of Ag filler and filler treatment on electrical, mechanical, thermal properties and fracture surface of silver-filled epoxy composites for electronic application. The study firstly investigated on the properties of composites prepared by different processing techniques, e.g., manual and homogenizer mixing as function of filler loading (0 to 8 vol. %). Based on better flexural and electrical properties given by composite prepared by homogenizer mixing, this technique has been chosen in sample preparation of composite as a function of different size and shape of the filler, e.g., CAgFs (in micron meter size) and CAgNPs (in nanometer size). Flexural strength of the composite prepared by silver flakes decreased with increasing of silver content while composite prepared with silver nanoparticles shows an optimum at 4 vol. % before decreased with increasing filler content. Electrical conductivity of both composites prepared by

silver flakes and silver nanoparticles show insulator-to-conductor behavior at 6 vol. %. Therefore, composite with hybrid filler (100F:0NP, 75F:25NP, 50F:50NP: 25F:7NP, 0F:100NP) were prepared at constant filler content (6 vol. %). Further studies on the effect of filler treatment by 3-aminopropyl triethoxysilane (3AMPTES) were conducted at 50F:50NP with the percentage of 3AMPTES were varied at 5 wt. %, 10 wt. % and 30 wt. %. Compared to untreated system, the treated Ag/epoxy composites demonstrate an improvement of ~ 8 % in electrical conductivity, ~13 % in flexural strength and ~ 42 % in storage modulus through presence of –Si-O-C-, N-H and C-H bonds which has been proved by FTIR analysis. However, there is no remarkable improvement in electrical conductivity, flexural and thermal properties could be observed as the content of 3AMPTES was increased.

CHAPTER 1

INTRODUCTION

1.0 Introduction

Thermosetting polymer resins are widely used as a matrix material in various composites. Owing to their densely cross-linked structure, they exhibit a number of superior qualities such as high glass transition temperature (T_g), high modulus, high creep resistance, low shrinkage at elevated temperature and good resistance to chemicals (Zunjarrao and Singh, 2006). Among the several available thermosetting polymers, epoxy resin is one of popular choice due to their ability to adhere to a wide variety of fillers and form a densely cross-linked molecular structure on curing which has led to their extensive use as matrix material in reinforced composite. The mentioned factors generally provide excellent stiffness, dimensional stability and resistance to chemicals (Zunjarrao and Singh, 2006). Epoxy resins were introduced to the world in 1946 at the Swiss Industries Fair (Chen et al., 2004). Since that time, epoxy compounds has been used in a wide variety of applications, such as adhesives, casting, tooling, surface coatings, and microelectronic encapsulants (Chen et al., 2004).

For decades, solder technology has played an important role in various levels of electronic packaging such as flip-chip connection (or C4), solder ball connection in ball-grid-arrays (BGA), and other direct chip attach (DCA) on a printed circuit board (PCB) (Li and Wong, 2006*b*). However, although soldering technology has matured through many decades, some issues associated with lead/tin (Pb/Sn) solders have become noticeable. From the environmental point of view, lead-containing

solders are harmful to the environment and human beings. Lead is highly toxic to human beings and even a small quantity can damage the brain, nervous system, liver and kidneys when ingested (Wong and Lu, 2000). For this reason, legislation and policies has been proposed in Europe to ban or limit the use of lead in solders. Following this tendency, great efforts have been made to develop alternative materials to replace current lead-based solder, which is lead-free solder (Mundlein et al., 2001; Li and Wong, 2006*a*).

However, despite avoiding the use of lead, lead-free solder still has some limitations, typically for fine pitch components. Miniaturization of electronic and photonic devices is a demanding trend in current and future technologies including customer products, military, biomedical and space application. Fine pitch interconnection is one of the most important technologies for device miniaturizations. The current solder paste technology used in surface mount technology (SMT) cannot meet the requirements of this very fine pitch interconnection due to their stencil printing resolution limit and bridging issues of solders, which is intrinsic characteristic of metal solders (Mundlein et al., 2001; Li and Wong, 2006*a*).

Besides that, other limitations of lead-free solder include the relatively high cost or limited availability of some candidate metals and metal alloys. Melting point of most lead-free alloy is generally 30-40°C higher than that of tin-lead alloy (approximately 183°C). Such a high melting temperature introduces many issues, such as increasing processing temperature, have to use more expensive substrates, higher components stress, pop-corning problem of the packages on printed wiring board (PWB) assembly and so on (Toon, 2005). Furthermore, thermal exposure at

this reflow temperature produces significant thermal strains in PCB after soldering, especially in the direction perpendicular to the surface of a PCB, where no structural reinforcement is made in that direction. Therefore, the residual thermal strains in an assembled PCB would cause distortions and reliability problems in electronic systems (Kang et al., 1998).

To overcome the problems regarding the use of lead-containing solder and lead-free solder, electrically conductive adhesives (ECAs) have been identified as a promising alternatives in electronics packaging applications (Wong and Lu, 2000; Haberland et al., 2001). ECAs mainly consist of organic or polymeric resin (e.g., epoxy, silicone, and polyimide) and metal fillers (e.g., silver (Ag), gold (Au), nickel (Ni), and copper (Cu)) (Li and Wong, 2006*b*). The polymeric materials in ECAs provide physical and mechanical properties such as adhesion, mechanical strength, and impact strength, while metal fillers conduct electricity (Jiang et al., 2006). The first thermoset polymer with silver filler was patented as an electrically conductive adhesive in 1956 (Lee et al., 2005; Lin et al., 2009), since then, conductive adhesives have been extensively studied especially for die attaching and terminal bonding of components.

Compared to traditional lead-containing solder technology, ECAs offer several advantages, e.g., fewer processing steps including fluxless bonding which eliminates the need for post-assembly cleaning and the disposal of detergent and flux residual, elimination of underfilling process since ECAs resin acts as an underfill that saves process time, low processing temperatures, and especially the fine pitch capability due to availability of small-size conductive fillers which enabling the miniaturization of electronic devices (Mundlein et al., 2001; Li and Wong, 2006*a*;

Mir and Kumar, 2008). The lower assembly temperature also negates the need for substrate materials that can withstand high soldering temperatures. These advantages furthermore lower the processing cost and allow the use of lower cost components and substrates (Li and Wong, 2006*b*). In addition, compared to lead-free solders, conductive adhesive systems exhibit greater flexibility, creep resistance, and energy damping (Wong and Lu, 1998), which can reduce the possibility of failures that occur in lead-free solder interconnections. Hence, electrically conductive adhesive are perceived as the next generation interconnect material for electronic packaging.

However, as a relatively new interconnection technology, conductive adhesive technology does have some drawbacks. Most of the limitations regarding the conductive adhesive mainly are associated with the reliability issues including lower electrical conductivity, fatigue life (Xie, 2000) or conductivity fatigue (decreased conductivity at elevated temperature and humidity aging or normal use condition) in reliability testing, limited current carrying capability and limited impact resistance (Perichaud et al., 1998), which negate the chances of ECAs from becoming a replacement materials for solders in electronic applications (Kang et al., 1998).

1.1 Problem statement

Currently, ECAs with micron-sized of silver flakes in epoxy resins has been widely used in electronic industries. However, with the advance in nanotechnologies, there has been a renewed interest in polymer/nanofiller composites because fillers in nanosize such as nanoconductive particles are expected to provide new and interesting properties. Incorporating nanotechnology into ECAs systems is believed

not only enables the ultra-fine pitch capability, but also enhances the electrical properties such as reducing the percolation threshold and improving the electrical conductivity. Investigation and research on the potential application of silver nanoparticles in epoxy composites is still motivating studies as there are variations in standard percolation theories have been observed in many systems and some of them remain largely unexplained. According to Sancaktar and Bai (2011), there are several factors which known to affect the magnitude of the threshold volume fraction, such as particle size distribution, particle shape, and pre-treatment of particle. Moreover, the types of conductive filler, the selection of matrix and processing condition also influenced the conductivity mechanism of composites (Brito and Sanchez, 2000; Battacharya, 1986). Therefore, different conductive adhesive systems will results in different adhesive resistivity behavior.

Besides of electrical property, size and shape of the particles also affected the mechanical and thermal properties of silver filled epoxy composite. Generally, the size, shape and also particle distribution in commercial nanoparticles that available in market cannot be controlled. They normally exist in relatively broad particle distribution with combination of variety of particle shape. The properties of this nanoparticle are dependent on the production methods, the selection of reactant, as well as processing condition which include reaction temperature and time. Therefore, a simple and cost effective synthesis process with controllable parameters is preferred in order to obtain high dispersive nanoparticles with narrow particle size distribution.

As the price of silver nanoparticles is relatively expensive compared to silver filler in micron size, hence, hybridization of silver flakes and silver nanoparticles is

believed as one of the method to reduce the production cost of ECA's. Furthermore, the hybridization of filler is aim to introduce synergistic effect and improves the electrical, mechanical as well as thermal properties. In addition, according to the literature, the previous studies were mainly focused only on the conductive properties including the conduction mechanism (Wong and Lu, 2000; Shimada et al., 2000), reliability issues such as increasing contact resistance of ECAs joint with increasing current densities, temperature and humidity (Kim and Shi, 2001; Sun, 2001) and the adhesion of the ECAs on the substrates (Zhang et al., 2003). Information regarding other properties, such as mechanical properties, thermal properties, e.g. coefficient of thermal expansion, and dynamic mechanical properties were less reported. The evaluation of these properties, e.g. mechanical and thermal properties are crucial factors for determining the reliability performance of this material since electronic devices may experience mechanical shocks during assembly and handling, and various environmental conditions including increasing temperature throughout their service life (Tee et al., 2007; Xu and Dillard, 2010).

1.2 Objectives of the present study

The objectives of present study are summarized as follows:

1. To synthesis silver nanoparticles via chemical reduction method.
2. To determine the effect of different processing method on electrical, mechanical and thermal properties of silver flakes filled epoxy composites
3. To identify the effect of different size and shape of silver particles on electrical, mechanical and thermal properties of silver filled epoxy composites

4. To investigate the effect on the hybrid size and shape of silver fillers on electrical, mechanical and thermal properties of silver filled epoxy composites
5. To determine the effect of 3AMPTES content of treated silver filler on electrical, mechanical and thermal properties of treated-silver filled epoxy composites.

1.3 Structure of thesis

The inscription of present study has been divided into five chapters. Chapter 1 gives general introduction regarding the silver nanoparticles and application of silver nanoparticles in polymer composites, especially as ECAs material, problems statement that occured in current technologies and objectives of the present study. Chapter 2 generally covered literature review including synthesis parameter, theory of percolation threshold for ECAs materials and factors affecting the electrical, mechanical as well as thermal properties of ECAs. Chapter 3 comprises a whole experiment procedure starting from information of raw material, design experiments on sample preparation and characterization. In Chapter 4, interpretation of the results and findings are proposed in order to get better understanding. Last but not least, Chapter 5 summarizes the conclusion of present study and also some recommendation for future works.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

In general, metal-polymer nanocomposites can be defined as a composite that consist of polymer as a matrix and metal nanoparticles as a reinforced element. On the other hand, definition of nanoparticles itself can be dependent on the materials, fields and application concerned. In the narrower sense, they are regarded as the particles that having a size from 1 to 100 nm (Vollath, 2008). Metal-polymer nanocomposite can be obtained by two different approaches, namely, *in situ* and *ex situ* techniques. In the *in situ* technique, metal particles are generated inside a polymer by decomposition or chemical reduction of a metallic precursor dissolved into the polymer while in *ex situ* technique, nanoparticles are first produced by chemical route and then dispersed into polymer matrices (Nicolais and Carotenuto, 2005).

Recently, research on the preparation, characterization, and application of metal nanoparticles has received increasing attention from many researchers in various fields. This is due to their extremely small sizes and large specific surface areas that exhibit novel properties in term of optical, physical and chemical properties which differ from the bulk properties (Sileikaite et al., 2006, Bhui et al., 2008). As example, there is a very strong interest in using nano-sized metals as advanced additives in plastic functionalization (Nicolais and Carotenuto, 2005). The embedding of nanoscopic metal structure into polymer matrices represents the simplest way to take advantage of some of the novel physical characteristics govern

by nano-sized metal such as plasmon absorption, near IR photoluminescence, supermagnetism, etc. and this system has a potential to be used in a number of application. They have various potential application as electronic, optical, and mechanic devices, magnetic recording media, superconductors, photographic suspensions, drug delivery, and so on (Xie et al., 2006; Chen and Wang, 2008; Jia et al., 2008). The presence of a very large filler-matrix interface area of nanoparticle could dramatically changes the polymer characteristic, e.g. glass transition temperature, crystallinity, free volume content, etc. These characteristics furthermore allowing further technologically exploitable in mechanical and physical properties, leading to special properties such as increased strength and/or increased chemical/heat resistance.

Although the addition of nanoparticles in polymer composites theoretically could improve the properties of the resulted composites, however practically, this advantage commonly marred by the nature of nanoparticles itself. The large surface of nanoparticles enhances interaction among the particles and hence, caused the particles agglomerations. In order to break these agglomerations, the processing methods in dispersing nanoparticles also become as a great challenge. Furthermore, morphology of the filler (e.g. size and shapes) also becomes a very important aspect as it profoundly influences the material performances. Therefore, it is important to study the potential factors that might control the resulted nanoparticles in term of sizes and shapes during synthesis process in order to allow tuning of nanocomposite properties.

2.1 Synthesis of silver nanoparticles

Among the various metal nanoparticles, silver nanoparticles have been most widely investigated (Suber et al., 2005; Guzman et al., 2008; Chen et al., 2009). Depending on their size and shapes, silver nanoparticles exhibit unusual optical, electronic, and chemical properties, which opening many possibilities for technological applications (Balan et al., 2007). Silver nanoparticles in particular, are able to interact efficiently with light by virtue of plasmon resonances, which are the collective oscillations of the conduction electron in metal. According to Hutter and Fendler (2004), plasma oscillation is the phenomena that free electrons is the metal oscillate cooperatively from their equilibrium position where the positive charge of metal (atomic nucleus that the positive charges are averaged) bind the ensemble of the free electrons as illustrated in Figure 2.1. Excitation of surface Plasmon by light at the incident wavelength where resonance occurs results in strong light scattering, in the appearance of intense surface Plasmon absorption bands, and an enhancement of the local electromagnetic fields.

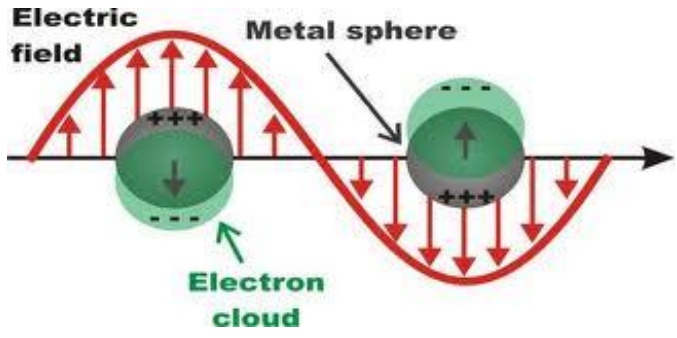

Figure 2.1: Illustration of localized surface Plasmon resonance for nanometer size metallic structure (Hutter and Fendler, 2004)

2.1.1 Synthesis method

In a nanoscale regime, chemical and physical properties of inorganic particles are highly dependent on geometrical factors such as a size and shape. Precise controls of such factors allow one not only to observed unique properties of nanoparticles but also to tune chemical and physical properties as desired. In order to do so, the most challenging issues concerned by researchers are regarding on the reproduce-ability of nanoparticles in term of uniformity in size and shapes with narrow size distribution. For these reasons, scientists have developed many techniques for synthesizing and characterizing new materials with at least one dimension on the nanoscale, including nanoparticles, nanolayers, and nanotubes. Still, the design and synthesis of nanoscale materials with controlled properties is a significant and ongoing challenge within nanoscience and nanotechnology as each synthesis process requires specific conditions for its optimization (Bonet et al., 1999; Manno et al., 2008).

Generally, metal nanoparticles can be prepared by two different methods, e.g., physical and chemical methods. In physical method, preparations of metallic nanoparticles include UV and IR radiation, aerosol technology and lithography (Kotthaus et al., 1997; Busmann et al., 1999). Metallic nanoparticles can also be prepared by assemble the atoms in the process of metal vaporization and subsequent condensation on various supports, or obtained through the treatment of the bigger particles in colloidal dispersion by means of colloidal mills, ultrasound, etc. Although physical methods are able to produce particles in nano sizes, however, only reports on chemical methods can be found abundantly in literatures. In chemical method, the main chemical way is the reduction metal ions in solution (chemical

reduction method) (Chou and Ren, 2000; Wang et al., 2005; Sileikaite et al., 2006). Other than that, there are variety of chemical routes that have been reported in literature such as electrochemical techniques (Bonet et al., 1999), photochemical reduction, liquid-liquid method (Cai et al., 2004), reverse micelle processes (Lin et al., 2001; Tamura et al., 2003; Xie et al., 2006; Eastoe et al., 2006), microwave plasma irradiation (Yin et al., 2004; Bang et al., 2007; Sheikh et al., 2009), sonochemical method (Zhu et al., 2002; Zhu et al., 2010) and polyol method (Nersisyan et al., 2003; Taguchi et al., 2008).

2.1.2 Chemical reduction method

Chemical reduction method is the most frequently route employed for the preparation of silver nanoparticles as it has stable colloidal dispersions in water or organic solvents (Sharma et al., 2009; Kholoud et al., 2010). This method generally utilizes three main items; a precursor, a reducing agent and a stabilizer or protective agent. Even though chemical reduction does have disadvantages in terms of toxic chemical usage which is harmful to the environment and health, however this method is known as the simplest method and has many merits such as mild reaction condition, low energy consumption, and simple operation procedure compared to other methods (Bhui et al., 2008).

In this synthesis technique, the chemical reduction that occurred initially leads to formation of primarily metal atoms or small (primary) particles from metal ions, which is followed by agglomeration into oligomeric cluster. These clusters eventually lead to the formation of colloidal metal particles (Kholoud et al., 2010). The reduction process of metal salt, e.g. silver nitrate with the presence of reducing

agent and surfactant could be illustrated as Figure 2.2. When the particle reaches the desired size, further growth is arrested by cooling the solution. Theoritically, the particle size and distribution of nanoparticles depend on the relative rates of nucleation and growth process. However, these rates are also influenced by the chemical reaction rates and the rate of protective agents adsorbing onto the colloidal surface to provide effective barrier against agglomeration (Lu and Chou, 2008).

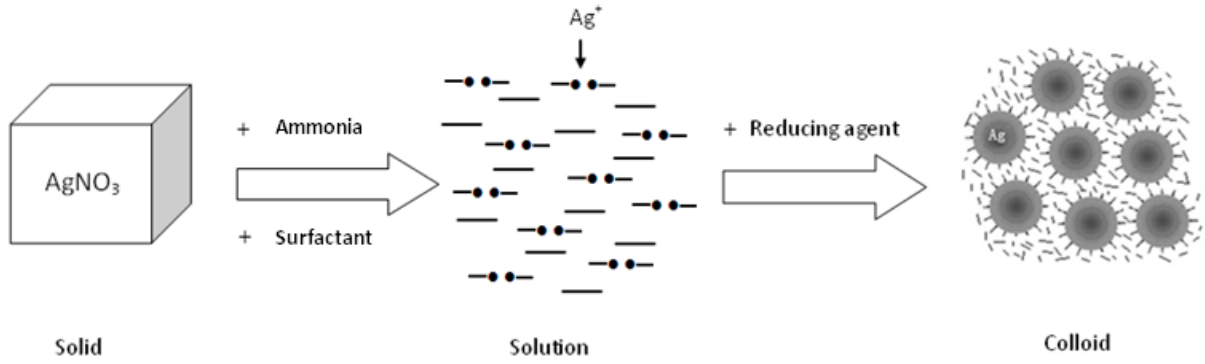

Figure 2.2: Schematic diagram of preparation process of nanometer Ag colloid (Liu et al., 2010)

2.1.3 Factors affecting the properties of silver nanoparticles

In synthesizing process, there are several factors that can affect the size, shapes as well as the properties of the nanoparticles. Studies have shown that the size, morphology, stability and properties (chemical and physical) of the metal nanoparticles are strongly influenced by the experimental conditions, the kinetics interaction of metal ions with reducing agents, and absorption processes of stabilizing agent with nanoparticles (Sharma et al., 2009). In addition, a rigorous control on the reaction parameters such as concentrations, reaction temperature, type of reducing agent; whether strong or mild, type of stabilizer, reaction time, pH, rotation per minute (RPM), amount and order on addition of reactants, could allow us control properties of the particles.

Chen et al. (2009) in their study investigated on the effect of silver salt concentration on the synthesized silver nanoparticle especially in term of the size produced. It is found that with the increasing concentration of silver nitrate (which acts as precursor) resulted on the increases size of silver nanoparticles. This observation is also supported by Yin et al. (2004) where the particle size distributions become broader and the average sizes increased with increasing the concentration of silver nitrate. This result is mainly attributed to the fact that the rate of spontaneous nucleation increases significantly more than the growth rate of silver nanocrystals. These small particles are energetically less stable and will spontaneously transform into large crystal following Ostwald ripening phenomenon in order to attain a lower energy state.

The selection of an appropriate reducing agent and stabilizer is also a crucial factor as size, shape and particles size distribution strongly depend on the nature of reducing agent and stabilizers. In synthesis process, there are variety of reducing agent that could be employed such as $NaBH_4$, sodium citrate, ascorbic acid, hydrazine dihydrochloride, potassium bitartate, ethanol, pyridine, DMF and poly(ethylene glycol). The introduction of a reducing agent causes the reduction of metal precursor. Reduction of metal salts requires adjustment of the reactivity of the reducing agent to redox potential of the metal. If the reaction rate is too fast, rapid formation of a large amount of metal nuclei will result in the too small particles to separate easily. If the reaction rate is too slow, it is very difficult to prevent the powder from agglomeration.

Examples of reducing agent that were used widely to prepare ultra fine metallic powder are borohydrate, hydrazine hydrate and formaldehyde. However, as

reported by Cai et al. (2004), the reducing power of borohydrate was believed too strong in order to obtain uniform size and monodispersed silver powder. Meanwhile, another reduction agent which is ascorbic acid has been reported having middle reduction power and efficient in acidic conditions (Suber et al., 2005). By using of the weaker reductant such as citrate, results in a slower reduction rate, but broadens the size distribution of particles. However it has been reported in Khan et al., (2011) that metal nanoparticles which prepared by the mild reducing agents was relatively more stable compared with those produced by excess of strong reducing agents.

In synthesis process, the choice of the surfactant is critical since it determines the stability, solubility, reactivity, dispersibility and even the size and shape of the nanoparticles during the synthesis (Balan et al., 2007). Surfactant is usually organic compound that are amphiphilic, which mean that they contain hydrophobic and hydrophilic groups. Hydrophobic can be referred to the physical property of a molecule that is repel from a mass of water while hydrophilic refers to a physical property of a molecule that can transiently bond with water through hydrogen bonding. A hydrophilic molecule is one that is typically charge-polarized and capable of hydrogen bonding which enabling it to dissolve more readily in water than in oil or other hydrophobic solvent. Hydrophobic and hydrophilic molecules are also known as non-polar and polar molecule, respectively (Merianos, 2001). As example, the use of chloride and citrate ions, cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) could chemically absorbed on growing crystals and initially control the growth rates by interacting through adsorption and desorption (Murthy et al., 1997; Zheng et al., 2003). Meanwhile, the influence of polyvinyl pyrrolidone (PVP) as a surfactant and mixing speed of reactants in synthesis of silver nanoparticles has been investigated by Wang et al., (2005). They reported the use of

PVP as dispersants which are; one is to generate complex compound with the precursor and control the process of the reaction and the other one is to protect particles from growth and agglomeration. They found that with the increases of surfactant, the changes in particles size are not obvious but the dispersibility becomes better. However, when the amount of surfactant is not enough, it cannot form a complete protection layer and this leads the particles to agglomerate easily. Apart of advantages offered by surfactant, they somehow cannot be easily removed from the surface of the metal colloids which unavoidably affect the physicochemical properties of the resulting nanoparticles (Balan et al., 2007; Yin et al., 2004).

2.2 Types of conductive filler

In preparing of composite material, the selection of filler is often made based on the desired properties of the final product. As example, electrically conductive adhesives (ECAs) owe their conductivity by the incorporation of high loadings of conductive filler. The choice of a conductive filler generally governed by the composite processing method, filler geometric arrangement and critical volume loading, which is needed to achieve the reliable electrical continuity and mechanical property (Sun, 2001). The common conductive fillers in ECAs can be divided into two categories which are carbon, and metal.

2.2.1 Carbon-based

Generally, the choice of carbon as filler in polymer matrix is mainly results from three kinds of requirements which is color, mechanical properties and electrical properties. However, for application of ECAs, carbon filler has been incorporated

into polymer matrix for the electrical purpose. There are varieties of conductive filler that fall in carbon category such as carbon black, carbon nanotube (CNT), graphite, synthetic diamond and etc. which have been used extensively in many research works. As an example, studies on the effect of CNT filler in polymer matrix has been done by previous researchers such as Geng et al. (2008), Li and Lumpp (2006) and Sandler et al. (1999) while studies on the effect of carbon black has been conducted by Schueler et al. (1997).

Schueler and co-workers (1997) studied on the correlation between the percolation threshold and shearing rate used to disperse the carbon black particles in polymer matrix. In addition to that, they used theory of colloid to describe the interactions amongst carbon black particles that dispersed in liquids as well as structure and dynamics of agglomerated particles formation. As a result, they found that the percolation threshold of carbon black filled polymer matrix not only depends on the particle size and fractal dimension but also on the shearing rate used. The recent discovery of carbon nanotubes offers a new opportunity to modify the electrical conductivity of polymer matrix systems. High aspect ratio provided by CNT has been used due to their unique characteristic which can conduct current easily at low filler content (Li and Lumpp, 2006). This observation was consistent with the finding reported by Sandler et al. (1999) where the percolation threshold was strongly depending on the particle shape and for CNT dispersed in epoxy matrix, it can be achieved at 0.04 wt. % of filler content.

2.2.2 Metal

Conductive filler used in ECAs that categorized in metal class can be as silver (Ag), gold (Au), copper (Cu), nickel (Ni), zinc (Zn), and etc. Each type of conductive metal filler owns their advantages and disadvantages. One limitation that rule out most metals to be used as conductive filler in ECAs is the formation of oxide layers. For example, aluminium powder cannot be used in ECAs because of its insulating oxide film. Meanwhile, metals such as nickel and copper have their own disadvantages that restricted them to be use as conductive filler even though they are cheap. Copper tend to become non-conductive after being oxidized due exposure to heat and humidity while high filler resistance and contact resistance showed by nickel has overcome its ability to resist oxidation (Wong and Lu; 1998; Bao et al., 2007).

Noble metals such as silver and gold have good conductivity but they are very expensive. However, considering the price and the conductivity offered by silver compared to gold, silver is widely used as conductive filler in industry application due to its high electrical conductivity, chemical stability, and lower cost. Silver also form both thin and relatively conductive oxides. Moreover, silver can be easily precipitated into a wide range of controllable sizes and shapes. In some application, metal-plated conductive particles have been used, especially in anisotropic conductive adhesives. The original intent of using plated particles is to reduce cost and there are various types of plated particles that have been specially designed for specific characteristics and end use. As example, silver and gold plating on non-metals such as glass and plastic are among the most common types of filler product.

Studies on the effect of metal filler filled polymer matrix have been reported by many researchers. For examples, Zhang et al. (2010*a*) studied the properties of Ag-coated Cu flakes filled epoxy composites, Kim et al. (2009) studied the electrical conductivity of a silver flake in thermosetting polymer matrix composite, Chan et al. (2009) studied the properties of copper filled epoxy composites, and Alvarez et al. (2010) studied the structural, electrical and percolation threshold of Al/polymethylmethacrylate nanocomposites. Furthermore, there also has been reported on the using of a low melting point alloy (LMPA) as the conductive filler (Li and Wong, 2006*b*; Wu et al., 2001). The intent of using LMPA is to let the particles form metallurgical bonds during the polymer cure to achieve a lower contact resistance. Table 2.1 listed the properties of common conductive filler used in ECAs.

Table 2.1: Properties of common conductive filler used in ECAs (Callister, 2000)

Types of conductive filler	**Density at 298K (g/cm^3)**	**Electrical Conductivity, σ at 298K (x 10^5 S/cm)**	**Coefficient of Thermal Expansion at 298K (ppm/K)**	**Thermal Conductivity at 298K (W/m-K)**
Gold (Au)	19.30	4.52	14.2	310
Silver (Ag)	10.50	6.30	18.9	429
Copper (Cu)	8.93	5.96	16.7	401
Nickel (Ni)	8.90	1.43	13.0	91
Aluminium (Al)	2.71	3.78	23.0	250

2.3 Conductive polymer in electronic applications

In general, conductive polymers can be classified into two types which are intrinsically and extrinsically conductive polymers. In intrinsically conductive polymer, it has extensive conjugation in the backbone which is responsible for conductance. This type of conductive polymer can be classified in two kind;

conductive polymers that having conjugated π-electrons in the backbone, e.g., polyacetylene, polyaniline, etc. or doped conducting polymers either p-doped (oxidative doping) or n-doped (reductive doping). Meanwhile, in extrinsically conductive polymers, conductivity property was achieved due to the externally added ingredients in them. This group also can be classified in two types; conductive element filled polymers and blended conducting polymers that prepared by blending a conventional polymer with a conducting polymer (Ahluwalia and Mishra, 2008).

In application, extrinsically conductive polymer that involves incorporating commercial metal filler, such as silver into thermosetting epoxy matrix is the most common used due to several reasons. In general, important polymer properties such as low density, strength, and impact resistance are reduced by the addition of metallic particles. Due to high density of metal relative to polymer and the lack of reinforcing ability of metal particles, it is desirable to minimize the concentration of metal used to improve the mechanical performance for the specified electrical properties. For that purpose, studies on various properties and possible application of metal/polymer composites have been conducted by many researchers (Perichaud et al., 1998; Busmann et al., 1999; Mundlein et al., 2001). However, the studies were more focused on conductivity property of the conductive polymer as it is the most crucial property that determines the application of metal/polymer composites in electronic industry. It is apparent that the applications of these materials in the electronic industry are very wide including die (chip) attach adhesives, electrostatic dissipation, electromagnetic interference shielding, conductive painting, flip-chip interconnections as well as surface-mount electronic component application. The details of some applications are discussed in the following sub-section.

2.3.1 Die (chip) attach adhesives

Figure 2.3 illustrates the application of die-attach polymer adhesive in electronic. The principal function of die attach adhesives is to mechanically attach the integrated chip (IC) to the substrates in a highly reliable manner (Li and Wong, 2006*b*). A good die attach material should fit to the desired functionality which is often governed by mechanical, thermal and electrical properties. In this application, sufficient adhesion is required to ensure the die remains fixed in place when it is subjected to assembly processing or during actual device service. The polymer-based adhesives offer many advantages such as lower stresses on IC due to low material modulus (both the storage and loss modulus) and curing temperature, ease of use in manufacturing environment, and low cost compared to inorganic adhesives (Li and Wong, 2006*b*).

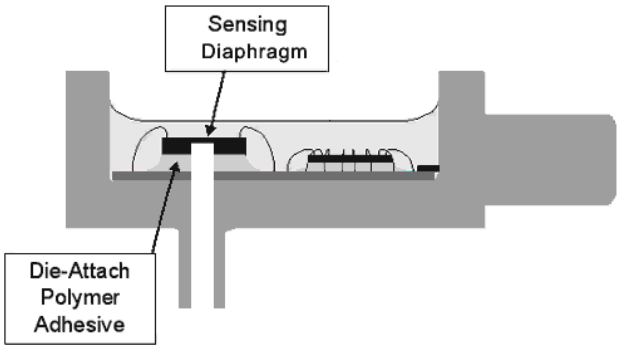

Figure 2.3: Application of die attach adhesives in electronic (Li and Wong, 2006*b*)

2.3.2 Flip-chip interconnection

In flip-chip interconnection, ICA can be applied in two different ways which are for flip-chip bumping and also flip-chip bonding. In flip-chip bumping, there is a variety of bumping compositions currently being used for forming electrical and structural interconnects between the chip and package. The bumps can be composed

of a single metal, an alloy or a combination of metals, alloys and polymers. Printing process typically involves a screen or stencil with openings through which bumps are deposited. During the printing process, the paste is typically dispensed some distance away from the stencil apertures as shown in Figure 2.4 (a). In flip-chip bonding, the transfer method has been used in order to get accurate pattern alignment. Studs or pillars are raised on either die or substrate. Then, the ICA is selectively transferred to the raised area by contacting the face of die or substrate to a flat film of the ICA paste which adheres to the prominent surfaces as shown in Figure 2.4 (b) (Li and Wong, 2006*b*).

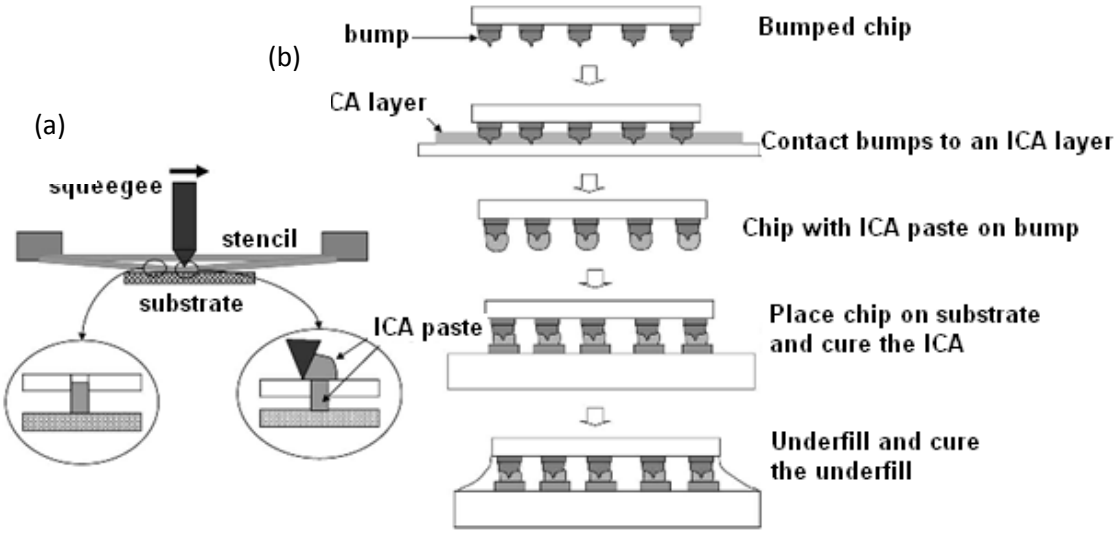

Figure 2.4: (a) Schematic diagram of printing process, (b) A flip-chip bonding process using ICAs (Li and Wong, 2006*b*)

2.3.3 Surface-mount electronic component technology (SMT)

SMT is the main technique for interconnecting chip components to substrate by packing and placing the components on the printed circuit board and using the reflow furnace to melt the solder alloy for the electronic system interconnection (Li

and Wong, 2006*b*). Figure 2.5 shows a scheme of several different components interconnected by surface-mount technology.

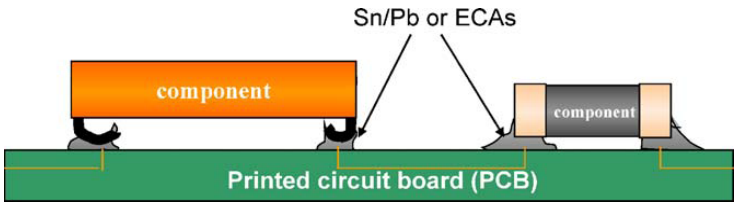

Figure 2.5: A schematic structure of surface mount interconnection (Li and Wong, 2006*b*)

2.4 Introduction of electrically conductive adhesives (ECAs)

As mentioned in Section 1.0, an electrically conductive adhesive (ECAs) is a composites of polymeric matrices and electrically conductive fillers (Wong and Lu, 1998; Jiang et al. 2006). As known, polymeric matrices have excellent dielectric properties and thus are electrical insulators due to their low concentration of free charge carriers (Psarras, 2005). The addition of conductive fillers will provide the electrical properties while the polymer matrix provides the mechanical properties (Kang et al., 1995). In other word, electrical and mechanical properties of ECAs are provided by different components which are different from metallic solders that provide both the electrical and mechanical properties (Jiang et al., 2006). Basically, as shown in Figure 2.6, ECAs can be categorized with respect to conductive filler loading level which is isotropic conductive adhesive (ICAs) and anisotropic conductive adhesives (ACAs) (Perichaud et al., 1998; Li and Wong, 2006*b*). The illustration of these ACAs and ICAs materials in electronic application are shown in Figure 2.7 (Li and Wong, 2006*b*).

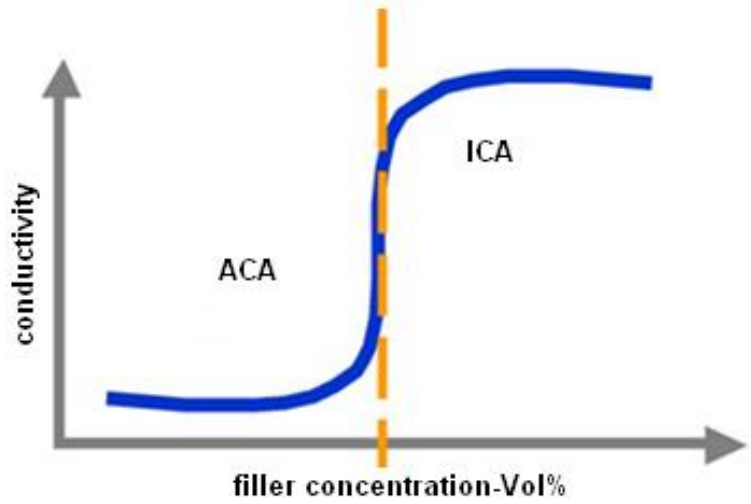

Figure 2.6: A typical percolation curve showing the abrupt increase in conductivity at the percolation threshold (Li and Wong, 2006*b*)

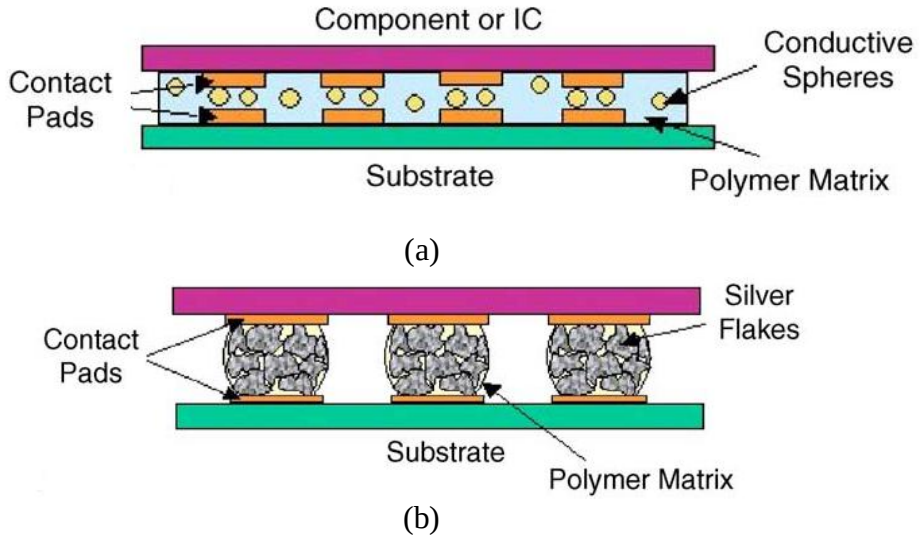

Figure 2.7: Schematic illustrations of (a) ACAs and (b) ICAs in flip chip bonding (Li and Wong, 2006*b*)

In general, both materials (ICAs and ACAs) are composed of insulating adhesive and conductive particle fillers although the concepts of these materials are different (Li and Wong, 2006*b*). ACAs provide uni-directional electrical conductivity in vertical or z-axis. This directional conductivity is achieved by using a relatively low volume loading of the conductive filler, which normally between 5 to 10 vol. %. The low volume loading is insufficient for inter-particle contact and prevents