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Conductive Polymer Composite for Electronic Packaging

by

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1.0 Introduction

1.0.1 Overview

Soldering technology using tin/lead (Sn/Pb) solders plays an important role in electronic packaging, such as flip-chip, solder-ball connections in ball grid arrays (BGA), and integrated circuit (IC) package assembly to a printed circuit board (PCB) (Kang *et al.*, 1998; Lu and Wong, 2000c; Li and Wong, 2004b). With advances in microelectronics, some issues associated with Sn/Pb 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 has been eliminated from gasoline and paint. Eliminating lead from electronic packages is underway (Kang *et al.*, 1998; Li and Wong, 2004a).

Another limitation of solder paste exists in its use for fine pitch components. The current solder paste technology used in surface mount technology (SMT) cannot handle this very fine pitch interconnection due to the soldering defects such as bridging or soldering balling (Li and Wong, 2004b; Kang *et al.*, 1998). Another technical limitation of using the Pb-Sn eutectic solder is the necessary high reflow temperature between 215 and 230°C. This temperature is higher than the glass transition temperature of the epoxy resin used in most polymeric PCB materials (Kang *et al.*, 1998). Thermal exposure at this reflow temperature produces significant thermal strains in a PCB after soldering, especially in the direction perpendicular to the surface of a PCB, where no structural reinforcement is made in that direction. Thereby, the residual thermal strains in an assembled PCB would cause distortions and reliability problems in an electronic system (Kang *et al.*, 1998). In the electronic industry, two groups of materials are being investigated currently as possible alternatives for lead-based solders, which are lead-free solders (Lu and Wong, 2000c) and electrically conductive adhesives (Toon, 2005).

Legislation and policies have been proposed in Europe to ban or limit the use of lead in solders, and the United States is very likely to follow this trend (Rao *et al.*, 2003). Following this tendency, great efforts have been made in the industry to develop lead-free and environmentally friendly soldering materials to replace lead-based solders. One alternative to lead-bearing solders is lead-free, low melting temperature metals and metal alloys. Some applications have been found in this area.

However, some limitations still exist in lead-free solder technology, including the relatively high cost or limited availability of some candidate metals, and the requirement for relatively high soldering temperature for some metal and metal alloys (Suraski and Seelig, 2001). The alloys replacing traditional tin-lead solder are generally of a higher melting point than those that they replace. The melting point of this alloy (217°C) is about 30°C hotter than that of the tin-lead alloy with the lowest melting point (183°C) (Toon, 2005). Processing at the higher temperature creates potential manufacturing problems. Hence, in complying with the forthcoming lead-free legislation, a number of end-users will encounter problems with the assembly of temperature sensitive components such as liquid crystal displays, electrolytic capacitors and optoelectronics (Suraski and Seelig, 2001).

The other alternative for lead-bearing solders is electrically conductive adhesives (ECAs) (Li and Wong, 2004a; Wu *et al.*, 2005). ECAs consist of a polymer binder that provides mechanical strength, and conduct electricity, typically through the addition of conductive or metallic fillers, such as gold, silver, nickel, copper, or carbon powder. They consist of metal powder filler – usually silver – that conducts electricity inside a polymeric resin. The resin, an epoxy, silicon or polyimide, provides mechanical properties such as adhesion, mechanical strength and impact strength (Toon, 2005).

One of the promising ECAs is an electrically conductive epoxy resin, which when cured, will form a permanent inflexible bond with most metallic substrates. Since the first thermoset polymer with silver filler was patented as an electrically conductive adhesive in 1956, conductive adhesives have been studied extensively for die attaching and terminal bonding of components. Nowadays, conductive adhesives containing conducting particles as fillers have a great potential to replace the Sn/Pb solders in chip packaging for environmental reasons (Lee *et al.*, 2005).

With the phasing out of lead-bearing solders, electrically conductive adhesives have been identified as an environmentally friendly alternative to Sn/Pb solders in electronics packaging applications. Compared to Sn/Pb solders, conductive adhesive technology offers numerous advantages over conventional solder interconnection technology including finer pitch printing, lower temperature processing, and more flexible and simpler processing (Lu and Wong, 2000c). Additionally, lower assembly temperatures negate the need for substrate materials that can withstand high soldering temperatures. These advantages bring lower processing costs, allow the use of lower-cost components and substrates, and facilitate size reduction in devices (Toon, 2005).

In addition, compared with lead-free solders, conductive adhesive systems exhibit greater flexibility, creep resistance, and energy damping (Wong *et al.*, 1998), which can reduce the possibility of failures that occur in lead-free solder interconnections. Therefore, electrically conductive adhesives are perceived as the next generation interconnection material for electronic packaging (Liu *et al.*, 1995). As a relatively new interconnection technology, however, conductive adhesive technology does have some limitations and drawbacks. Some reliability issues including limited impact resistance (Rao *et al.*, 2003; Lu and Wong, 2000c), increased contact resistance upon thermal cycling, and weakened mechanical strength in various climatic environmental conditions, lack of reworkability, conductivity fatigue, limited current-carrying capability and silver migration are several major obstacles currently preventing ECAs from becoming a general replacement for solders in electronic applications (Kang *et al.*, 1998). As a result, conductive adhesives are currently used only in low-power devices such as driver chips for liquid crystal displays (Toon, 2005).

Metal filled polymer composites are getting acceptance for the past few years, mainly due to concerns about the environment. For example, silver-filled thermosetting polymers were first patented as electrically conductive adhesives (ECAs). ECAs have been explored as an environment friendly interconnection technique, one of two potential alternatives (the other one is lead-free solder) towards current tin/lead solders. Metal-filled polymer composites possess unique characteristics where their electrical characteristics are close to the properties of metals, whereas the mechanical properties and processing methods are typical for plastics. The achievement of metallic properties in such composites depends on many factors; filler particle shape, size, filler distribution within the polymer matrix, the interaction between the filler surface, and the contact resistance between adjacent particles. The filling of a polymer with metallic particles results in an increase of both electrical and thermal conductivity of the composites obtained.

The behavior of composites made with an insulating matrix and conductive filler is quite interesting and extremely important to understand. The incorporation of metallic filler into polymer matrix results in shifting the electrical resistance from dielectric to metallic behavior over a very narrow range of filler concentration as shown in Figure 1. This transition phenomenon is called the percolation threshold where certain continuous structures of fillers are formed. Theory of percolation threshold predicts a filler concentration threshold where the composite system makes a transition between tunneling and conductor-filler ohmic conduction. Below this percolation point, tunneling prevails, while beyond it, the conductor-filler carries the current.

Increase in filler loading resulting 'close proximity' of conductive filler particles, thus electron can travel the polymeric gap in between the conductive particles, allowing current to flow, for example by hopping or tunneling effect. Generally, excess metal particles are not necessary if the metal particle content in the past-threshold region. The percolation behavior is primarily affected by the particle size, the shape of the filler and filler particle distribution. For example, using smaller particle size helps to reduce the minimum metal content required to reach the percolation threshold value. Therefore, there is lot more works currently being done to evaluate the use of metal nanoparticles into polymer matrix.

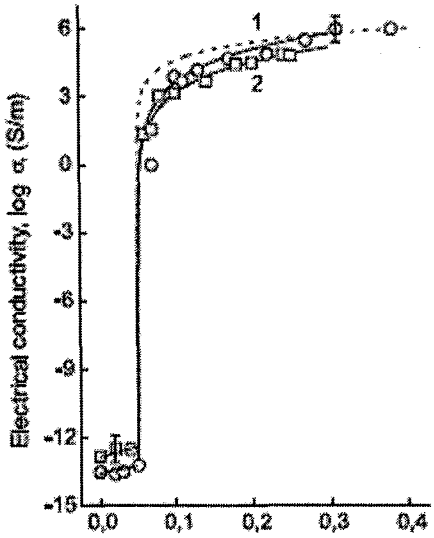


Figure 1: Percolation threshold resulted from incorporation of filler into polymer matrix

1.0.2 Electrically Conductive Adhesives (ECAs)

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 (Ye *et al.*, 1999; 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).

There are mainly two types of ECAs, anisotropic conductive adhesives (ACAs) and isotropic conductive adhesives (ICAs). Particles in flake form usually used to produce ICA (Figure 2), whereas ACA is being fabricated by incorporating the spherical form particles into polymer resin (Figure 3).

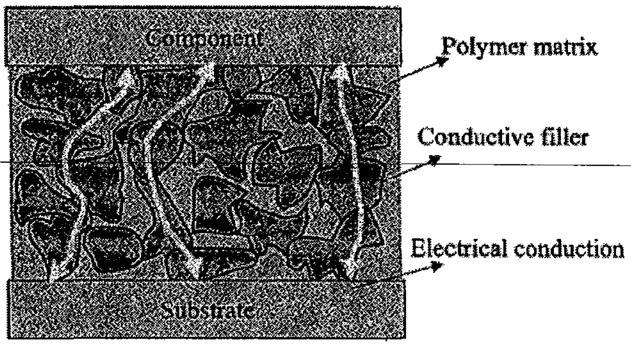


Figure 2: A cross section of an isotropic conductive adhesive (ICA) junction between silver flakes (Li *et al.*, 2004a)

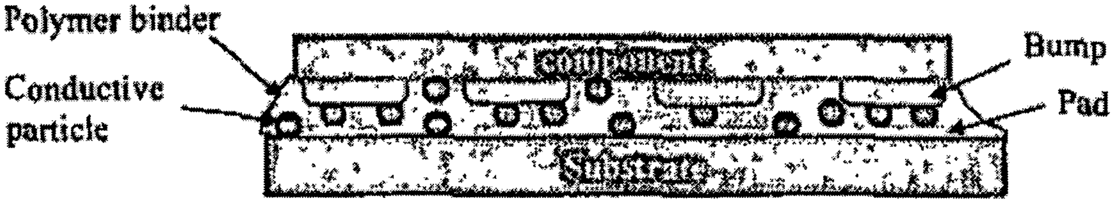


Figure 3: A cross section of anisotropic conductive adhesive (ACA) junction between spherical silver particles (Li and Wong, 2004b)

ICA 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 is based on the percolation theory (Figure 4).

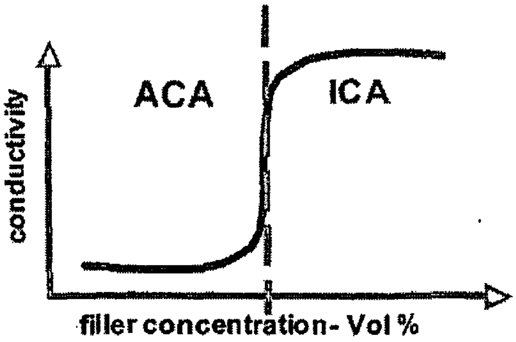


Figure 4: Percolation phenomenon of ECAs (Li and Wong, 2004b)

For ACAs, the loading level of conductive fillers is below the percolation threshold (P_c), and the low volume loading is insufficient for inter-particle contact and prevents conductivity in the X-Y plane of the adhesive. Therefore, they provide a unidirectional electrical conductivity in the vertical or Z-axis. The typical conductive fillers are in spherical form (Li and Wong, 2004b). ACAs are now being used to connect flat panel displays, tape-automated bonding (TAB), flip chips and fine pitch surface-mounted devices (SMDs).

ICAs consist of metallic particles (normally in flake form) in a polymer binder (Li and Wong, 2004b). Typical nanosized filler loadings is less than 7 vol.% (Busmann *et al.*, 1999). At these loadings, the materials have achieved the percolation threshold and are electrically conductive in all directions after the materials are cured. The most common ICAs are silver-flake-filled thermosetting epoxies which are typically provided as one-part thixotropic pastes (Li and Wong, 2004b). They can provide both electrical and mechanical interconnection between components after they are cured. Because the mechanical strength of the joint is provided by the polymer binder, the challenge in a formulation is to use the optimum metal filler loading without sacrificing the required strength.

The electrical conductivity is established primarily from more intimate contact between silver flakes, and silver flake with bonding pad, caused by the curing shrinkage of the polymer matrix (Fan *et al.*, 2004). When nanoparticles are incorporated into adhesive systems, the conduction mechanisms are mainly resulted from the effect of electron tunneling and thermionic emission (Fan *et al.*, 2004; Ye *et al.*, 1999). ECAs can be used instead of traditional solder bumps in flip chip bonding. The advantages of adhesives include lower process temperature, fine pitch capability, lead-free process and materials, flux-free process and materials, ability to bond on different substrates (such as glass) and simple process flow (Wong *et al.*, 1997; Li *et al.*, 2004a; Li and Wong, 2004b). However, comparing to mature solder technology, adhesive technology is still developing. Many issues associated with this technology, such as moisture absorption, silver migration (Li *et al.*, 1993), relatively lower conductivity and unstable contact resistance (Li *et al.*, 2004a), have not yet been understood satisfactorily (Wong *et al.*, 1997; Li *et al.*, 2004a).

1.0.3 Silver nanoparticles/epoxy composites

There are a limited number of production methods being used to fabricate silver nanoparticles filled epoxy composites. These are generally consisting of in situ and ex situ methods. The in situ method involves the introduction of metal ions in monomer or polymer solution. The ions are then reduced to form metal particles. Ex situ techniques involve making the metal nanoparticles, passivating their surface, and then dispersing them into solution that is polymerized (Nicolais and Carotenuto, 2005). The most common method of ex situ technique involves incorporating commercial nanosized silver powder into thermosetting epoxy matrix and then cures it to obtain silver nanoparticles/epoxy composites.

Silver-filled thermosetting polymers were first patented as electrically conductive adhesives in the 1950s (Fan, *et al.*, 2004; Lu and Wong, 2000a). 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). The following topics discussed about the effect of incorporation of silver nanoparticles in thermosetting epoxy resin and the conductive mechanism of silver nanoparticles in the nanocomposites system.

1.1 Experimental Methodology

The present research dealt with the production of polymer nanocomposite made of epoxy resin filled with 70-nm-sized silver (Ag) particles via high frequency (40 kHz) sonication technique. Figure 5 simplifies the overall research process flow, which had been basically divided into three phases. Phase I involves raw materials analysis. Phase II is mainly made up by two stages: the first stage is to produce specimens with untreated silver filler in epoxy resin, whereas the second stage is to produce treated silver nanoparticles-filled epoxy composites. Phase III encompasses the characterizations of the silver nanoparticles-filled epoxy composites.

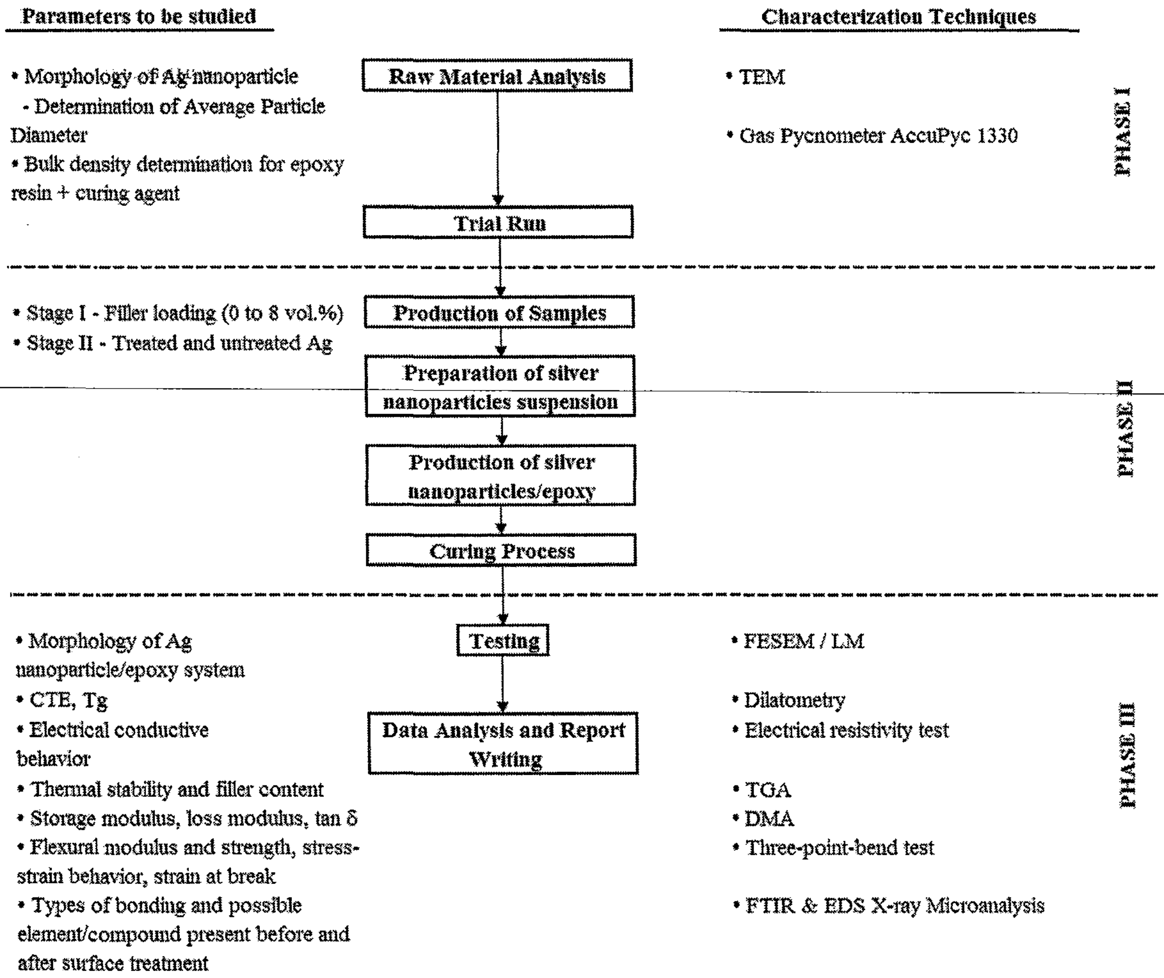


Figure 5: Overall Process Flow of the Present Research

1.2 Results & Discussion

The objectives of the present research is to investigate the effect of Ag filler concentration and chemical treatment on electrical and mechanical properties of the resulting composites. Electrical resistance measurement was done in room temperature using direct current (DC). The flexural properties of composites was carried out to determine the ability of the composites to sustain and work under flexural loading. These two findings were focused and reported in this report.

1.2.1 Effect of filler loading on untreated composites

1.2.1.1 Electrical properties

The electrical properties of composite materials of metallic filler particles embedded in polymer matrices strongly depend on the concentration and morphology of the particles (Busmann *et al.*, 1999). The electrical resistance shifts from insulator to conductor behavior with increasing metal content (Swapan, 1999; Busmann *et al.*, 1986; Zhang and Zeng, 1997), whereas solid filler materials in general tend to deteriorate mechanical properties of such composites (Busmann *et al.*, 1999; Chisholm *et al.*, 2004). Therefore, filler systems with a low percolation threshold are preferred in especially the application as isotropically conductive adhesives (ICAs). The cured composite incorporated with 8 vol.% of silver nanoparticles gives the lowest volume resistivity of 1.35×10^{2} Ω-cm. The dependence of the volume resistivity of the composites on silver nanoparticles content is shown in Figure 6.

Generally, the volume or bulk resistivity of the composites decreases as the Ag filler concentration increases. The curve indicates a typical resistivity curve for composites doped with nanosized conductive fillers. As expected, the unfilled specimen (0 vol.% Ag nanoparticle) having the highest volume resistivity of 4.71×10^{5} Ω-cm. The electrical resistivities show an obvious decreasing trend when 4 vol.% and 5 vol.% nanoparticles are introduced in the epoxy. For instance, the composite filled with 4 vol.% of Ag nanoparticles exhibits a volume resistivity of 3.46×10^{4} Ω-cm and the resistivity drops to 3.68×10^{2} Ω-cm at 5 vol.% of filler concentration. Therefore, the transition regime from high to low resistivity is found to be occurred at a range of filler concentration of 4 – 5 vol.%.

After 5 vol.%, the further reduction of resistivity is not so obvious. In other words, further increment of filler amount after 5 vol.% does not help much in improving the conductivity of composites. The critical volume fraction of Ag nanoparticles (V_c) for which the composite undergoes an insulator-conductor transition is then determined at 5 vol.%, as shown in a drastic drop of curve in Figure 6. Above 5 vol.%, the composite will behave like a conductor.

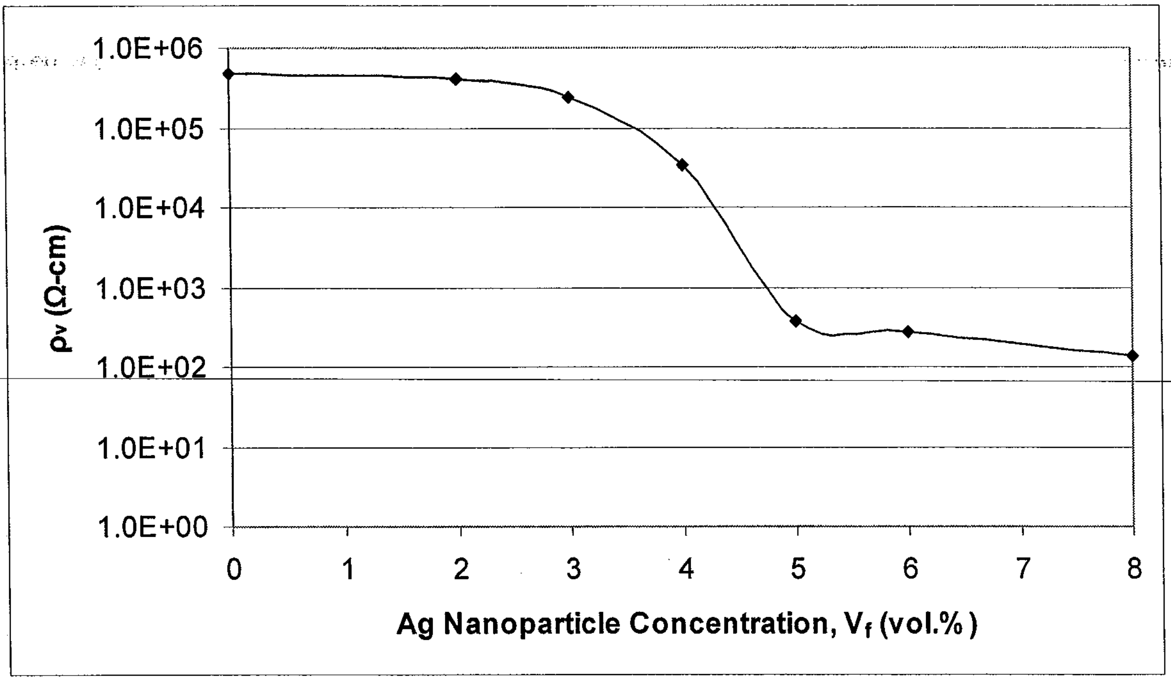
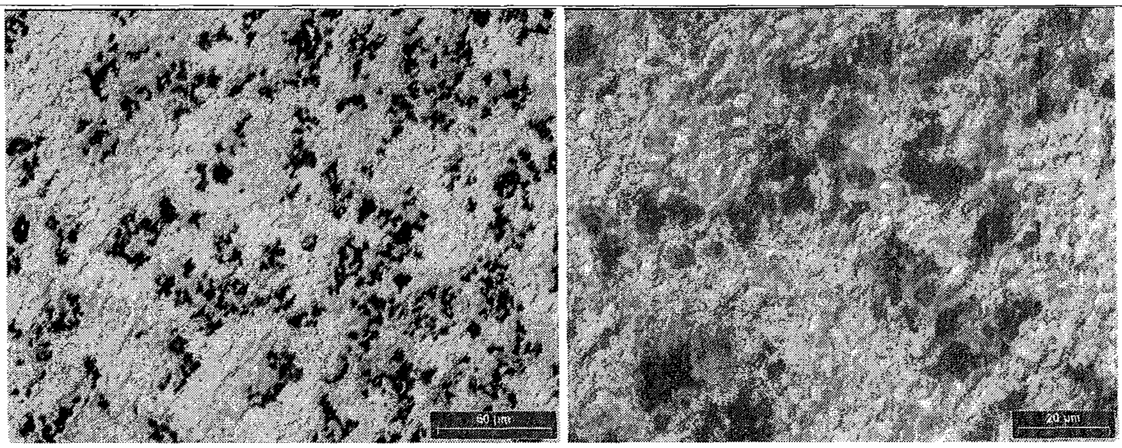


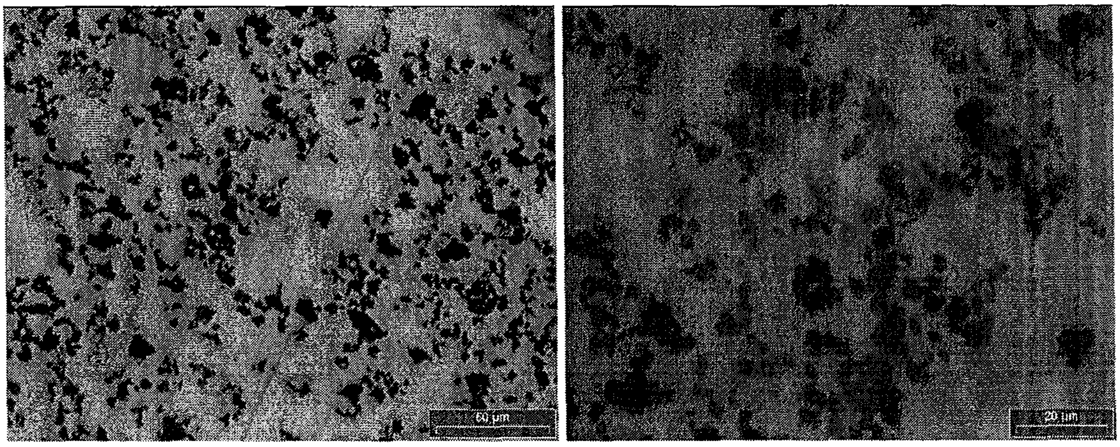
Figure 6: Dependence of volume resistivity, ρ_v of Ag nanoparticles/epoxy composites on the concentration of Ag fillers. Note that the insulator-to-conductor transition occurs at a critical filler concentration of 5 vol.%.

Experiments were limited to $V_f \leq 8$ vol.% because for higher concentrations there was no further improvement in electrical properties (Busmann *et al.*, 1999; Gonon and Boudefel, 2006). Higher filler concentrations may risk for electrical short at the nearby bonding pad during electronic packaging application. A low percolation threshold is even more preferred in applications like isotropically conductive adhesives. Commercially available adhesive for uses in electronic industry are generally filled with more than 25 vol.% of Ag flakes in micron size (Busmann *et al.*, 1999). Busmann and coworkers (1999) had developed a novel nanoscale metal/polymer matrix composite made by the dispersion of porous silver powder into a polymer matrix and led to a reduction of the percolation threshold to less than 7 vol.%. The critical volume fraction that has been determined in the present electrical study is approximately 5 vol.%. It is clear that the percolation threshold determined from experimental data does not deviate from the range of percolation threshold mentioned by Busmann and coworker (1999).

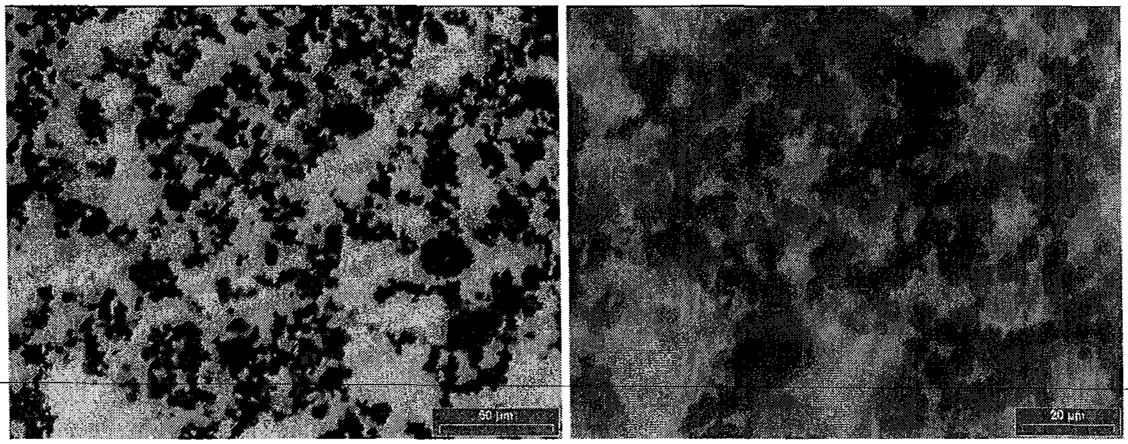
The morphological study was done using light microscope. Figure 7 is a series of micrographs taken under light microscope at several magnifications for 3 vol.%, 5 vol.% and 8 vol.% of untreated system. It is clearly shown in Figure 7 (a) and (b), the 3 vol.% of untreated Ag nanoparticles are dispersed in the epoxy system with a significant separation by the insulating matrix. At higher magnification, it can be observed that there is no Ag nanoparticles network being formed. The lumps of particles are separated several micrometers of insulating matrix. Insufficient filler amount is the main reason for much lesser formation of physical contact between fillers. The absence of particle networks and physical contact among fillers has led to the high electrical resistivity behavior for 3 vol.% untreated system.



(a) 3 vol.% (Magnification: 310×) **(b) 3vol.% (Magnification: 625×)**



(c) 5 vol.% (Magnification: 310×) **(d) 5 vol.% (Magnification: 625×)**



(e) 8 vol.% (Magnification: 310×) (f) 8 vol.%(Magnification: 625×)

Figure 7: Optical micrographs on 1-µm cross section of untreated Ag nanoparticles filled epoxy at filler loading of (a) – (b) 3 vol.%, (c) – (d) 5 vol.% and (e) – (f) 8 vol.%

The separation between lumps of Ag nanoparticles by insulating matrix is significantly reduced by the increase of untreated filler content from 3 vol.% to 5 vol.%, as shown in Figure 7 (c) and (d). In 5 vol.% of untreated system, the Ag nanoparticles are sufficient enough to have intimate contact, resulting in a Ag nanoparticle network. This networking is essentially a continuous linkage between Ag nanoparticles or lumps, connecting from all direction, from bottom to top of the specimen. According to percolation law, the electrons may find the ease of transportation through the conducting network formed in the bulk of 5 vol.% specimen, in compared with that experienced in 3 vol.% untreated composite. The higher amount of filler creates higher possibility for the occurrence of particles intimate contact in the matrix system, where the filler occupied larger area in the composite system (Figure 7 (b) and (d)). This gives a clear indication that the perfect Ag nanoparticles network in 5 vol.% untreated system has led to the noteworthy insulator-to-conductor transition to be occurred at 5 vol.% of filler concentration.

Higher filler loading in a reduced volume fraction of matrix in 8 vol.% untreated system is expected to have larger area to be occupied by Ag nanoaprticles. Figure 7 (e) and (f) provide a good indication for the occurrence of higher extent of Ag nanoparticles agglomeration. It is clear to be observed that the size of the Ag lumps is much bigger than that being found in 3 vol.% or 5 vol.% untreated system. The agglomerated Ag lumps may be the indicative for the degradation of flexural properties for 8 vol.% untreated composite. The filler-matrix interaction is significantly replaced by the domination of filler-filler interacton at higher filler loading. The bulk volume of the composite is almost fully occupied by the Ag lumps. The rigid bonding between fillers may be the contributor to embrittlement of composite in 8 vol.% system, as compared with ductile neat epoxy and 4 vol.% untreated system. However, the Ag lumps is well-arranged in the matrix system to form a much intimate contact and wider of conduction network. This is in contrast to the micrographs of 3 vol.% untreated system, where almost all of the lumps are significantly in contact in 8 vol.% untreated system. The formation of better Ag network indicates the achievement of the highest DC conductivity in 8 vol.% system. The increase in conductivity is, however rather slower than the trend predicted by percolation threshold theory. This might due to very small amount of nanovoids formation in the Ag lumps that already sufficient enough to restrict minority of electrons traveling for conduction. This is thus the conductivities of composites do increase after critical filler loading, V_c due to greater extent of particles contact but in a rather slowly rate in compared with theoretical data.

1.2.1.2 Flexural Properties

Mechanical property such as flexural properties of silver nanoparticles-filled epoxy composites were investigated in the composite composition range of 0 to 8 vol.% of Ag nanoparticles in the present study. High flexural modulus and strength are two of the critical parameters of a high performance conductive adhesive. Without adequate flexural strength, the conductive adhesive cannot survive the significant bending loads encountered during assembly, handling and throughout the product life.

Figure 8 shows the flexural stress-strain curves for three typical composites filled with 0, 4 and 8 vol.% of silver nanoparticles. The shape of the stress-strain curve gives a clue to the material's behavior. A hard, brittle material shows a large initial slope and fails with little strain. A soft and tough material, on the other hand, exhibits a very small initial slope, but strain hardens and withstands larger strains before failure. A material's stress-strain curve also indicates the overall toughness of the material. The area under the curve, in units of MPa, is a measure of a material's toughness. The greater that area is, the tougher the material is, and the greater the amount of energy required to break it.

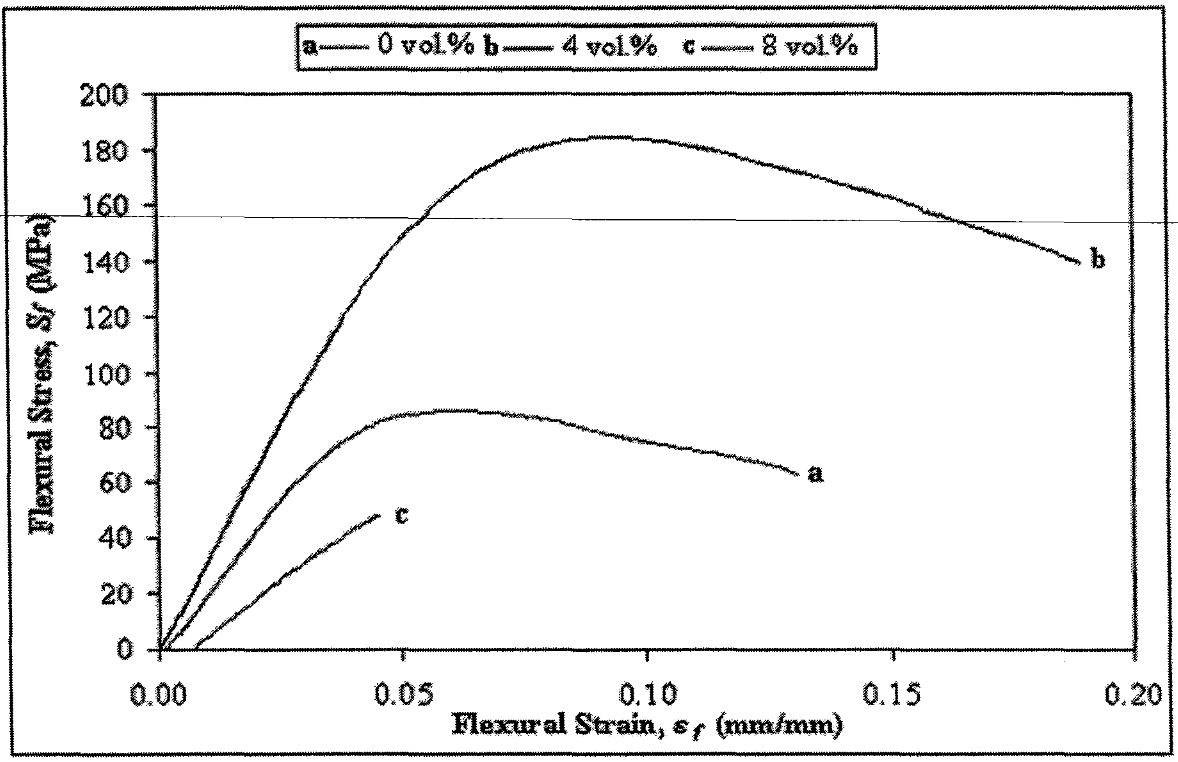


Figure 8: Typical flexural stress-strain curves for composites at two significant filler loadings in comparison with that of unfilled specimen

Curve (a) represents the flexural stress-strain response of neat specimen without filled of Ag nanoparticles. The property of neat specimen is somehow located in between that of 4 vol% Ag-filled and 8 vol% Ag-filled composites. Neat specimen shows its ductile fracture after achieving ultimate flexural strength. The material shows yielding before fracture.

The ductility of composite increases as filler concentration increases. It is observed that the system with 4 vol.% Ag incorporation has the highest flexural modulus (3993MPa) and strength (117 MPa) among the seven systems indicated in Figure 8 and 9. Gain in strength and stiffness of 4 vol.% system is around 22 % and 26 % respectively over the neat specimen. Curve (b) in Figure 8 shows a significant improvement in strength and modulus for 4 vol.% system. The area under curve (b) is the largest among the three systems, where the toughness of this system is the highest. The composite fails after achieving yielding. The 4 vol.% of Ag/epoxy system is therefore classified as a strong and tough material.

However, above 4 vol.% Ag, the flexural strength and modulus drops as filler concentration increases. Figure 9 and 10 clearly show the decreasing trend can be. The stress-strain behavior of 8 vol.% system indicates that this system experiences a typical brittle fracture (Figure 8, curve (c)). It fails at much lower stress and little strain without significant elongation on the composite before failure, in comparison with neat specimen and 8 vol.% system. This composite is determined as a low strength and brittle material. The ductility of composite is believed to be reduced above 4 vol.% introduction of Ag. Further increment of Ag filler after 4 vol.% results in the transition of stress-strain behavior from ductile to brittle. It also can be seen that by increasing filler concentration from 4 vol.% to 8 vol.%, there is no proportional improvement in flexural properties. Rather, there is a very nominal increase in modulus (+8.72%), and a significant reduction in strength (-6.23%) with 8 vol% Ag/epoxy composite over that of neat specimen.

It could be seen that Curve (c) does not originate from zero. It is strongly believed that the specimen was under pre-strain condition before being loaded in bending mode. This might due to the technical mistake done during characterization where the specimen was pre-strained by most probably the load-pointer when it was placed on the supports.

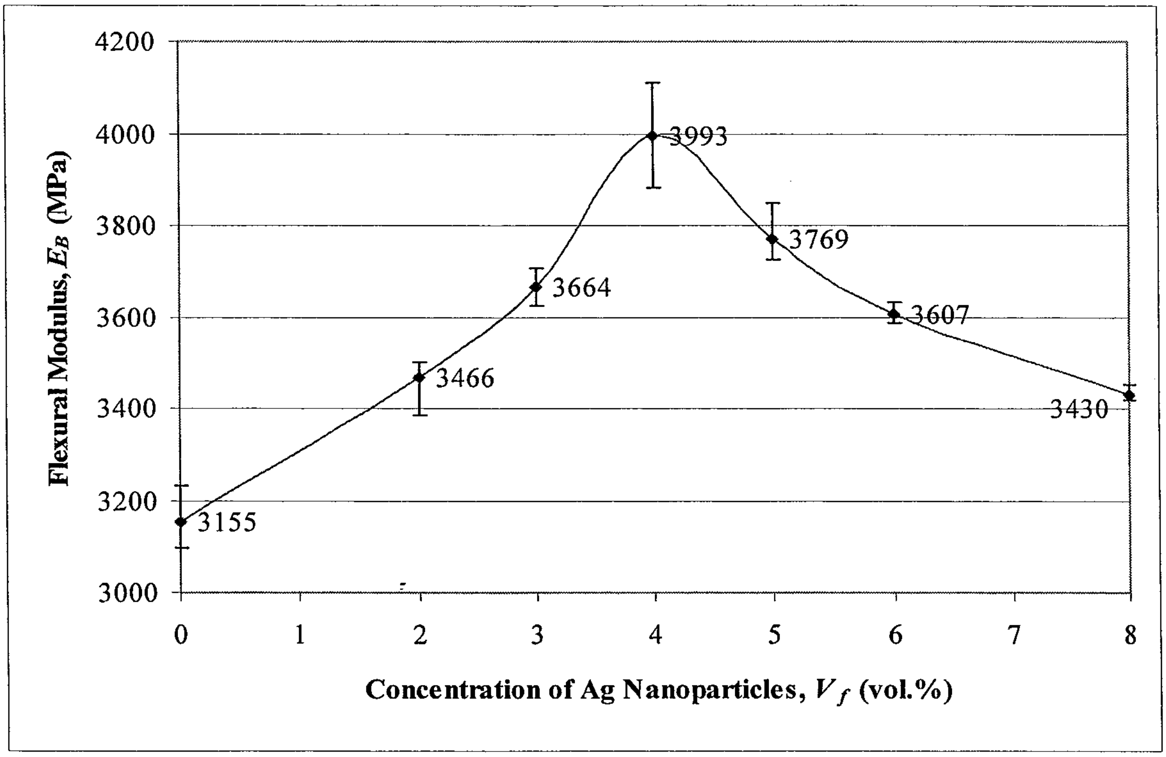


Figure 9: Moduli of elastic in bending are studied as a function of Ag nanoparticles concentration

The results of flexural test on modulus and strength obtained are parallel with the previous study reported by Chisholm, *et al.* (2004) where a decreasing trend in flexural modulus and strength in epoxy-based composites after achieving maximum flexural properties at 1.5 % of SiC filler concentration. Busmann *et al.* (1999) did also supported in their article that solid nanofiller materials in general tend to deteriorate mechanical properties of the composites.

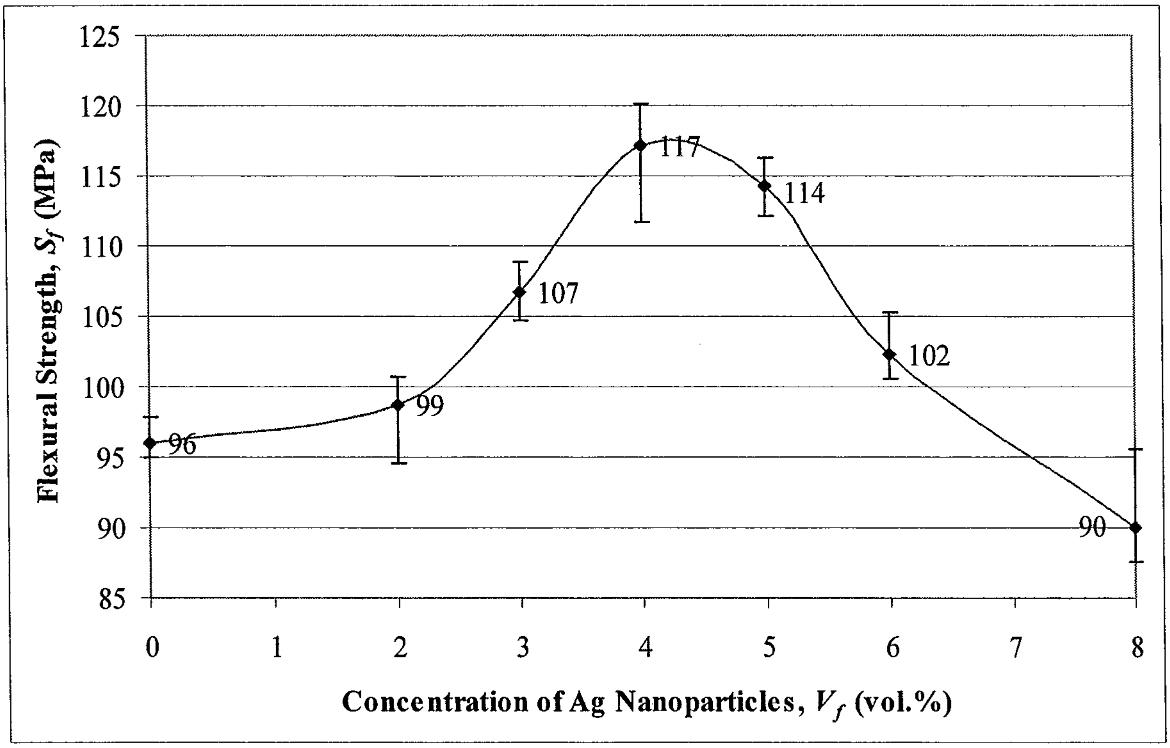


Figure 10: Flexural strength versus filler concentration of Ag nanoparticles/epoxy composites

The enhancement in flexural properties as filler loading increases from 0 to 4 vol.% indicates that the Ag nanoparticles tend to strengthen the materials. It is believed that the nanoparticles tend to reduce void content of the composite and thus translate into increased of 20 to 30 % flexural properties. The rigid and incompressive silver nanopowders do not leave sufficient space for compressive deformation of epoxy resin to take effect. When incorporated into epoxy resin, the Ag nanopowder leaves a reduced degree of room for compressive deformation of epoxy. The observed improvement of properties might also attribute to the use of ultrasonic wave for mixing. Ultrasonic mixing utilized high energy of sonic waves to force an intrinsic mixing of particles with the matrix via sonic cavitations (Xia *et al.*, 2000). Wang and coworkers (2000) had proven that the nanoparticles filler can redisperse more effectively by ultrasonic irradiation than by conventional stirring. The 4 vol.% of Ag is the optimum amount of filler that may create the maximum interaction of filler-matrix to effectively transfer loads from matrix to filler that stay in intimate contact. A strong interface layer is believed to be formed in between filler and matrix. However, at filler concentration higher than 4 vol.%, the adding of filler deteriorate the flexural properties of composites, especially at filler loading as high as 8 vol.%. It is believed that higher filler loading may lead to filler-filler interaction that resulting in agglomerates (Chisholm *et al.*, 2004), which restricted in the formation of well-dispersed Ag nanoparticles throughout the epoxy resin and decreased the degree of ductility. However, the microstructural study may prove the behavior of composite as filler concentration increases in microscopic scale.

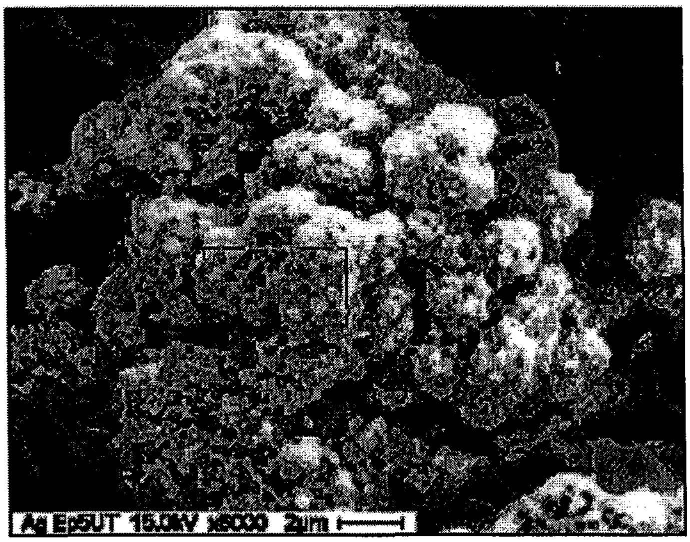
1.2.2 The effect of silane-based coupling agent

In this section, the effect of surface modification of Ag nanoparticles with a silane-based coupling agent, 3-aminopropyl triethoxysilane on the electrical and mechanical properties of the resulting composites is investigated. Two filler loadings (4 vol.% and 5 vol.%) have been selected for the second phase of study because these filler have displayed a reasonably good balance of electrical and mechanical properties in the first phase of study. The effect of surface treatment on 4 vol.% and 5 vol.% of silver nanoparticles in epoxy composites were investigated through electrical and mechanical properties.

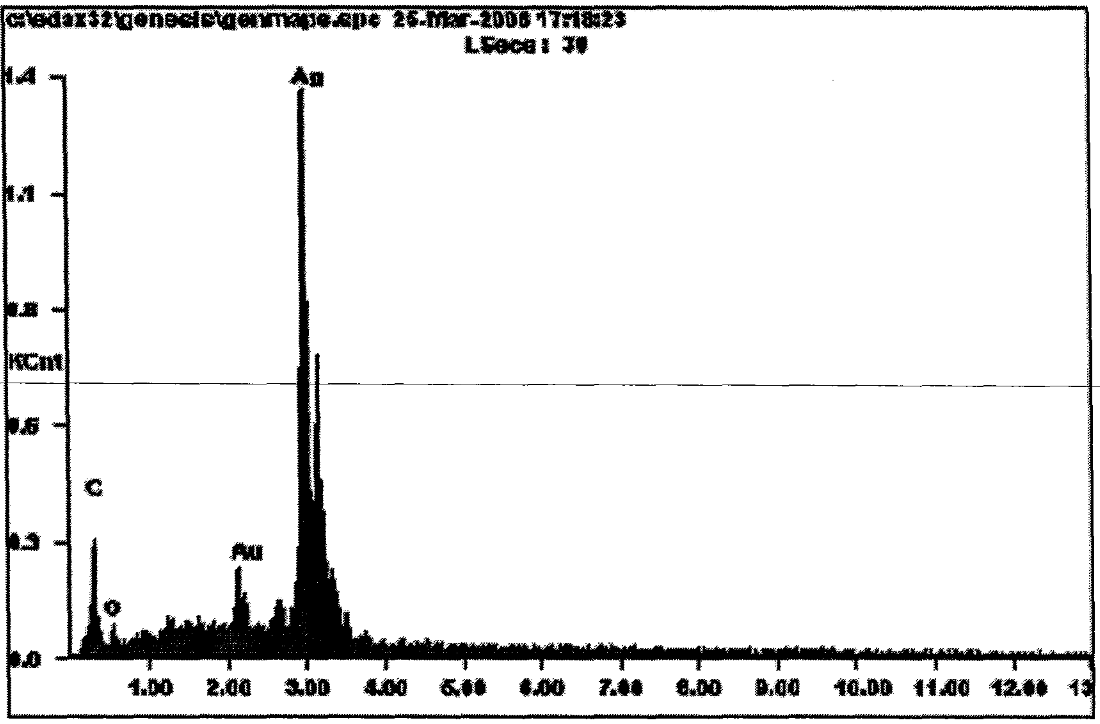
1.2.2.1 Elemental Analysis by EDAX

EDX analysis is implemented to indentify the presence of silicon (Si) element on the surface of Ag nanoparticles after chemically treated by 3APTES silane coupling agent. It is believed that with the adding of 3APTES silane coupling agent, the Ag nanoparticles are supposed to be coated with a thin layer of Si-based compound originated from the silane coupling agent. After incorporated into epoxy resin and curing, the Si element is supposed to remaine in the composite system at the interface of filler and matrix.

Figure 11 and 12 are the EDX spectrums obtained after analyzing untreated and treated systems, respectively. The EDX spectrum is just a plot of how frequently an X-ray is received for each energy level of electrons. An EDX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen. Figure 11 (b) and 12 (b) reveal that Ag is the most concentrated element in the composite at the selected area. It is noteworthy that the treated system shows the detection of Si element on the fracture surface of the composite. The peak is detected at a much lower concentration in compared with the peak of Ag element. It is reasonable as the 3APTES silane coupling agent is employed at a level of 1 % by weight referred to the weight of Ag nanoparticles filler that being introduced into the epoxy system. The elements of carbon (C) and oxygen (O) are identified may be contributed from the organic matrix itself and the added silane coupling agent. Since the specimen is polymeric material, a thin conducting layer of gold (Au) must be coated on the surface of the specimen to facilitate the capture of clear image of Ag nanoparticles. Therefore, as expected, the Au element was detected in the two EDAX spectrums is not surprising. It is definitely not originated or contributed by the specimen itself, and therefore is neglected during spectrum analysis. The EDAX analysis reveals that there is a high possibility of the formation of Si-based compound at the interface of Ag fillers and epoxy matrix, which leads to the enhancement in electrical and flexural properties.

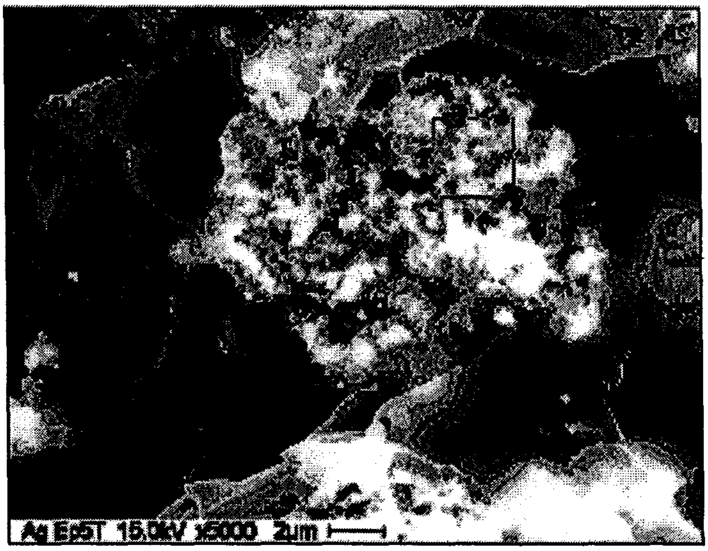


(a)

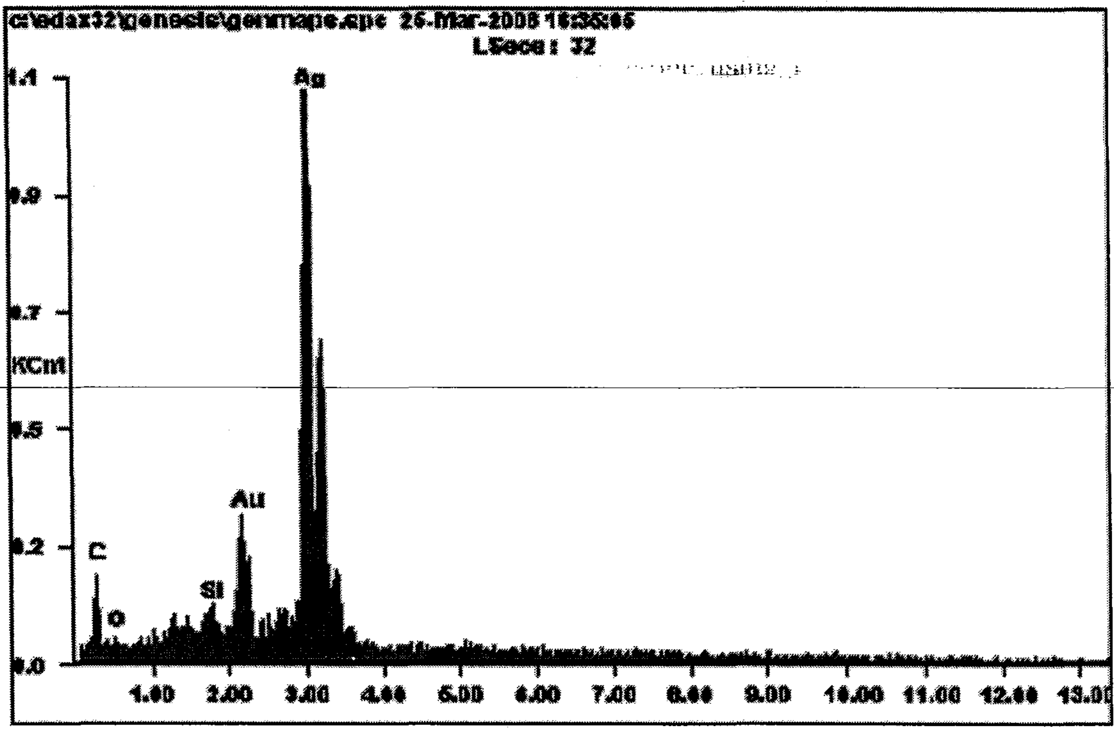


(b)

Figure 11: EDAX analysis on 5 vol.% of untreated Ag-filled epoxy composite: (a) Spot taken for EDAX analysis at micron scale (magnification: 4k×), (b) EDAX spectrum shows the absence of Si element on the surface of Ag nanoparticles (Au is the gold coating on the surface of specimen).



(a)



(b)

Figure 12: EDAX analysis on 5 vol.% of treated Ag-filled epoxy composite: (a) Spot taken for EDAX analysis at micron scale (magnification: 3.5k×), (b) EDAX spectrum shows the presence of Si trace on the surface of Ag nanoparticles (Au is the gold coating on the surface of specimen).

1.2.2.2 Electrical Conductivity

As discussed earlier, the volume resistivity of Ag nanoparticles filled epoxy composites relates to the volume fraction of filler particles and the particle size as well. Conduction behavior is also dependent on the creation of conducting contacts between metallic filler particles as predicted by percolation theory. The filler surface is thus playing a vital role in determining the processing behavior and properties of composites. In the present research, the commercial Ag nanoparticles are treated with a silane-based coupling agent called 3-aminopropyl triethoxysilane (3APTES). According to Tan *et al.* (2005) and Rothon (2003), the use of coupling agent may beneficially modify the surface of fillers, and thus optimize composite processing and properties. The volume resistivity measurements were made on two specimens filled with 4 vol.% and 5 vol.% of treated Ag nanoparticles. Table 1 shows the resistivities and conductivities of the treated and untreated specimens at the same filler concentration. The resistivity of 4vol.% system shows that the adding of 3APTES silane coupling agent has decreased the resistivity drastically and dramatically from 3.46×10^4 to 1.33×10^2 Ω-cm. At the critical filler concentration (5 vol.%), the composite records a much lower resistivity (2.51×10^{-1} Ω-cm) after surface modification of Ag nanoparticles. The result suggests that the coupling agent also affects the DC conductivity of the composites. This is in accordance with the previous work done by Tan *et al.* (2005), where the resistivity of a typical ECA sample showed that with the adding of KH-570 silane coupling agent, the resistivity decreased dramatically. The authors predicted that the drastic changes were probably due to the improvement of silver flakes' dispersivity in the matrix and the improved adhesion between fillers and matrix. It is suggested that good adhesion of filler-matrix and filler-filler minimize the gap between filler-filler and filler-matrix. The presence of gap may contribute to certain degree of resistance to the conduction process. On the other hand, the good dispersivity of nanosized Ag filler increases the possibility of single particle dispersion throughout the matrix. This promotes the conduction via electron traveling from particle to particle across a potential barrier (insulating matrix). Good dispersion of fillers may also well-arrange the fillers, yielding particle-particle physical contact, where nano-defect or agglomeration does not take place between particles. These may make a great contribution for the conductivity improvement.

It is noteworthy that the highest conductivity is achieved in the 5 vol% treated Ag filled epoxy system at 3.99 S/cm. The adding of 3APTES silane coupling agent to 5 vol.% system has significantly improved the DC conductivity of composite by 1470 times (Table 4.7). The drastic shift of conduction behavior from 4 vol.% to 5 vol.% system is also being observed after surface modification of Ag nanoparticles. It is again being proved that the critical Ag filler loading (V_c) that make the transition of insulator-to-conductor is determined at 5 vol.% concentration. Below V_c, the 4 vol.% system also shows an enhancement in conductivity for about 260 times as a results of the presence of 3APTES silane coupling agent in the composition of composite. A more obvious comparison in conductivity is made and shown in Figure 12.

Table 1: Comparison of the measured volume resistivities and calculated conductivities for 4 and 5 vol.%, treated and untreated silver-filled epoxy systems

Filler Loading (vol.%)	Ag Nanoparticles Surface Modification	Volume Resistivity, ρ_v (Ω-cm)	DC Conductivity, σ (S/cm)	Enhancement in Conductivity (times)
4	Untreated	3.46×10^{4}	2.89×10^{-5}	-
	Treated	1.33×10^{2}	7.54×10^{-3}	261
5	Untreated	3.68×10^{2}	2.72×10^{-3}	-
	Treated	2.51×10^{-1}	3.99	1470

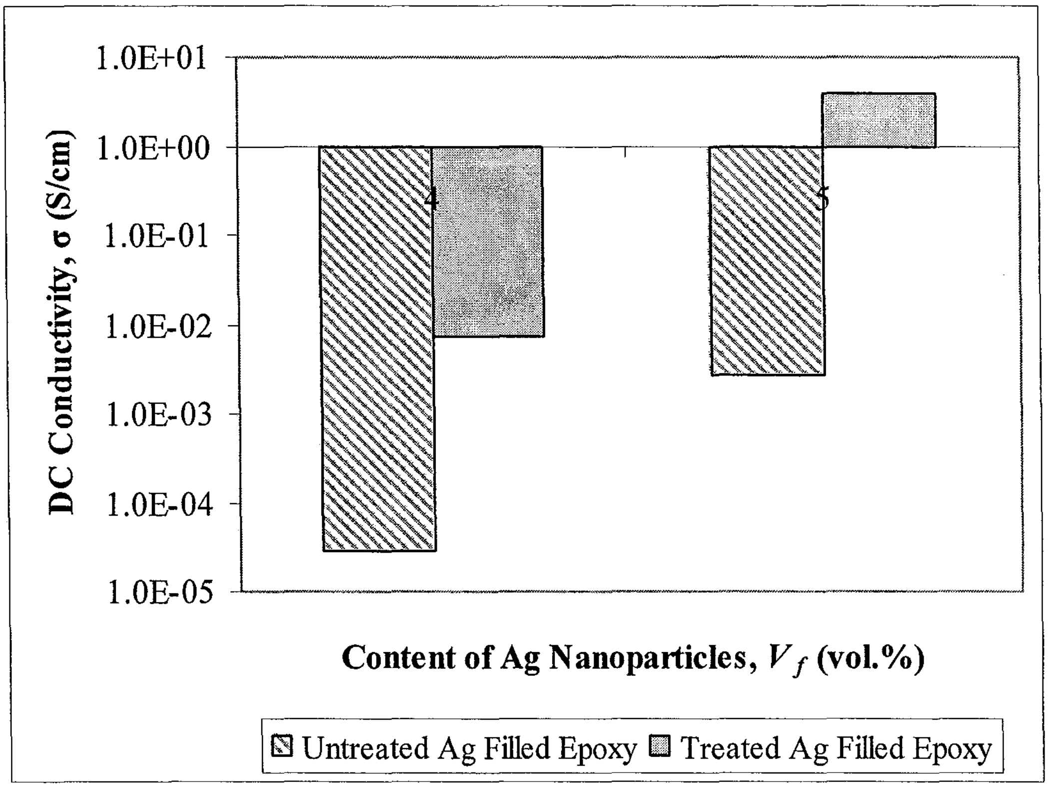


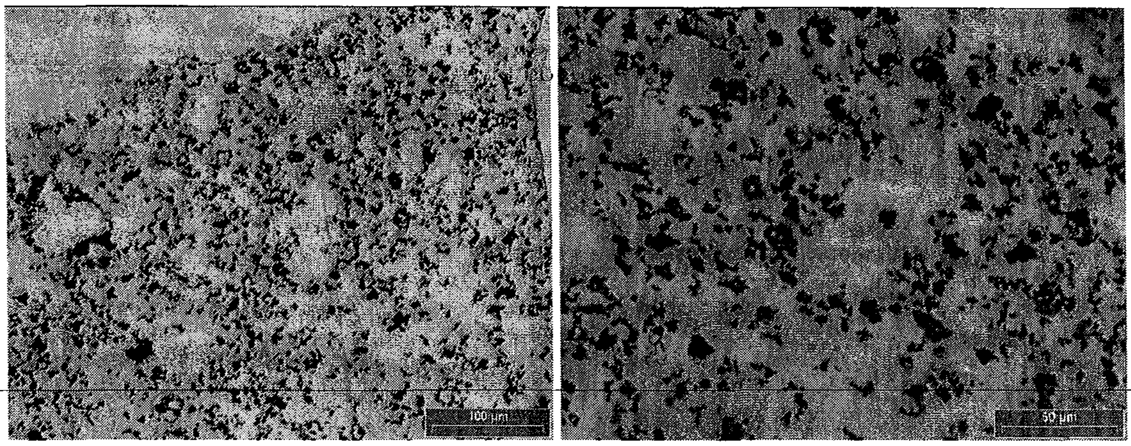
Figure 13: Comparison in DC conductivity of treated Ag filled epoxy systems and untreated Ag filled epoxy systems at 4 and 5 vol.% filler concentration

The above mentioned enhancement in conductivity is most probably due to the improvement of dispersivity of silver nanoparticles in the matrix by the aid of ultrasonic cavitation, and the improved adhesion between fillers and matrix. The significant changes should be correlated by observing and studying the microstructures of the composites, and determining the presence of types of chemical bonding between fillers and matrix. The observation of dispersivity of Ag nanoparticles at 5 vol.% of untreated and treated filler concentration, respectively, were done using light microscope. The specimens are cut in cross section of thickness in order to investigate the extent of Ag nanoparticles dispersion throughout the volume of bulk composites.

It is exciting and noteworthy to report that the dispersivity of Ag nanoparticles in epoxy matrix system is remarkably improved after the surface treatment, by observing the difference in the distribution of 5 vol.% of fillers in micrographs shown in Figure 14 (a) and (b) (untreated system) and Figure 14 (c) – (e) (treated system). The degree of agglomeration of Ag nanoparticles is significantly reduced. The Ag nanoparticles are dispersed uniformly throughout the matrix. In untreated system, although the conduction network of Ag is formed in 5 vol.% composite, the fillers are distributed inhomogeneously along the boundaries of epoxy grains, forming a so-called cellular structure (Gonon and Boudefel, 2006). This cellular structure tends to agglomerate the filler along the thin path of epoxy grain boundaries. The 5 vol.% untreated system conducts current via the cellular structure of Ag conduction network.

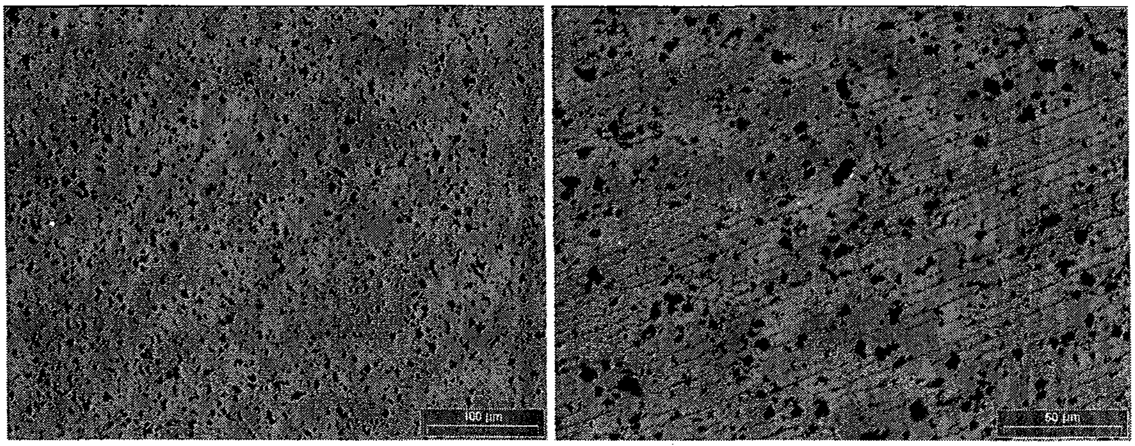
When the surface of filler is chemically modified, the filler-matrix interaction is enhanced, leading to the well-disperse of Ag nanoparticles in the matrix. The dispersion of Ag nanoparticles may lead to intimate contact of fillers with most probably a much minimum amount or volume of nanovoids within the contact. This increases the possibility of very narrow separation (< 10 nm) between two single Ag nanoparticles due to the reduced degree of particles agglomeration.

Figure 14 (e) shows an increase of Ag dispersion in the matrix. It is, therefore suggested that the conduction mechanism in the 5 vol.% treated composite may be dominated by both percolation threshold theory and electron tunneling effect. This might be the reason for the noticeable enhancement in electrical conduction behavior. It is believed that electron conduction through tunneling effect does contribute to the drastic enhancement in conductivity of 5 vol.% of treated Ag filled epoxy system.



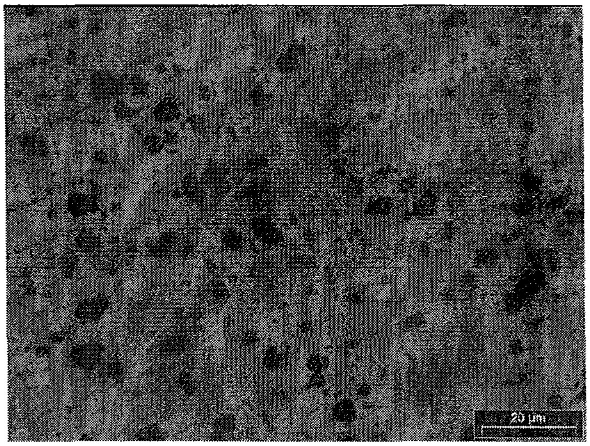
(a) 5 vol.% of untreated Ag (Magnification: 155×)

(b) 5 vol.% of untreated Ag (Magnification: 310×)



(c) 5 vol.% of treated Ag (Magnification: 155×)

(d) 5 vol.% of treated (Magnification: 310×)



(e) 5 vol.% of treated (Magnification: 625×)

Figure 14: Light microscopy micrographs reveal the degree of dispersivity of untreated and treated Ag nanoparticles in epoxy matrix system for: (a) – (b) 5 vol.% of untreated Ag, and (c) – (e) 5 vol.% of treated Ag

1.2.2.3 Flexural Properties

Referring to Figure 15, the system filled with 4 vol.% treated Ag achieves the highest flexural modulus at 5456 MPa. Meanwhile, the 5 vol.% treated Ag system records a slightly lower flexural modulus at 5049 MPa. The small difference in the drop of flexural modulus for the both systems can be seen in the figure. It is found that with the adding of only 1 wt.% of 3APTES silane coupling agent, the flexural modulus of the 4 vol.% system shows remarkable enhancement for about 37 %, in comparison with that of filled with untreated Ag system. The coupling agent also give rise to approximately 34 % of improvement in modulus for the system with 5 vol.% treated Ag. These great enhancements imply that the surface modification of Ag nanoparticles with a 3APTES silane coupling agent that being employed at levels of 1 wt.% referred to the Ag filler might improve the adhesion between matrix and fillers by most probably the formation of chemical bonding between fillers and matrix surfaces.

Mohd Ishak and coworkers (1998) had shown significant increase in modulus with the addition of 1 % coupling agent. They noted that the three main factors that affecting the composites' modulus were filler modulus, filler loading and filler aspect ratio. Normally, high stiffness composite requires filler particles of high modulus and high aspect ratio (the ratio of the major to the minor dimension of a particle), and preferably at high filler loading. Since all of those factors have been kept as constant in the first phase of the present research for 4 and 5 vol.% untreated system, it can be inferred that the presence of 3APTES silane coupling agent has led to a significant improvement in the filler-matrix interfacial bonding. This will obviously results in an increase in the efficiency of stress transfer from matrix to the filler, which consequently gives rise to higher modulus.

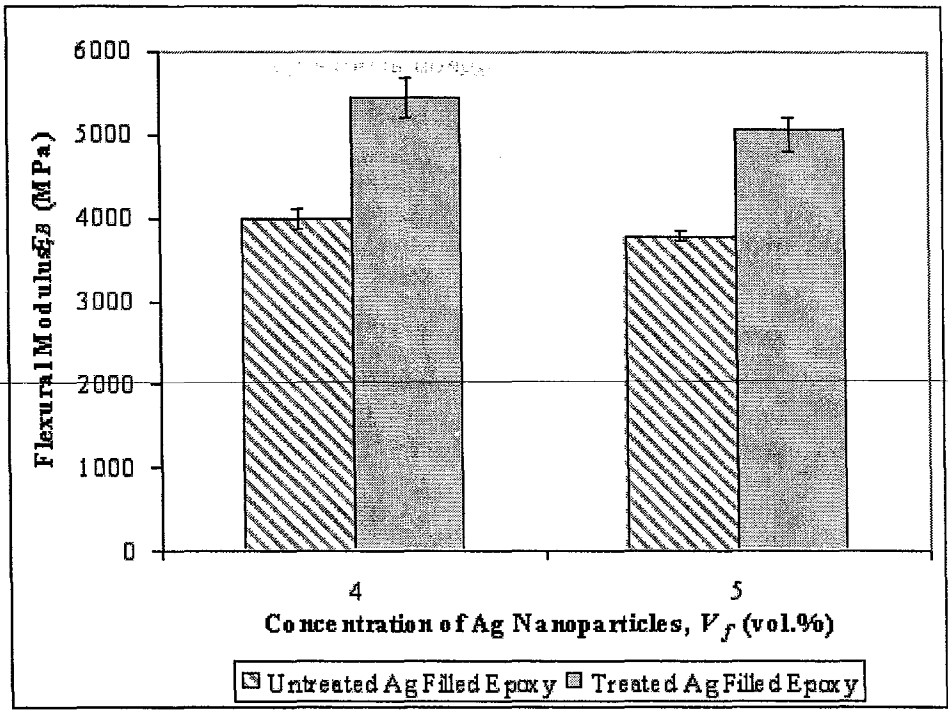


Figure 15: Flexural modulus versus Ag filler loading for treated and untreated Ag filled epoxy systems at two selected filler contents of 4 and 5 vol.%

The comparison has been made on the flexural strength of composites filled with treated and untreated Ag fillers. The effect of the silane-based coupling agent on the flexural strength of the specimens is shown in Figure 16. The overlapping of Y error bar in Figure 16 reveals that there is no significant reduction in strength as filler loading increases. The optimum strength can be achieved with a filler loading ranging from 4 to 5 vol.% of Ag nanoparticles. The employment of 3APTES silane coupling agent in 4 to 5 vol.% range of filler concentration gives similar effect and degree of enhancement in strength. It is predicted that a noticeable increase in strength might be observed in higher filler loading composites, such as in 6 to 8 vol.% systems. The enhancement in flexural strength is probably due to the improved adhesion between matrix and fillers via the formation of interface. A strong interface facilitates the transmission of mechanical energy (in this case, the flexural loading) from the polymer matrix to the fillers. It increases with the strength of chemical bonding between the fillers and the matrix. The coupling agent functions as molecular bridge at the interface of dissimilar polymer binder and fillers, resulting in the formation of covalent bonds across the interface, which improves the flexural properties of the composites (Tan *et al.*, 2005).

Reinforcement depends on the transmission of mechanical energy from the matrix to the filler. It increases with strength of chemical bonding between fillers and the matrix.

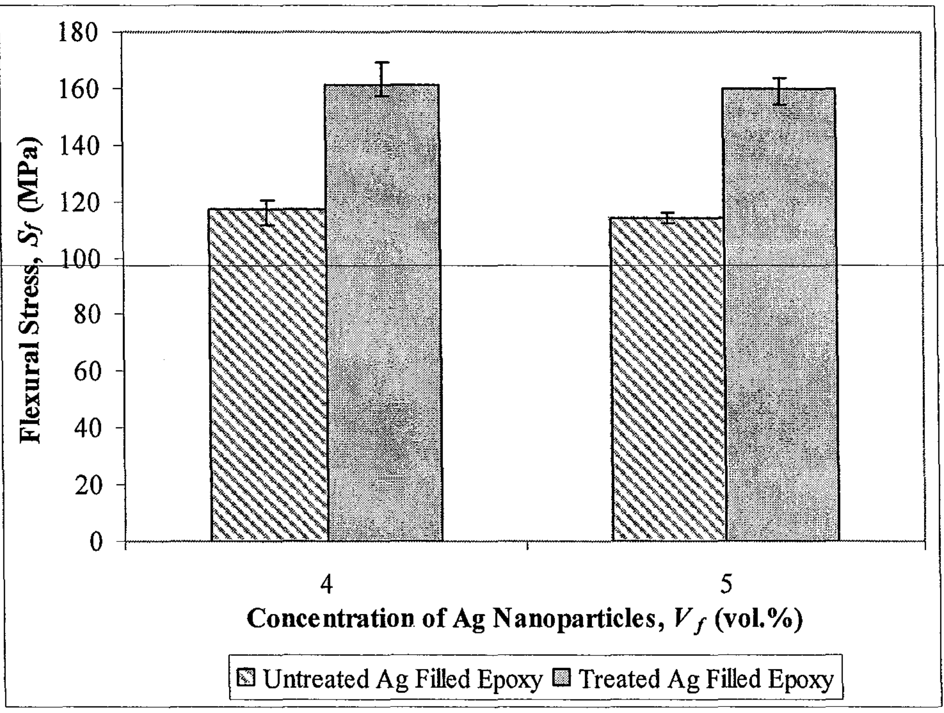


Figure 16: Flexural stress versus Ag filler loading for treated and untreated Ag filled epoxy systems at two selected filler contents of 4 and 5 vol.%

2.0: To synthesis silver nanoparticles

2.1 Introduction

Metal nanoparticles have gained much attention in recent years due to their further potential applications in optical and electronic devices. Due to their small size, these crystallites exhibit novel material properties that largely differ from the bulk properties. Many reports on quantum size effect on photochemistry, non-linear optical properties of semiconductor or the emergence of metallic properties with the size of the particles have appeared during the past. Silver has received much attention, since it has the highest thermal and electrical conductivities of all metals; compare to gold, nickel, copper, etc.

2.2 Methodology

In this study, the fabrication of silver nanoparticles via green synthesis was carried out. The final product was characterized by transmission electron microscopy (TEM) and particle size analysis. Figure 17 generally summarizes the method used in the production of silver nanoparticles.

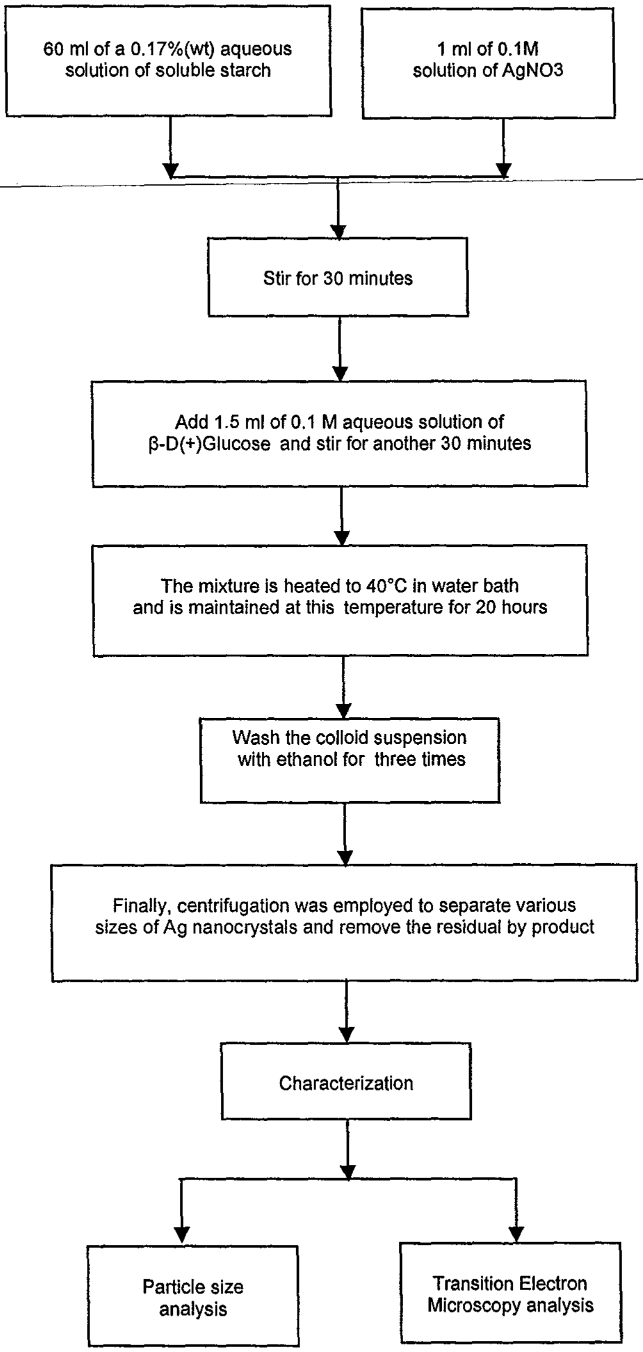


Figure 17: Green method to produce silver nanoparticle

2.3 Results and Discussion

A particle size analysis was carried out by using TEM observation. A statistic calculation was carried out to obtain the average diameter of Ag nanoparticles, as shown in Table 2. Figure 18 is a histogram summarized the distribution of particle size or diameter. The histogram reveals that there are 41.1% of particle having diameter in the range of 40 to 60 nm, and 15.3% of particles having a size from 60 to 80 nm. However, there are some signs of particle agglomeration being observed, as shown in Figure 19 and 20. The agglomeration of particles takes place by joining up the particles in a manner of continuous chain. It can be seen clearly that particles come in contact with each other in sequence which leading to the formation of a continuous linkage.

Table 2: The statistical analysis of Ag nanoparticles calculated from 470 particles

Statistic Parameter	Reading
Sum of Ag diameter (nm)	26897
Total number of Ag nanoparticles being measured and observed	470
Average Diameter (nm)	57.23
Maximum Diameter (nm)	133
Minimum Diameter (nm)	7

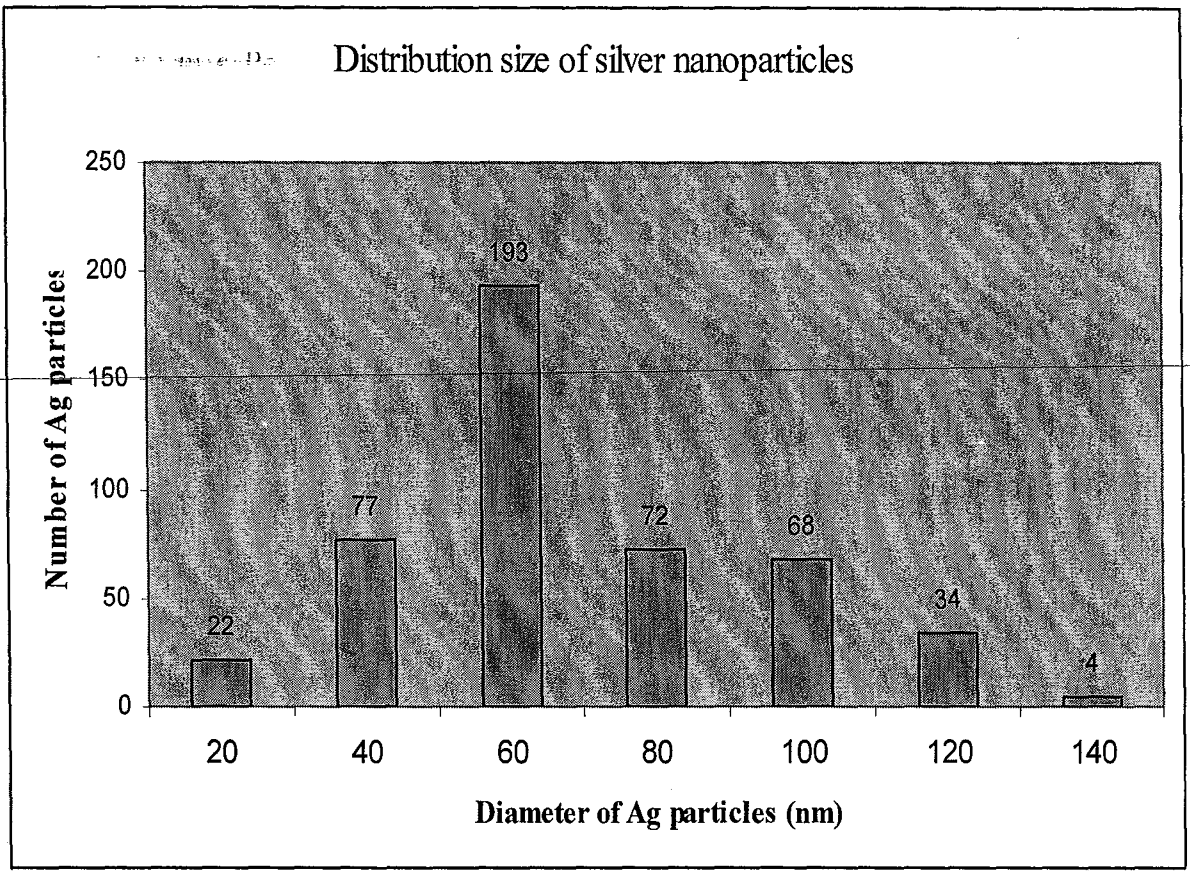


Figure 18: Particle size distribution with respect to diameters of silver nanoparticles.

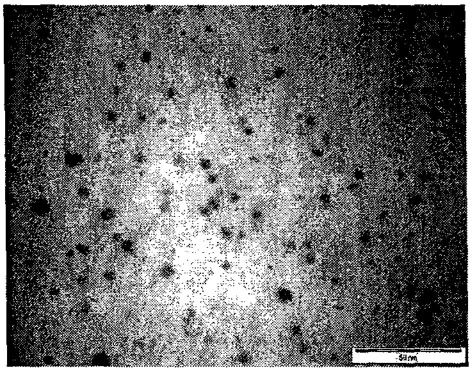


Figure 19: TEM image of silver nanoparticles at 50nm scale

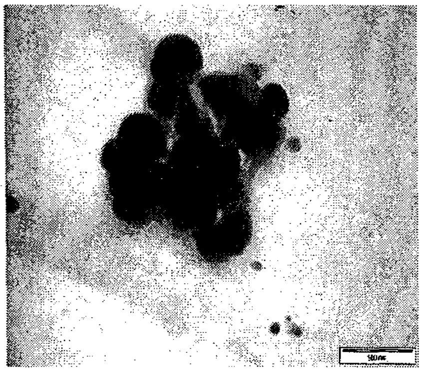


Figure 20: TEM image of silver nanoparticles at 100nm scale.

4.0 Conclusions

The following conclusions are based on the findings reported from the investigation done in the present research.

- The electrical measurement shown that DC conductivity of untreated 70-nm-silver nanoparticles-filled epoxy composites increases with filler concentration. The insulator-to-conductor transition is found to be occurred at a filler loading of 5 vol.% of silver nanoparticles. This critical filler loading is termed percolation threshold (V_c). Below percolation threshold, the composites are behaving like perfect insulator as unfilled epoxy system. The 5 vol.% Ag/epoxy composite managed to achieve a DC conductivity at 2.72×10^{-3} S/cm. No remarkable improvement in DC conductivity above 5 vol.% of filler concentration.
- In untreated Ag/epoxy composites, the nanometer-sized particles can more easily migrate and segregate along the grain boundaries of epoxy matrix, giving rise to an inhomogenoues distribution of fillers (cellular structure). The addition of 3APTES silane coupling agent to the composites has extensively enhanced the homogeneous distribution of silver nanoparticles in the epoxy. The well-dispersed filler and the least problem of agglomeration throughout the matrix have led to the noticeable enhancement in electrical conductivity of the composites. There is no cellular structure can be observed in treated Ag/epoxy composites. The insulator-to-conductor transition is still found to be occurred at 5 vol.% of Ag filler concentration. The 5 vol.% of treated Ag/epoxy composite reported a conductivity of 3.99 S/cm.
- Nanoparticles loading into the base matrix are found to be optimal around 4 vol.% to derive maximum gain in the mechanical and thermal properties of the structural composites for both treated and untreated Ag/epoxy composites. The improvement in flexural properties after surface treatment of filler is about 33 – 37 % over untreated Ag/epoxy composites. The drop in flexural and thermal properties of 5 vol.% of treated Ag/epoxy composite is not significant after achieving maximum properties in 4 vol.% treated system. Therefore, an optimum Ag filler loading that balance up the electrical, thermal and mechanical performance of an Ag/epoxy composite falls at 5 vol.%.

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Publications

International Journal

1) D. I. Tee, M. Mariatti, A. Azizan, C. H. See & K. F. Chong, (2007) Effect of Silane-based coupling agent on the properties of silver nanoparticles filled epoxy composites. *Composites Science & Technology 67, 2584-2591*

Presentation in International Conference

1) D. I. Tee, M. Mariatti, C. H. See, K. F. Chong, Study on the Electrical Property of Silver (Ag) Nanoparticles Filled Epoxy Composites for the Application of Electrically Conductive Adhesives (ECAs) in Electronic Packaging, International Electronic Manufacturing Technology (IEMT 2006), Putra Jaya, 8-10 November 2006
2) D. I. Tee, M. Mariatti, A. Azizan, C. H. See and K. F. Chong, Thermal and electrical conductivity properties of silver nanoparticles filled epoxy composites for the application of electrically conductive adhesives (ECAs), 12 Asian Chemical Congress (12 ACC), Kuala Lumpur, 23-25 August 2007.