

**AN INTRODUCTION TO
ELECTRICALLY CONDUCTIVE ADHESIVES**

by

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1. INTRODUCTION

Electrically conductive adhesives (ECAs) can be employed in a wide variety of applications to provide both a mechanical bond and an electrical interconnection between a device lead or chip carrier and a circuit board contact pad. This dual functionality is achieved by composite materials composed of metallic particles dispersed in an adhesive matrix. (Note that those materials are different from the inherently conductive polymers, such as polyacetylene, polyphenylenes, etc.) There are several types of conductive adhesives divided by their morphology, metal filler percentage, and processing requirements: isotropic conductive adhesives (ICAs), which conduct electricity equally in all directions like solder pastes; anisotropic conductive adhesives (ACAs), which conduct only in the Z-axis with the alignment of device and substrate conductor pads under heat and pressure; anisotropic conductive adhesive films (ACAFs), which are the film versions of ACAs; heat seal connectors (HSCs), which have customized built in circuitries; and non-conductive adhesives (NCAs), which obtain mechanical bonding from the adhesives and electrical connection from the metal contact spots [1-2].

ECAs (mainly solventless conductive epoxies) have been used as the major die attachment materials for silicon chips to lead frames [3]. They are the materials of greatest commercial importance, with about 80% of the overall die attach market [4]. Conductive silver pastes have also been used for decades to form circuit and component terminal bonding in the hybrid industry. ACAs are mainly used to interconnect flexible circuit connectors, tape automated bonding (TAB) packages, and bare IC chips to glass panels for liquid crystal display (LCD) interconnection technology. ICAs have drawn more and more attention for their potential uses for solder replacement in surface mount technology (SMT). This introductory paper is focused on the ICAs due to their similar assembly process with reduced steps to the

conventional SMT using solder pastes and no requirements for capital equipment investments for potential applications.

ECAs offer several advantages over solder. They are environmentally friendly, eliminating the lead (Pb) and flux associated with normal soldering processes, and their associated cleaning/disposal problems, reducing coefficient of thermal expansion (CTE) mismatch design limitations, and offering lower temperature processing and less complicated assembly processes. However, a better understanding of the design, reliability, material, and manufacturing characteristics of various conductive adhesive technologies must be achieved before an assessment of their leverages as a component attachment replacement can be made. The processing parameters, such as temperature, pressure, cure time, and material pot and shelf life are critical to the success of making reliable electrical and mechanical interconnections at time zero and during the life cycle. At this stage, they are not ready to replace solder throughout the electronics industry due to questions that remain concerning the electrical and mechanical reliability of the adhesive joints. Their implementations are currently limited to low cost applications and specialty applications where solder cannot be used. Research and development in the past has evaluated both the electrical and mechanical reliability of these materials for specific electronic packaging processes [5-25]. However, adhesive technologies are still in developmental stages in comparison with the mature solder technology. There are many challenges still to be answered, and insights to be gained. No material and process has been found to provide a high junction/joint stability to gain widespread acceptance or universal applicability. Both mechanical and electrical degradation have been observed which vary with component/board metallizations, type of component, lead configurations, and severity of the test procedures. Common approaches in current research are that isotropic conductive adhesives are stencil printed or syringe dispensed to the printed circuit board (PCB) substrates, and the surface mount devices (SMD) are placed and the assemblies cured. Reliabilities during accelerated life times are tested after processing and assembly, and component lead and PCB metallizations are varied to get the optimum combination for the ECA application. Extensive process and reliability data are generated and published from these experiments. Sometimes there are different experimental results from different investigators even with the same adhesive, and this is mainly caused by the large process variables involved during the assembly and cure process. Therefore, basic and applied studies of the process, structural, and material characterizations are critical for the successful applications of the ECA technology.

2. FUNDAMENTALS OF ELECTRICALLY CONDUCTIVE ADHESIVES

Isotropically electrically conductive adhesives (ICAs) of resistivities less than $1 \times 10^{-2} \Omega\text{-cm}$ are formed from high resistivity polymers by mixing the polymer matrix with metal fillers. Two types of polymer conventionally used are thermoplastic and thermosetting, each with advantages and disadvantages. If a very large amount of filler is required for conduction, the polymer material's strength and elasticity may be degraded. It is therefore important to use the minimum quantity of conductive filler to achieve the

required degree of electrical performance. Percolation theory predicts a ‘critical’ filler concentration, at which a three-dimensional network is established and conductivity increases suddenly by several orders. Thereafter, conductivity changes slowly with increase in filler concentration [26-27]. The more recent commercial ICAs have volume resistivities around 10^{-4} Ω -cm, which is one order of magnitude higher than that of solders. Figure 1 shows the electrical resistivity variation with metal filler concentration in a nickel-sphere filled epoxy system [9], which displays the general percolation transition trend.

Filler particles may come in the form of spheres, fibers, flakes or granules, but the optimum geometry is that which provides minimum critical filler concentration for low resistance, the best contact between neighboring metallic particles, and strongest adhesion to the polymer, i.e. flakes, due to their high surface to volume and aspect (L/W) ratios [27]. Small particles are better than large, providing more particle to particle contact, greater conductivity and consistency of product [28].

ICAs are most typically filled with silver flakes. For lower cost adhesives, nickel filled systems offer lower conductivity, and the copper-filled systems may be unstable after exposure to high temperatures due to oxide growth on the particle surfaces [29].

ICA composites have some immediate advantages over solder as a means of electrically conducting attachment of chip or package lead to board pad. The first is a reduction in processing steps for surface mount device manufacture from nine nominal steps using solder to only five [30] (Figure 2). They also eliminate environmentally harmful Pb and flux removal solvents [31]. However, there is still a lot of research needed to be done to find the optimum PCB pad metallizations and component lead finishes for ICAs.

Small, thin, surface mount plastic packages experience exceptionally high stresses intensified by soldering at over 220°C. ICAs offer lower processing temperatures, reducing problems associated with solder joint fatigue and stress induced cracking, and decreasing stress on heat sensitive components. Typical ICAs cure at temperatures ranging from 80°C to 150°C, but some two-component ICAs can be cured at room temperature [32]. ICA coefficients of thermal expansion are more closely matched than solder's to that of epoxy-fiberglass, and offer a more compliant attachment, minimizing failures with high flexibility, creep resistance, and stress dampening [33].

ICA silver particles around 5-15 μ m in size facilitate finer line resolution than is possible with the 20-45 μ m metal particles found in solder pastes. Solder paste flow after printing also restricts the line resolution, whereas ICAs have little or no flow during cure [33].

While ICA costs are roughly three times those of solder, the difference is more than offset by reduced weight use, lower capital equipment cost, and reduced numbers of production steps required to complete a soldered assembly. And price reductions can be expected from the higher volume production levels necessary for wide-scale solder replacement. The epoxy technique offers quicker production throughput, due to shorter processing times and less handling of assemblies [33, 34, 37].

ICA drawbacks include moisture absorption and silver migration [30]. Non-selective wetting by currently available ICA materials cannot provide the same self-alignment feature as solder does. Rework is not as convenient as for solder, but is possible with various techniques. Another possible production problem (air entrapment) requires careful mixing/handling.

Anisotropically conductive adhesives (ACAs) provide both electrical and mechanical interconnections between electronic components and the supporting substrate. Conduction in these materials is restricted to the Z-axis, i.e. perpendicular to the plane of the substrate, while maintaining electrical insulation in the X-Y plane. ACAs can be a dispensable or stencil printable paste, or a pre-processed dry film. The last is termed an anisotropic conductive adhesive film (ACAF), also called Z-axis conductive film (ZAF). A typical bonding configuration is shown in Figure 3. The ACA provides a new material system for solder replacement as the interconnect for flip chip and surface mount technology besides ICAs. These ACAs offer numerous advantages in surface mount assembly, including low temperature process, fluxless bonding which eliminates the need for cleaning, lead-free formulations and low cost [36-37]. The anisotropic nature of these materials makes them excellent candidates for very fine pitch components [38]. For chip on glass applications, the high temperature reflow process of solder might destroy the liquid crystal and the glass. Consequently most current ACAF applications involve flat display interconnections for LCD's [39-43], but industry predicts that there will be more and more non-LCD applications in the future [44-47].

ACAs become conductive in one direction only after they have been processed under heat and pressure and with the alignment of the corresponding conduction pads. The requirements of the complicated processes and specific bonding equipment are the main drawbacks of these materials compared with solders and ICAs. However, these materials are applied over the entire area between the device and substrate, and mechanical strength of the bonding is enhanced by the larger bonding area.

In general, ACAFs are prepared by dispersing conductive particles randomly in an adhesive matrix at a concentration far below the percolation threshold. The particle density in the adhesive is controlled to provide enough particles on the device conduction pads to ensure reliable electrical contact; on the other hand, few enough particles are present to avoid pad connections in the X-Y plane [36, 48]. Spherical particles are used, which provide lower percolation probabilities than the same concentration of flakes (which are used in isotropic adhesives) [45]. The dispersion consistency is extremely important to prevent opens or shorts.

ACAFs can be based on a thermoplastic adhesive, a thermoset adhesive, or a combination of the two. The main advantage of thermoplastic adhesives is the relative ease of repair operations [49]. The curing reaction of thermoset adhesives is not reversible, so it is therefore hard to remove components and repair interconnections. The ability to maintain strong and robust adhesive bonds at high temperature is the main advantage of these materials. Because of the advantages and disadvantages to both thermoplastic and thermoset formulations, most manufacturers try to optimize performance by blending the two to

combine the application and rework ease of a thermoplastic adhesive with the performance characteristics of a thermoset adhesive.

The purpose of the conductive particles is to provide contact area as well as to overcome any nonplanarity of the substrates. In order to provide contact area, either the bond pads or the particle must deform. This localized deformation at the contact interface is also desirable in that it serves to disturb any thin oxide layers formed on the connector that would interfere with the connection [42].

The conductive particles may be solid metal, metal coated glass spheres or metal coated polymer spheres. Hard solid spheres may not deform to any great degree and only touch at the points of tangency. Metal coated polymer composite particles are flattened during bonding. This flattening increases the effective surface area of the particle. The ideal metallurgy should also be ductile, and resistant to corrosion or oxidation. Silver offers moderate cost, high electrical conductivity, high current carrying ability, and low chemical reactivity, but problems with electromigration may occur. Gold is the ideal material, with high cost for large-volume productions. Plated particles may offer the best combination of properties at moderate cost [36].

For fine pitch applications, the conductor pad sizes and conductor spacings are decreasing. As a result, it becomes more difficult to maintain electrical X-Y insulation with a specific ACAF. The maximum conductive particle size for the adhesives affects the minimum conductor spacing. The reduced conductor widths cause difficulties to accommodate lateral misregistration between pad and conductor and decrease the number of particles in the interconnection as well. The particle loading density in the film determines the number of conduction particles in the pad interconnection. The pad heights and particle size, together with any compliance in substrate or particles, help decide the ZAF thickness. Because oxides on conductors can interfere with electrical contact, the conduction pad is usually electroplated with oxide resistant coatings, such as gold, to minimize surface oxides before the bonding operation.

Significant process parameters for ACAF bonding are temperature, load, tacking time, and cure time. The substrate pads are preheated to a temperature below the ACAF's curing temperature, but high enough to partially soften the film so that it has the ability to flow and fill void volume. The bonding load should be high enough to allow the conductive spheres to make good physical contacts between component and substrate conductors; but not high enough to crack the component or the particles in the ACAF. Finally, the tacking time should be sufficient to produce a good initial cure so that the component does not shift during the final cure process [36].

3. MATERIAL AND STRUCTURAL PROPERTIES OF ECAS

3.1 Polymer Matrix and Metal Fillers

There are two types of electrically conductive polymers: intrinsically conductive and metal-filled polymers. Although intrinsically conductive polymers based on polyacetylene- and polyphenylene-

compounds have potential to be candidate materials [50], problems still remain with processability, mechanical properties, and stability. They have relatively higher resistivity ranges. Polyacetylene based materials usually have a resistivity range from 10^{-3} to 10^4 Ω -cm, and polyphenylene groups have a resistivity range from 2×10^{-3} to 10^3 Ω -cm. Metal filled polymer composites are the subject of this paper. They were first patented as electrical conductive adhesives in the 1950's [51-52]. For electronic bonding applications, the metal filled composites should be one-component pastes capable of curing under a variety of manufacturing circumstances in 1-2 minutes at 150°C ideally. Finely divided gold, silver, and copper appear frequently in conductive adhesives for bonding to electronic components. Epoxy resin systems are generally used in adhesive formulations. Recent patents [53-54] have given empirical data for establishing specific blends of two or more particles sizes for optimum results: good adhesion and high electrical conductivity. For a random distribution, 35-40 vol.% metal will effect a large drop in electrical resistivity. Silver, gold, palladium, copper, nickel, and carbon fillers have produced adhesives with typical properties as shown in Table 1 [55]. The volume resistivity and lap shear strength change as a function of silver weight percent from 10^{14} Ω -cm and 20.0 MPa at 0% loading down to 640-0.023 Ω -cm and 11.7-10.2 MPa at 70-75% loading, respectively [56].

Two types of polymers can be used as the adhesive matrix: thermosets and thermoplastics. Thermoset materials do not flow at high temperatures due to the interlocked structure after cure. They are materials that are initially monomers or prepolymers, which polymerize during process (curing). Three-dimensional cross-linked molecular structures are formed after curing as a result of the physical links or branch points that tie the polymer chains together. The relative number of branch points is called the cross-link density, and materials with high cross-link densities tend to be stiffer but more brittle. The degree of chemical conversion at which the cross-link structure first forms is called the gel point and the phenomenon is know as gelation [57]. The material cannot flow as a true liquid after gelation. Viscosity depends upon molecular weight and increases during the polymerization reaction, and effectively goes to infinity at the gel point. Thermoplastic materials consist of long polymer chains that have few side branches, and the chains are not physically linked. They can flow at a high temperature since they do not process the cross-link network structures that prevent flow of thermoset polymers. The properties of these materials depend on the structure of the backbone chain. High temperature engineering thermoplastics have been introduced that rival the performance of thermoset. They can withstand the temperatures of soldering operations without physical deformation and flow because they possess exceptionally rigid chain structures that resist large scale molecular motion until very high temperatures. They are amorphous glasses, such as polyetherimide and polyethersulfone.

Thermoset epoxy resins are the most common polymer matrices used for conductive adhesives. The epoxies based on the diglycidyl ether of bisphenol-A (DGEBA), which is synthesized by reacting bisphenol A and epichlorohydrin, are the common materials for liquid adhesives. The chemical structure, reaction, and typical conditions for the preparation of DGEBA are shown in Figure 4. DGEBA epoxy has

an epoxide functionality of 2 for its average molecular weight of 380. Modification to the base resin usually consists of varying the epoxy equivalent weight or increasing the viscosity. The main ingredients of an epoxy system consist of the resin and the hardener(s). Sometimes an accelerator is added to facilitate curing, leading to the desired reaction products at desired temperatures. Notice the bisphenol A resin contains active three-member rings. Ring opening reactions with hardeners produce highly cross-linked structures in a curing process. Hundreds of compounds (hardeners) have been found effective, resulting in different rates of curing, different reaction products and product properties. They can be grouped into three major categories: catalytic (Lewis acids and bases), amines (aliphatic and aromatic), and anhydrides [58]. In the case of anhydrides, tertiary amine accelerators, or catalysts, are added to promote curing. Aliphatic amines generally cure rapidly and can react at low temperatures. Elevated temperature cures are often required of aromatic amines, as the functional groups are tied to more rigid moieties. Epoxy curing involves sequential opening of the three-member rings. Each can form two chemical bonds with hardeners. Therefore, the original DGEBA molecule theoretically serves as a cross-linking point, connecting four branches. The viscosity of the resin first decreases as temperature increases. Meanwhile, as the extent of cure reaction increases, the polymeric structure becomes cross-linked. At the gel point, the increased cross-linking causes the material viscosity to rise greatly and further flow is prohibited. As a consequence, the system cures and stiffens, and the material is no longer processable.

The viscosity of the epoxy matrix affects settling of the metal particles during cure. Some thixotropic agents can be added in to increase the viscosity of the system and minimize settling of the particles [59].

The metal filler usually chosen is metal powder of size less than 20 μm in diameter. Narrow particle size distributions require greater concentrations of particles to exceed the percolation threshold for electrical conduction than broad size distributions [59]. The importance of the size distribution data is related not only to the breadth of particle size but also to the mean particle diameter.

Grinding and breaking of the metals takes place in combinations of ball mills, impact mills, and gyratory mills. Screening and air classification will separate the particle sizes. Minute amounts of contaminants from the grinding machines must be expected.

Several factors influence the use of metal fillers. Silver is the most conductive of the frequently used metals, although it is also expensive. Some researchers have explored the use of copper or other low-cost materials instead of silver, but their results have largely proved unsatisfactory. One problem is that oxides and other films on the particles' surface are non-conductors and therefore dramatically change the electrical properties of the composites. This effect is most significant with the smallest particles. Therefore, only metals with high corrosion resistance, such as silver or gold, can be used. Nickel is also of interest because of its low rate of oxidation. Silver coated plastics or glass particles can be used as a metal filler [59], but the mixing processes have been known to fragment the fragile silver coating, reducing metal-to-metal contacts. Electrical properties of the composites made from the coated particles are very sensitive to processing conditions. Very thin silver coated layers are unsuitable.

The properties of the metal filled polymers are affected not only by the material properties of the individual phases and percentage of filler, but also by the particle shape, size, distribution, orientation, state of adhesion between the filler and matrix, and the amount of particle agglomeration. The tensile modulus of the composites can be increased as a result of the metal fillers. Generally, as the filler loading increases, the composite modulus increases; the ultimate strain decreases; and the ultimate strength increases. However, for filler concentration greater than the percolation threshold, too much metal filler could deteriorate the mechanical properties. This is explained by the mismatch in the coefficient of thermal expansion (CTE) of the filler and matrix and by the occurrence of a stress concentration zones around the filler particles. Stress concentration at the filler boundaries can cause premature failure in filled polymeric materials. Fillers often decrease energy dissipation peaks; they do not shift the glass transition temperatures, but broaden the region at high filler concentrations.

3.2 Structure of the Composites

Two main approaches have been employed to process the metal-filled polymers: dispersions of metal powders in thermosetting or thermoplastic resins, and mixtures of metal and polymer powders compacted by cold or hot pressing. The resultant structures of composites are either 'random' or 'segregated' distributions [27, 60]. By varying the metal filler volume percentage and metal particle and polymer particle size ratio, four basic microstructures can be generated as shown in Figure 5: (A) random and isolated, (B) random but continuous, (C) segregated but isolated, and (D) segregated and continuous. The term 'segregated' denotes that microscopic dispersed particles are being restricted into the boundaries of much larger primary particles. From the macroscopic point of view this distribution is random too. In the random packing methods (Figures 5(a) and (b)), continuity relies strictly on the possible contact between contiguous sites as explained by percolation theory [61-62]. This applies to the metal filled resin systems and for the similar particle size and shape metal/polymer compacted mixture systems. Particles may occupy any sites in the resin matrix, or either a metal or polymer site in the compacted systems. In contrast, in the segregated distribution, the chance of forming a conduction network is increased by restricting the volume which any metal particle can occupy from the entire field of view to only the interproximal contacts or the intersites of the polymer particles. The metallic particles are thereby segregated into a reticulated structure, which is most likely to occur in compacted metal and polymer powder systems processed by powder metallurgy compression molding.

Here 'random' and 'segregated' describe the geometry which results in terms of the polymer and metal particle size ratio R_p/R_m ; (R_p is the radius of polymer particles, and R_m is the radius of metal particles.) whereas 'isolated' and 'continuous' represent the continuity of the dispersed powder phase in terms of V_c , the critical volume percentage of dispersed material required for continuity. As a result of the segregated geometric arrangement, the loading percentage required to achieve continuity is dramatically reduced. The electrical resistivity shows a transition from a non-conductor to a conductor at the critical

volume loading V_c equal to 35-37% in a random composite structure with silver-bakelite mixtures ($R_p/R_m \approx 2$) [63]. On the other hand, for the segregated composites with polyvinyl chloride and nickel or copper mixtures ($R_p/R_m = 30$), V_c could be reduced to 6% [64]. Figure 6(a) illustrates electrical resistivity versus filler percentage for both segregated and random structures [64]; Figure 6(b) shows the different microstructure and geometry in these two composites which have similar conductivities [27, 63]. Notice here the segregated structures are for the special case of dry-blend powders being compacted into a form by pressure and subsequently fused by sintering in place at an elevated temperature. This type of processing can be directly compared to introducing a random mixture of particles into a resin matrix followed by subsequent solidification. Another way to form a segregated metal network in a plastic matrix is to deposit a continuous metal coating on plastic particles. Techniques which rely on segregating the conductive medium into a continuous network achieve the goal of reducing the volume concentration of conductor needed without compromising the mechanical properties of the composites. Unfortunately, the techniques used to achieve the segregated network involve special processing methods which do not lend themselves to high volume production.

The main factors controlling the properties of the metal-filled polymer systems are particle size ratios, particle shape, polymer viscosity, and oxide layer thickness on the metal particles. The relative particle size ratio plays an important role in determining continuity. Figure 7 [60] shows the inverse character of this relationship based on both the theoretical and practical minimum mean number of contacts per metal particles. This spherical model gives the extent of particle size ratio variation on continuity from the segregated mixtures with high particle size ratios and random mixtures with low particle size ratios. For the metal and polymer particle mixture systems, the volume/surface area occupied by the polymeric phase and the surface area/volume possessed by the metallic phase should be maximized. Spherical polymeric particles would minimize the potential contact surface area while maximizing the volume displaced; and flake-shape, needlelike, or fibrous metallic particles would increase the surface/volume ratio. The critical volume loading for continuity decreases as the aspect ratio of the metal filler increases. Therefore, excessive shear of the metal particles in the mixing processes should be avoided to prevent the increase of V_c by the decreased aspect ratio (L/W). The early set viscosity of the pre-polymers is critical for the metal filled ester or epoxide composites. If a metal is too dense relative to the fluid medium, it will result in rapid and differential sedimentation. The metal particles must remain in suspension until the polymerization reaction can sufficiently increase the polymer viscosity. The oxide layers naturally formed on the metal filler surface will significantly degrade the electrical and thermal conductivity even if there are no extraneous contaminants on the metal surfaces. The conduction through the thin insulating layer is controlled by electron tunneling processes, or by the degenerate semiconductor conduction of some metal oxides.

Silver flakes are randomly distributed in the polymer mixture for electrically conductive adhesive systems. The commercial ICAs all have randomly distributed structures as described above. Silver volume percentage is around 25-35%. The segregate distributions normally occur in the metal/polymer

powder particle compacted systems, and the polymer particles need to retain their geometric identity after compressing to segregate the metal particles. Although this seems inapplicable in the ICA systems, the low metal filler volume percentage (6%) required to achieve conduction in the segregated structure is very attractive. Spherical glass and silica fillers have been used in encapsulant materials to reduce the coefficient of thermal expansion (CTE) of the epoxy matrix to match the CTE of silicon die and PCBs. By the combination of silica and metal fillers in a resin system, the CTE of the conductive adhesive as well as the metal filler concentration can be reduced. This will increase the mechanical performance and reduce the cost of ICAs. Similar structures with tin spheres and silver flake fillers have been found in commercial conductive adhesives.

4. ELECTRICAL CONDUCTION MECHANISMS AND THEORY

The addition of a conductor to an insulator affects the electrical properties of the composite according to the degree of filling and proximity of conductive particles to other conductive particles. Three situations are possible: no contact between conductive particles, close proximity, and physical contact [65]. When the conductive particles are isolated, the conductivity of the composite is changed only slightly. The composite remains an insulator, although its dielectric properties may change significantly [66]. When the conductive particles are in close proximity, electrons can penetrate the thin gap (<10 nm) between the particles. The process of electron transport across an insulator gap is referred to as tunneling. The metal-insulator-metal structure in the metal filler contact area is our main interest. Considerable work has been done on comparable electrical contact behavior [67]. The tunneling effect is extremely sensitive to the gap width (thickness of the film) and height of the potential barrier to be penetrated, and these quantities are never exactly known, so the calculations are typically and necessarily made with approximations and simplifying assumptions about the applied voltage, the temperature (zero or finite), and the shape of the potential barrier between the conductors. The exponential dependence of the tunneling resistance on the gap width and the insulator potential barrier height shows the importance of maintaining close proximity between adjacent conductive particles, and of the insulator film type between the metal fillers.

Another condition is that the metal fillers physically contact each other to form a continuous network throughout the composite. The composite conducts through the particle network by the conduction mechanism of the metal particles (band-type conduction). Band and tunneling conduction can be differentiated by the AC and DC behavior of the composites [68]. A composite which conducts by a tunneling mechanism will exhibit a higher AC conductivity than DC conductivity.

In highly loaded composites actual touching does occur [65], where the current-voltage characteristics of such composites are linear (ohmic). The non-ohmic behavior observed in other composites is due to the electron tunneling mechanism. However, claims refuting the above statement [69] show that even composites with resistivities as high as $10^7 \Omega\text{-cm}$ exhibit linear voltage-current

characteristics except at the electrodes. The total non-ohmic behavior of composites is claimed to be caused by extended space charge distributions near the electrodes. These space charge distributions are generated by local polarization of the matrix material [69].

Actual physical metallic contacts or tunneling conduction between metal particles possibly co-exist in the metal-filled polymer system, depending on filler loading, processing conditions, polymer-metal wettability, and temperature. An organic lubrication layer (fatty acids) is usually applied to the silver surface during manufacture of the silver flakes to avoid flake aggregation when milling. Residual acid layers might still remain on the silver flakes in the conductive adhesives. Possible chemi-sorbed oxide or sulfide layers and polymer layers wetted on the metal particles may also exist. These film layers will contribute to the tunneling conduction especially before the cure of the adhesive matrix.

Isotropically conductive adhesives (ICAs) are typically formed by loading silver flakes into an adhesive matrix such that the percolation threshold is exceeded. Electrical connection is provided by the continuous network of metal particles. The discontinuous electrical property change of the composite is normally explained in terms of the metal filler concentrations by percolation theory. The point where the electrical resistivity decreases dramatically is called the percolation threshold. Above the percolation threshold concentration, networks of chains of conductive particles are formed throughout the composite [61], although this network does not necessarily imply physical contact between adjacent particles. The percolation model is normally analyzed statistically by Monte Carlo techniques. This approach has not been completely successful in predicting the performance of real composites.

The probability of a continuous network being formed by filler particles in a matrix is related to the statistical average number of contacts each particle makes with neighboring particles and the maximum number of contacts per particle that are possible [70]. At the critical point of network formation, $C_p = P_c Z$, where C_p is the critical number of contacts per particle, P_c is the critical probability of network formation, and Z is the maximum number of possible contacts, or coordination number. Values of Z for several packaging arrangements of spherical particles are listed in Table 2 [63, 70, 71]. From these values of P_c and Z , the critical average number of contacts per particle for network formation, C_p , has been calculated as 1.5 for each case investigated. One of the disadvantages of the percolation model is that it requires a specified lattice from which the statistical analysis of P_c is made. In a truly random situation a lattice cannot be specified. Guland [63] showed experimentally that the value of C_p for a random dispersion of spheres in a matrix is 1.5. For spherical particles, C_p is apparently a constant.

The volume percentage of metal filler in a matrix is dependent on the average number of contacts per filler particle ($C_p = f(P_c)$). The linear relationship was assumed [72]: $f(P) = PZ / P_m$, where P_m is the maximum packing fraction of the filler in the matrix. Combining the above two equations, $P_c = C_p P_m / Z$. For a random mixture of spheres C_p equals 1.5, $Z = 6$, and $P_m = 0.637$. Therefore, P_c is 0.159. This value is much lower than the experimental values. Jantzen [71] proposed $f(P) = \{ZP/(1-P)\} \{(1-P_m)/P_m\}$. At the critical loading for network formation: $P_c = \{1 + (Z/C_p) (1-P_m)/P_m\}^{-1}$. For the random

sphere case as above, P_c is 0.305. This represents the point at which network formation begins and the sharp drop in resistivity starts. These equations do not adequately account for preparation technique, particle size distribution, or particle-particle interaction effects.

Predictions for flakes, fibers, and other irregular shapes are even less well developed. For irregular fillers with a completely random distributions, the critical value of P_c is the same as for spheres [73].

Effective conductivity σ_e of composites which have different filler shapes and geometry have been developed recently, such as two-phase materials with long parallel cylinder fills [74]; suspension of hard sphere systems [75]; hard-sphere dispersion systems [76]; and aggregates of anisotropic grains [77].

The calculation of the effective electrical conductivity of two-phase heterogeneous material from its microscopic structure is a problem which has received lots of attention. For arbitrary phase properties and volume fractions, theoretical techniques basically fall into two categories: effective-medium approximations and rigorous bounding techniques [78]. Comparatively, there is a depth of work on the determination of effective properties from computer simulations, especially for continuum models (e.g. distributions of particles in a matrix).

Conventional approaches are to obtain σ_e by simulation, solving the local governing differential equations for the fields (electrical, temperature, and concentration, etc.), subject to the appropriate boundary conditions at the multiphase interface of the computer-generated random heterogeneous system, using numerical procedures such as finite differences, finite elements, or boundary elements. The solutions obtained for a sufficiently large number of such random configurations are then collected to yield the configurationally average fields and hence the effective properties [75].

A number of methods have been employed to predict the effective conductivity σ_e of disordered two phase materials. Perturbation expansions [79] for σ_e in the terms of the parameter $(\sigma_2 - \sigma_1) / \sigma_1$ have been used by several investigators. Another approach which has received considerable attention is the method of bounds [80]. The computation of upper and lower bounds for σ_e requires microstructural information in the form of two- and three-point correlation functions. The effective conductivity has also been calculated by numerically solving the many-particle conduction problem directly. These calculations are useful for testing the validity and merits of various approximate analytic methods: they are, however, computationally time consuming.

Commercial ICAs contain silver flake volume concentrations greater than the percolation threshold in order to achieve good electrical conduction reliably. Percolation theory is useful to explain the macroscopic conduction in these materials. More detailed conduction models must include processing and geometric effects during the adhesive processing and cannot be developed from percolation theory alone. After mixing, conductive adhesives do not always establish electrical conduction immediately, and some such as silver filled epoxy systems, may have very high resistivities before cure [81]. Electrical conductivity develops only after cure and the final resistance is dependent on the cure process. It is

important to understand the basic microstructural development of the conduction network during the processing of the adhesives. Not much work has been focused on the structure and process related conduction models, or on the microscopic conduction mechanisms between the silver flakes of conductive adhesives. A better understanding of the conduction mechanisms in the conductive adhesive systems is necessary. A conduction model combining the microscopic contact effects between flakes and macroscopic percolation conduction, including the silver filler size distributions and orientation effects, has been developed [82-84].

4. MAIN ISSUES OF ECA APPLICATIONS

Although electrically conductive adhesives have potential usage and various advantages over solder for SMT and microelectronics applications, issues and problems still remain to be solved in order to successfully implement ECAs for solder replacement in electronics assemblies.

SMT requires short process times, high yield, high component availability, reliable joints for different components, visual inspection of joints, and capability of repair [85]. ECAs will not be a drop-in replacement for solder in the existing surface mount production lines. First, it will not be cost effective to do so. Special component lead plating and board conduction pad metallizations need to be optimized for conductive adhesives. Standard materials, components and assembly equipment for specific applications need to be developed combining the material vendors', research organizations', and application companies' efforts together. Mechanical bonding strength and electrical conductivity cannot be compromised for the new material development. Fine pitch and thinner lead trends have improved both the pick and placement machine accuracy and the stencil printing process (the laser etched or electroplated stencils and precise stencil printing machine). ECAs have more rigid process requirements for positioning due to their non-selective wetting and lack of self- alignment. Currently major concerns for using ECAs for SMT are the limited availability of components and substrates designed for adhesives, and the lack of methods to predict life-time reliabilities and their relationship to the accelerated life time tests performed as solder joints. Different electrical and mechanical failure mechanisms require one to monitor these properties separately during life-time tests. There are difficulties to inspect the adhesive joints and judge the quality of the joints from visual and x-ray inspection methods, which work for solder joints perfectly. Repairability and reworkability of adhesive joints need to be investigated and improved.

Adhesion strength between the component leads, adhesives, and board terminal metallizations is one of the most critical properties for high volume SMT applications. Large quad flat package (QFP) and plastic leaded chip carrier (PLCC) packages bonded on PCBs experience failure when drop (mechanical shock), shearing, and bending tests are performed on the entire assembly [86], due to limited contact area (ICAs filled with 30% silver by volume reduces the actual adhesive bonding area further) between the component leads, adhesives, and the PCB conduct pads. Electrical conductance of the adhesive joints degrades under humidity exposure [87]. Interfacial and contact resistance increases especially on non-

noble lead and board pad finishes under accelerated life time tests. Assembly and cure processes of ECAs are also critical for a reliable adhesive joint. [84, 87]. Stencil printing parameters should be optimized relating to the specific ICA viscosity. Cure processes need to be studied to ensure the complete cure of the adhesive joints. New snap cure ICAs are developed to match the cycle time of solder reflow, and the manufacturers' recommended cure schedules for these materials are 3-5 min. at 150°C. The actual cure time needed is still longer than that of solder reflow. ECAs also have adhesive shelf-life and pot-life limitations, and freezer storage requirements for the one-component silver filled epoxies. Some manufacturing issues associated with the adhesives have been investigated [88]. Adhesives face bleed and slump problems when dispensing or stencil printing if the processing is not optimized, and overall the process windows are narrow, which may be overcome by the newly developed materials with promising rheological properties.

As silver is the most common metal filler used in the conductive adhesives, potential problems associated with silver migration in hazardous environments have been investigated [11, 14, 19]. Silver migration is a process by which silver is transported as ions under the influence of an electric field and is re-deposited as metal on the other side across an adjacent insulator. Electrical bias voltage and moisture presence in the system are major conditions for silver migration to occur. Water (humidity) is necessary for the effect. Silver ions are dissolved and move in the water films [67]. Migration will increase with the increased voltage across the insulators. A 'threshold voltage' for specific test conditions would be expected, below which silver migration will not occur.

Test circuits with parallel conductive lines with spacing from 0.8 mm down to 0.1 mm were biased with 5 V and 12 V in 85°C/85% RH for 168 hours. No migration and indication of migration could be identified under microscopic investigation. Insulation resistance measurements support the visual test [11]. Surface insulation resistances (SIR) were monitored between the 0.65 mm pitch QFP pads under 5 V bias in 60°C/90% RH for 1000 hours continuously [14]. No evidence of silver electromigration was visible after the humidity test. Alloys containing palladium and platinum for preventing silver migration are used in most thick film inks, but pure silver is used in the conductive adhesives. Authors [11,14] claimed that silver filled epoxies differ substantially in composition compared to silver inks used in the hybrid industry. In the adhesives, the silver particles are wetted and surrounded by and encapsulated in an epoxy resin, which upon curing, flows and covers the silver flake before it sets to a hard impenetrable shield. Extensive work on silver migration has been done for ACAs for fine pitch applications [19]. Accelerated temperature, humidity, and bias (THB) tests were performed at 85°C/85% RH with voltage biases (10 V, 50 V, and 100 V) across 0.1 mm spaced interdigitated conductors. The test results [19] showed significant metal migrations, and the enhanced electrical field stresses (10^2 to 10^4 V/mm) were proposed as the driving force for failure. Metallic silver dendrites grew between 200 to 1000 hours. Under electric field stress, silver atoms from particles attached to the anode easily dissociated into silver ions, and the Ag^+ ions then migrated to the cathode and deposited to form the roots of the silver dendritic tree. The silver ions also

reacted with $(OH)^-$ and form the dark brownish silver oxides or hydroxide. Corrosion was initiated at a few spots on the anode and one spot at the cathode. At the end of silver migration, a silver dendritic tree had formed with the root anchored at the cathode and several branches linking the anode. Notice that the materials of interest were ACAFs for fine pitch flip chip application under severe THB test conditions. The loading density for the ACAF also contributes to the migration, because silver particles exist between the conductors. Compared with the cases discussed earlier of ICAs for SMT applications, the test conditions and the spacings between the electrodes are different. In summary, the silver migration issue is dependent on the application condition, adhesive matrix, and type of conductive adhesives (e.g. ICAs or ACAs). It is probably less important with the coarse pitch SMT components, but it needs to be considered especially for very fine pitch direct chip on board application.

5. CONCLUSION.

This paper has been prepared with the specific purpose of providing general, and to some degree historical, background to the other ECA papers also contained in this issue of the *International Journal of Microelectronics Packaging*. These provide a good mix of electrical, mechanical, and thermal properties and hence also problems, and in this sense are representative of the field. They have all been drawn from the recent *Second International Conference on Adhesive Joining and Coating Technology in Electronics Manufacturing* [89].

One of the essential elements of an introductory review is a bibliography to provide an introduction to the literature. The citations above can be supplemented in specific areas. There is a growing emphasis on the role of processing parameters [90] on eventual electronic properties by the development of microstructure under cure [91-93]. For those wishing to pursue conduction models further, the literature is extensive, but the primary issue of inter-particulate conduction is unresolved [94-109]. ACA conduction modeling is rather more straight-forward [110-114]. Finally, it is worth noting that very high conductivity ICAs are appearing at the laboratory development stage [115, 116].

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Captions to figures and tables

Figure 1: Resistivity versus filler volume concentration [9].

Figure 2: Production step comparison of ICAs versus solder pastes in SMT [30].

Figure 3: Illustration of the ZAF interconnection.

Figure 4: The typical reaction pathway and condition for the preparation of DGEBA [58]. (a) Synthesis of Diglycidyl Ether of Bisphenol A. (b) Chemical structure of DGEBA.

Figure 5: Schematic illustration of the influence of particle size ratio R_p/R_m and volume percentage on the microstructure of aggregates [60].

Figure 6: (a) Influence of the filler content on electrical resistivity of a random and a segregated particulate distribution [64]. (b) Micrographs of the actual geometries of the random (\blacklozenge) [63] and segregated (\bigcirc) [27] distributions.

Figure 7: Theoretical (----) and practical (——) minimum requirements for continuity [27] (The hatch region represents the zone of continuity.).

Table 1: Typical properties of metal-filled adhesives [55].

Table 2: Critical contacts per particle determined from bond percolation theory.

TABLES

Table 1: Typical properties of metal-filled adhesives [55].

Properties	Lap shear strength (MPa)	Specific gravity (g/cm^3)	Thermal conductivity (W/m-K)	Thermal expansion (ppm/ $^{\circ}\text{C}$)	Volume resistivity ($\Omega\text{-cm}$)
Value	5.49-14.9	2.9-3.4	1.44-7.21	45-55 ($<T_g$)	4×10^{-4} - 5×10^{-2}

Table 2: Critical contacts per particle determined from bond percolation theory.

Lattice Type	Z	P_m	P_c	C_p
Face-centered cubic	12	0.74	0.125	1.50
Body-centered cubic	8	0.68	0.183	1.46
Simple cubic	6	0.52	0.254	1.52
Diamond	4	0.34	0.389	1.56

Random	6	0.637	----	----
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FIGURES

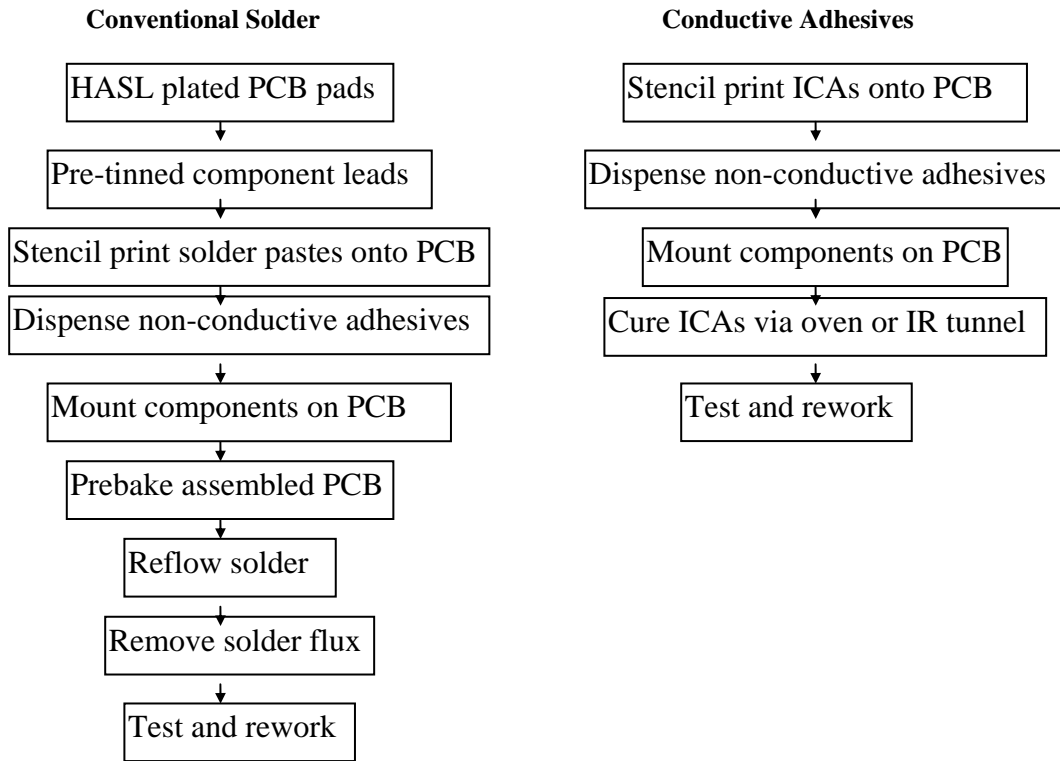


Figure 2: Production step comparison of ICAs versus solder pastes in SMT [30].

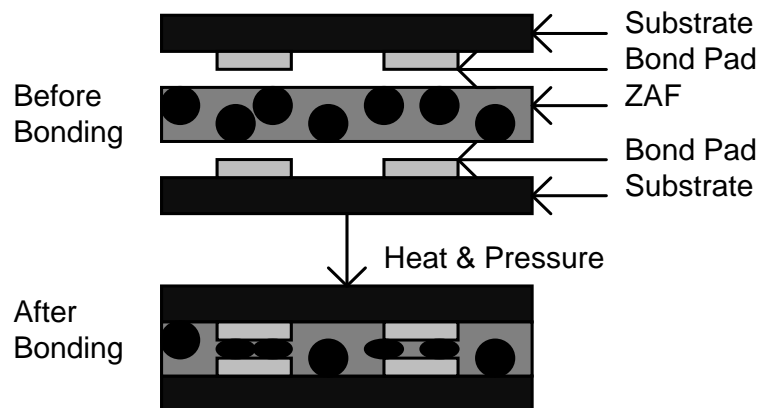


Figure 3: Illustration of the ZAF interconnection.