

ELECTRICAL CONDUCTION MODELS FOR ISOTROPICALLY CONDUCTIVE ADHESIVES

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An electrical conduction model was developed by understanding the microscopic conduction between the Ag flake particles and macroscale conduction explained by the percolation theory. The contact resistance between Ag flakes is mainly contributed by constriction resistance and tunneling resistance. The constriction resistance is controlled by the actual contact spot area (metallic contact), which is dependent on the contact force between flakes. The tunneling resistance is dependent on a barrier film thickness. Large contact pressures may cause a break of the tarnish or organic films on the flakes and induce new metallic contacts. The material hardness, pressure between particles and particle contact sizes are important parameters controlling the contact resistance.

Computer simulations were performed to predict the percolation threshold and particle size effects. Resistivities of the composites were calculated by resistor network simulations incorporating contact resistance and particle size distribution effects. The model predicts that the resistivity decrease with the stress developed during the cure process of the conductive adhesives and with broad particle size distributions.

1. Introduction

Isotropically conductive adhesives (ICAs) are typically formed by loading Ag 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 in terms of the metal filler concentrations is normally explained by percolation theory. The point where the electrical resistivity decreases dramatically is called the percolation threshold. Above the percolation threshold concentration P_c , networks of chains of conductive particles are formed throughout the composite.¹ Commercial ICAs contain Ag 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 Ag filled epoxy systems, may have very high resistivities before cure.² Electrical conductivity develops only after cure and the final resistance is dependent on the cure process. It is important to understand the basic microstructure development of the conduction network during the processing of the adhesives. Little work has been focused on the structure and process related conduction models, or on the microscopic conduction mechanisms between the Ag flakes of conductive adhesives. A better understanding of the conduction mechanisms in the conductive adhesive systems is necessary.

The purpose of this conduction model study is to provide guidelines for design and process rules for ICA materials by relating the physical and processing properties of the material to the electrical performance of adhesive joints, and to get a better fundamental understanding of the composite system. The

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ICA systems studied consist of Ag flakes in an epoxy matrix.

An organic lubrication layer (fatty acids) is usually applied to the Ag surface during manufacture of the Ag flakes to avoid flake aggregation when milling. Residual acid layers might still remain on the Ag flakes in the conductive adhesives. Transmission electron microscopy (TEM) work³ has been done to identify the flake-to-flake contact areas, flake size distributions, and orientations in the adhesive joints. Oxidation on the flakes has been investigated. Preliminary results show that no Ag oxide is formed on the flake surfaces. Auger analysis was used to investigate the surface elements on the Ag flakes.

Computer simulations were used to generate random or partially oriented structures based on experimental observations of the adhesive joints and particulate geometries. Percolation conduction networks were developed and the computer identified the macroscopic scale contact types based on simplifying assumptions. Microscopic scale contact effects (such as pressure dependent contact resistance between flakes, tunnel conduction through a polymer insulation films or other absorbed films, broken contacts, or connections caused by coefficient of thermal expansion (CTE) mismatch during temperature changes) were derived more analytically, based on similar assumptions. The shrinkage during epoxy cure can be included in the computer model by changing parameters of the dimensional effects. Thermal and residual stress development during cure is considered in the microscopic contact effects. Computer models combining the microscopic analytical contact resistance model with the macroscopic Ag flake percolation network, and with geometry and orientation effects included, give the resistance range of adhesives based on some simplified assumptions.

2. Theoretical and Numerical Model Approaches

Microscopic investigation of the materials shows that all dimensions of the conducting regions are much greater than the room temperature mean free paths of conduction electrons in Ag. If all dimensions of the conducting region are larger than the electron mean free paths, we can ignore the effect of finite flake dimensions.⁴ The random distribution of the Ag flakes in the epoxy matrix modifies the conductivity of a sample or joint in several ways. Isolated conducting regions cannot contribute to transport, so that

only the connected part of the conducting material, Ag, (a volume fraction about 25–35% for commercial materials,) is of interest. (The Ag volume percentage is calculated from the manufacturer's specified Ag weight percentage and the constituents' densities.) The optimal arrangement would be if the connected regions were arranged in regular layers parallel to the applied field. This yields an upper bound ratio of the conductivity of the composite to the bulk conductivity of the metallic part being equal to P_c . But in an actual composite, this bound is far from reality, and many percolation connection clusters consist of useless dead ends, with current flowing predominantly through a fraction of the sample which is significantly less than P_c . Calculating the conductivity caused by a continuous percolation cluster at $P > P_c$ requires a knowledge of the internal structure of large clusters.⁵ Figure 1 shows an illustration of a percolation cluster formed between two contact electrodes. In this cluster, the ellipsoidal particles represent the Ag flakes (only two orientations) in the epoxy matrix. Here we can see that many flakes will not carry current, and these flakes on the cluster are called "dangling" or "dead ends". These dead ends contribute to the percolation cluster density but not to its conductivity, so the conductivity is not proportional to cluster density (filler density). When all the "dead end" flakes are removed, only the "backbone" is left for conduction. The 'backbone' consists of two types of connection. One is a single connected path, and removal any one of these connections will break the whole connection between the electrodes. The other is the multi-connection parallel paths in the "backbone", and removal of one of these will still allow the current to flow through other connection paths. For the illustration example in Fig. 1, the percolation

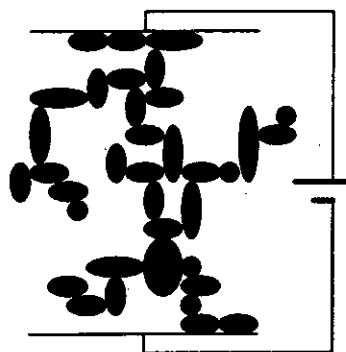


Fig. 1. Illustration of an Ag flake cluster between electrodes.

cluster consists of total of 36 flakes, with 17 flakes contributing to the "backbone"; 8 of these are critical single contacts. There are lots of non-percolation clusters existing in the material as well, so the total Ag flake volume percentage is much larger than the Ag flake percentage which contributes to the actual critical conduction paths. Figure 1: Illustration of an Ag flake cluster between electrodes.

To calculate the resistance of the percolation cluster, also called a "random resistor network", Kirchhoff's Rules state that for every loop of conductors the sum of the voltages is zero, and that for every site the sum of the current flowing into it is also zero. The resulting system of coupled linear equations for the voltages at every site can be written as

$$I_i = \sum_j (V_j - V_i) \sigma_{ij},$$

where V_i is the voltage at site i , I_i is the external current going into the site i (it is nonzero only at the external terminals, and zero on all other sites) and σ_{ij} is the conductance of the connection between the nearest neighbor sites i and j .

The computer simulation program developed first generates the random occupied sites for the Ag flakes. The program then counts and identifies the percolation clusters, and gives the common cluster identification number and calculates the number of flakes in these particular sites. Each cluster is checked to see if there is connection between the top and bottom electrodes. If any two sites at opposite electrodes have the same cluster identification number, the sample is determined to percolate in the direction perpendicular to the electrodes. These properties are generated according to the specified filler volume percentage. The resistor networks are established after the continuous percolation clusters are identified. The resistivity of the system is calculated by a program which solves the resistor network equations by iteration and finite difference methods.

The above percolation treatment of the Ag filled conductive epoxy systems can only explain the macroscopic conduction. The microscopic level conduction processes between adjacent Ag flakes are more complicated and are related to the processing and constituents of the composites. The conduction within the composite is controlled principally by ohmic conduction within the Ag flakes (R_{Ag}), by constriction resistance at the contact spots (R_c), and by quantum mechanical tunneling between the particles (R_t).⁶ The internal stress built up during the cure of the epoxy system will also contribute to the

conduction. The thermal expansion difference between the filler and epoxy resin will change the relative magnitude of the various processes discussed above.

The continuous Ag flake network past the percolation threshold consists of the "backbone" chains for conduction.⁷ The resistance through the "backbone" consists of a large number of resistors combined in series and parallel. This system can be solved by Kirchhoff's Rules with computer iteration. The resistance between the individual contacts depends on the metal filler surface condition, and on mechanical properties of the filler which are related to the contact areas controlled by interparticulate forces. The particle sizes and distribution will change the percolation "backbone" structure and hence the resistor network and number of contacts involved. These resistances will be counted based on the resistor network conductivity calculation which combines contact effects and percolation processes.

3. Results and Discussion

3.1. Theoretical consideration between contacts

The conductivity of the metal filled epoxy system depends on the filler metal and the inter-particle contacts even if the same percolation "backbone" structure is developed in the matrix. The commercial metal filled adhesives have resistivities several orders of magnitude larger than the resistivities of the filler metals, especially for Cu and Ni fillers. Al particles are not used in these systems because of their hard and continuous insulating oxide layer on the surface. Ag filled adhesives have relatively low resistivity and dominate the commercial conductive adhesive range. The individual particle-to-particle contact paths in the percolation "backbone" linkage make an important contribution to the resistivity of the composite material.

The particles' contact resistance normally consists of the particle contact constriction resistance and a tunneling resistance.⁸ The constriction resistance R_c is the consequence of the current flow being constricted through small conducting spots. An alien film in the contact may give rise to an additional resistance R_t . Theoretically one may expect that the discontinuity of the crystal lattice order in the contact will reflect electrons and produce a transition resistance. However, such resistance is extremely small and similar to the resistance of grain boundaries in polycrystalline materials.⁸ The contact areas

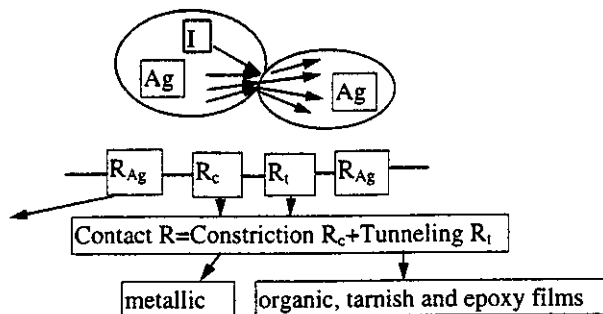


Fig. 2. Illustration of contact resistance between silver flakes.

between adjacent flakes are normally formed by the epoxy curing force. This surface area could be partly covered by insulating tarnish films and only a fraction of it has metallic or quasimetallic contact. A quasimetallic contact is covered with a thin film that is penetrable for electrons by means of the tunnel effect, and consequently produces a relatively small film resistance. Figure 2 illustrates the three types of resistance. We are neglecting the other possible contact conduction mechanism here (i.e. through a degenerate semiconducting surface oxide).

Tarnish films on metals are known to form almost instantly upon exposure to normal atmosphere.⁸ Ag oxidizes to Ag_2O at room temperature only in presence of ozone. Ag_2O is soft, easily removed mechanically and decomposes at 200°C. It seldom disturbs the performance of contacts. In a normal atmosphere Ag obtains a dark, resistive film of Ag_2S . Ag_2S begins to decompose at about 360°C. Ag has a tendency to sulfidize and the Ag sulfide is not protective. It grows steadily but slowly because the concentration of the attacking gas is usually small. Sulfidation is controlled by the scarce rate of arrival of active sulfur atoms to the surface. A 10⁻⁹ concentration of H_2S in air is considered to be harmful. The resistivity of Ag_2S at room temperature lies between 105 and 10¹⁰ Ω m, depending on the state of its lattice structure. This is the same resistivity range as copper oxide. Ag_2S is softer than the matrix metal. Its hardness is about half that of the pure Ag (about 1.5×10^8 N/m²). Therefore, the Ag_2S film is easily damaged at contact, providing a relatively good conductance through metal spots. From processed Ag flakes, residual organic films may remain on the surface after milling, which is purposely deposited for dispersion or dedusting reasons. In the Ag filled epoxy system, the flake itself may be completely cov-

ered by a thin epoxy film. All these three films may be present in different thicknesses, providing an insulating layer between flakes. For thin films on the order of less than 10 nm, quantum mechanical tunneling can occur, resulting in lower resistivities. The potential barrier is proportional to the work function of the conductor and the thickness of the film.

There is always sufficient time to allow a deposit of normal (chemisorbed) oxygen layers on Ag. Observation of contacts between Ag rods⁸ shows that the conductance versus load P curves have sudden changes of the conductance to high values. For the Ag filled epoxy system, resistivity of the matrix decreases dramatically during cure and continues decreasing with further cure and cool processing.² These jumps were attributed to the intricate nature of the formation of a metallic spot. The contact is first formed merely elastically and the conductance through the film is due to the tunnel effect. With increasing load, the load carrying hump breaks down, disrupting the film and producing a clean contact spot. At further increasing load, there may be new rupturing of the film on the same hump due to new plastic yielding which would result in enlargement of the already existing metallic spot. Or, other humps may collapse too, and new spots may be generated. Very likely both phenomena will happen during one jump.

The constriction resistance is derived from the principles of ohmic conduction and electric field theory⁸ and can be expressed by $R_c = \rho/2a$, where a is the radius of the flat contact area and (is the metal particle resistivity. The constriction resistance increase with temperature will be less than that of the bulk metal. The temperature factor is approximately $(1 + 2/3\alpha T)$, where (is the temperature coefficient of resistivity of the contact metal, and T is temperature change. The tunneling film resistance⁸ is expressed by $R_t = \eta/A_c$, in the case of the insulating film distributed uniformly over the contact area A_c , where $\eta(\Omega \cdot \text{cm}^2)$ is the resistance across one cm² of the film.

The load bearing area which is the sum of all the contact spots can be generated mainly by elastic deformation. Two types of deformation can occur: elastic recoverable and plastic permanent deformations. Because of the unevenness of the surfaces, plastic deformation will happen in some areas. Combining these two effects, the contact force $F = \xi H A_c$, where $0.2 < \xi < 1$ and H is the "contact hardness". The contact spot area A_c is a function of the applied

contact load F between particles and of the deformation that occurs as a result of the applied pressure. Good electrical contact is made with combinations of elastic and plastic deformations. $A_c = F/\xi H$, and for most systems $\xi = 0.7$.⁸ For Ag-Ag contacts, H is approximately $2.5 \times 10^8 \text{ N/m}^2$ at room temperature. This H depends on the temperature, and the time of the stress due to continued thermal diffusion of atoms under influence of the stress. The constriction resistance R_c slowly decreases with time and pressure. The essential cause for this decrease will be the strain in the structure, produced around the contact by the stress when the contact is made, enlarging the contact surface. From observation of the TEM results,³ for one material with small Ag flakes around $1 \mu\text{m}$, the contact diameter is around 200 nm . Hence, typically, the contact resistance R_{contact} ,

$$\begin{aligned} R_{\text{contact}} &= R_c + R_t \\ &= \rho/2a + \eta/A_c \\ &= \rho 0.5(3.14\xi H/F)^{1/2} + \eta\xi H/F \\ &= 0.89\rho(\xi H/F)^{1/2} + \eta\xi H/F \end{aligned}$$

and the contact resistance is dependent on the particle size, the force applied between them, and the intrinsic properties of the conductive filler. We have $\rho_{\text{Ag}} = 1.7 \times 10^{-8} \Omega \cdot \text{m}$, $\xi = 0.7$, $H = 2.5 \times 10^8 \text{ N/m}^2$, $\eta_{\text{Ag}} = 0.3 \times 10^{-10} \Omega \cdot \text{m}^2$,⁹ and F is the contact force between the flakes in N, so the above equation becomes

$$\begin{aligned} R_{\text{contact}} &= R_c + R_t \\ &= \rho/2a + \eta/A_c \\ &= 0.89\rho(\xi H/F)^{1/2} + \eta\xi H/F \\ &= 2 \times 10^{-4}/F^{1/2} + 5.25 \times 10^{-3}/F(\Omega). \end{aligned}$$

The contact resistance changes with contact force between Ag flakes is shown in Fig. 3. The above case is based on the assumption that the contact is covered by a thin layer of film where the contact resistance is actually dominated by the tunneling resistance factor. In real conductive adhesive systems, the contact between the Ag flakes after cure is expected to have mainly metallic contact, because the tarnish film (Ag_2O and Ag_2S) and organic acid layer are all easily broken due to the stress induced during the curing and cooling process. From the TEM results, after cure the Ag flake contact diameter a is very small, which causes the tunnel resistance to be too large if calculated from the above equation. So the contact resistance is mainly contributed by the constriction resistance between metallic contacts

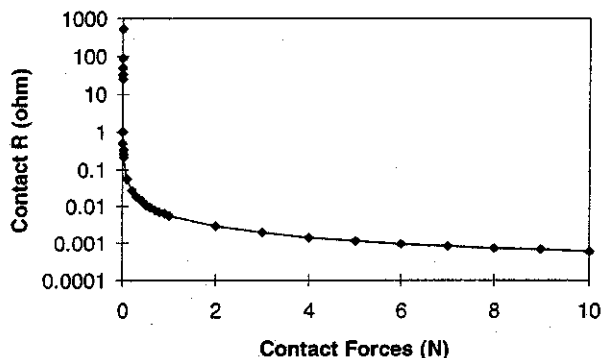


Fig. 3. Contact resistance change versus contact force.

after the adhesive curing process. Large resistivity before cure is contributed by the insulating film on the silver flakes and dominated by tunneling resistivity effects, and also some insulated contacts (if the film thickness is too larger for electron tunneling) in the critical path of the percolation "backbone" cluster.

3.2. Numerical simulation and resistivity calculation

Two-dimensional simulations were first conducted. Ag flakes were assumed to be in square or rectangular shapes. The model first simulates the percolation cluster according to the particle filler percentage. Different size filler particles were used, one group is monosized particles with variable size and

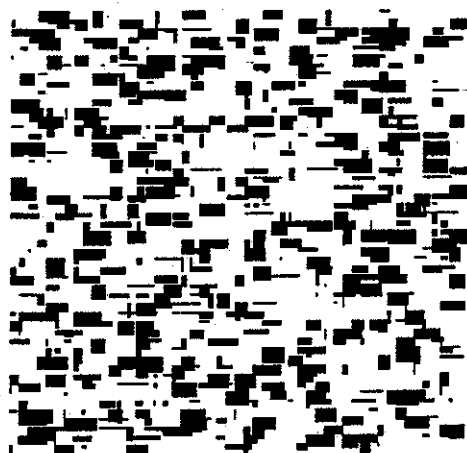


Fig. 4. Representative percolation cluster with size distribution of rectangular shaped particles.



Fig. 5. Connected percolation cluster after P_c .

shape parameters, and the other group is particles with uniform size distributions. The maximum cluster sizes were calculated, and as was the percolation threshold, with different particle size, shape and distributions. Figure 4 shows a representative matrix (100×100) filled with particles with size distributions ($< 5 \times 5$) below the percolation threshold P_c ($P=24\%$). Figure 5 is the representative cluster distribution for the connected cluster with $P > P_c$, ($P = 40\%$). Table 1 shows the representative results of the percolation threshold P_c changes with the particle sizes, shapes and distributions based on a two-dimensional simulation on a 80×80 matrix. The calculated maximum percolation cluster sizes increased dramatically above the percolation threshold, although many of the particles mainly contribute to the dead ends. The percolation cluster size does not increase in the same trend as the conductivity of the material does, which is very consistent with the theory results.¹ The two-dimensional simulation shows that the larger size particles need a relatively high percolation threshold, and the rectangular shape also increases the P_c .

Resistivities of the composite matrices were calculated by solving the linear equations of Kirchoff Rules with computer iterations. The Ag flake resistivity is $1.7 \times 10^{-6} \Omega \text{ cm}$, with the epoxy assumed to be $1 \times 10^{10} \Omega \text{ cm}$, and contact resistances are calculated (constriction and tunneling resistances) dependent on the contact forces. The calculation results are shown in Fig. 6 for different monosize particles and in Fig. 7 for particles with different size distributions. The results show that particles with distributed sizes show a lower resistivity transition point and also lower resistivity. Particles with broad size distributions have the same effects. Figure 8 shows the contact resistance effect on the resistance of the composites. The model here assumes the contact resistance and contact force are the same for any of the two Ag flake contacts, which is independent of the particle size and distribution, only the contact area is change by the contact forces.

3.3. Summary

The contact resistances between the Ag particles were considered. Three different films mainly exist on the Ag surface, and they are residual organic films, tarnish films (Ag_2O or Ag_2S), and a thin epoxy layer. The contact resistance is contributed by the constriction resistance and tunneling resistance. R_c is induced by the small contact spots and restriction of the current flow, and tunneling resistance R_t is caused by the very thin layer on the Ag flakes besides the metallic contact spots. The contact pressure and force applied on the Ag flake contacts have very important effects on the contact resistance. Pressure will enlarge the metallic contact spots area by elastic and plastic deformation and also potentially break the organic and tarnish films to produce fresh metallic contacts. These will all decrease the contact resistance between the particles and hence reduce the resistivity of the conductive adhesives. Experimental results² of the conduction development during cure show further resistivity decreases after

Table 1. Percolation threshold and continuous cluster size with different particle sizes.

Particle Sizes	Two-Dimensional P_c (%)	Percolated Cluster Size
2×2	55	1900
4×2	75	838
4×4	64	535

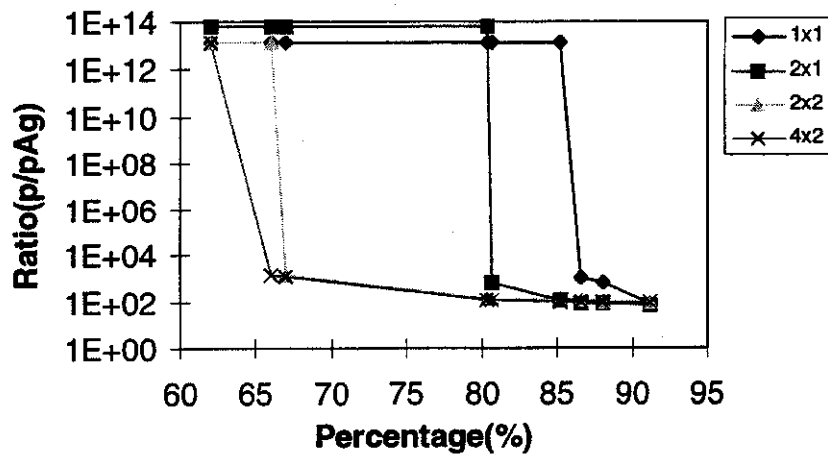


Fig. 6. Ratio of resistivity (ρ/ρ_{Ag}) versus metal filler percentage for monosize particles.

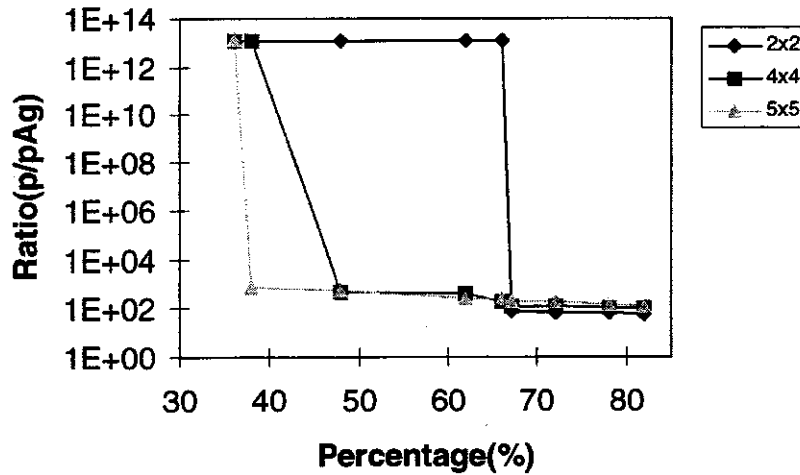


Fig. 7. Ratio of resistivity versus filler percentage for random size distribution.

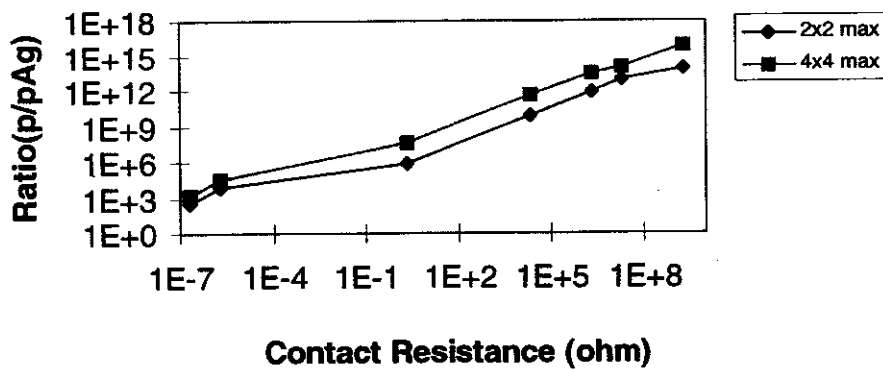


Fig. 8. Ratio of resistivity versus contact resistance.

continued cure can be expected, mainly caused by the increased pressure and stress between the particles resulting in the reduced contact resistance. Environmental scanning electron microscopy (ESEM) hot stage investigation² did not show any large scale Ag flake movement during curing. This tells us that the percolation clusters already exist in the matrix, and the sudden conduction development is mainly caused by the residual stress and epoxy cure shrinkage induced stress on the Ag flake contacts. This may contribute to one or more linkages in the critical cluster "backbone" paths.

Computer models calculate the particle size, shape, distribution effects on the percolation threshold and cluster sizes. The resistivities of the composites were also calculated by considering the contact effects and particle size effect. At this stage, the model development work has not been completed yet. More useful and realistic 3-D models will be developed and the real joint structure will be considered. Computer simulation programs in C and FORTRAN will be made available.

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