Materials Characterization, Conduction Development, and Curing Effects on Reliability of Isotropically Conductive Adhesives

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***Abstract*—Three commercially available, silver filled, snap cure isotropically electrically conductive adhesives for surface mount applications were selected for study. Fundamental material characterizations were conducted on these materials, including thermal analysis [differential scanning calorimetry (DSC), thermo-gravitational analysis (TGA), and thermo-mechanical analysis (TMA)], rheological, and dynamic mechanical analyses. Microstructural investigations [scanning electron microscopy (SEM), transverse electromagnetic (TEM), Auger)] were performed to identify the silver flake size, distribution, and contact morphology. These analyses were related to the cure process and electrical conduction mechanisms of isotropically conductive adhesives (ICA's).**

The resistivity of these materials was monitored during cure and related to the cure kinetics of the epoxy matrix. The resistivity decreased dramatically ($>$k$\Omega \cdot$cm to m$\Omega \cdot$cm) around a specific temperature with ramp cure and over a narrow time range ($<$10 s) with isothermal cure. Successive heating (25–150 °C) and cooling cycles yielded different degrees of consecutive resistivity decreases for these materials which were cured according the manufacturer's recommended schedules. Microstructure development during cure was studied with a hot stage in an environmental scanning electron microscope (ESEM) to relate morphological changes with the observed changes in resistance. No significant structural changes and silver flake movements were noticed during cure. The conduction development was accompanied by breakage and decomposition of the tarnish, organic thin layers which cover the silver flake surface, and by the enlargement of the contact area between silver flakes by thermal stress and shrinkage during the epoxy cure. The temperature coefficients of resistance (TCR) were measured for these materials; the TCR is closely related to a conduction mechanism dominated by constraint resistance between the flakes or by the silver flake metallic conduction.

The resistivity and interfacial resistance of these materials with bare copper and gold plated pads (with five selected cure schedules) were measured through 85 °C/85% RH exposure up to 900 h. The bulk resistivity decreased in the first 100 h of exposure and did not change with humidity; however, the interfacial resistance increased with the copper pads for some materials. This is caused by the oxidation of the copper pads due to moisture attack.

***Index Terms*— Coefficient of thermal expansion, differential scanning calorimetry, environmental scanning electron microscope, gelation, isotropically conductive adhesives, temperature coefficients of resistance, thermo-gravitational analysis, thermomechanical analysis, vitrification.**

I. Introduction

ISOTROPICALLY conductive adhesives (ICA) are particle filled polymers. The filler particles are electrically conductive and must form a continuous bridge between two electrical terminals to function. The filler particles are almost always silver. Silver particles are used because of their low and stable resistivity (1.6 $\mu\Omega \cdot$ cm). The matrix or binder materials typically used in the electronics industry are epoxies. Epoxies are used because of their exceptional combination of stability, strength, toughness, adhesion, and chemical resistance.

ICA's have been used for many years in the electronics industry to form electrical interconnects between adherends. The electronics industry has shown renewed interest in ICA's as it has migrated from through-hole to surface mount technology and now to no-clean solders. Still further interest has been developed with the anticipation of legislation on lead.

The factors limiting general ICA application have been materials cost, inadequate strength, poor reliability and an inadequate understanding of processing conditions.

This paper focuses on the influence of cure on resistivity, joint resistance and reliability. Novel analytical methods were developed to define the cure conditions that produce optimum electrical properties and stability.

II. Processing Conditions

Past studies [1] have focused on the overall system or process performance with a given set of designs, materials, process parameters, and cure schedules (Fig. 1). In order for the results from this type of study to be meaningful each process step needs to be optimized to meet the requirements of the subsequent process steps; including the application and cure of the interconnection material. The designs and process parameters typically used were optimized for SnPb solders and not for ICA's. Even though ICA's have been around for a long time they still have only seen limited use. As a result there are no readily available design guidelines and process parameters,

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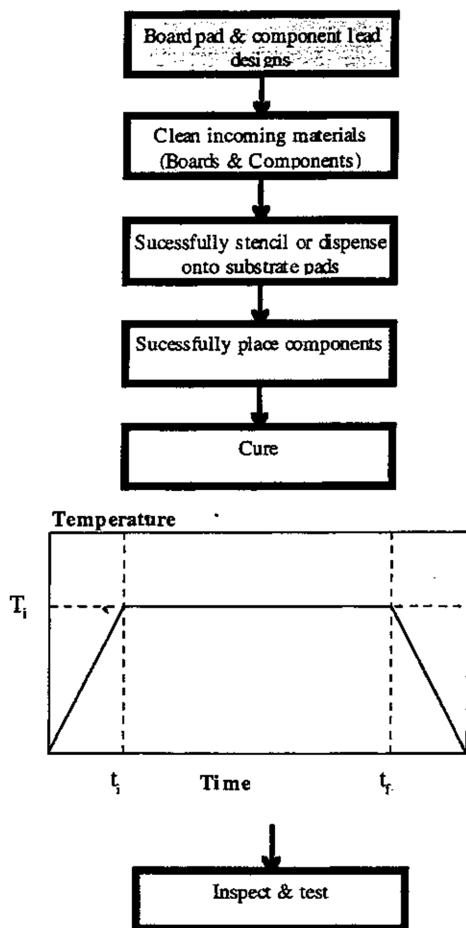

Fig. 1. Schematic process overview.

as there are with solder, for working with ICA's. To further confuse the issue each ICA supplier uses a proprietary epoxy blend with a recommended cure schedule that has probably not been optimized for the intended application; the suppliers readily admit to this.

Therefore, a set of experiments and analytical techniques were designed to be independent of board design, application method and component placement. This allowed the evaluation of cured properties in a given application without these other process dependencies. Thermal analysis techniques accomplish this, but do not take into account the interaction with the adherends. The novel tests developed factor in the adherend, its surface condition and its interaction with the ICA.

III. Cure Kinetics

The most common epoxy resin system used is made by condensing epichlorohydrin with bisphenol A (diphenylol propane) and is cured with a polyamine. The curing of epoxy is complex and several steps are involved. Cure begins with the formation and linear growth of the polymer chains that then begin to branch, and then crosslink. As cure proceeds the molecular weight increases rapidly and eventually the chains become linked together into networks of infinite molecular weight. The transformation from a viscous liquid to an elastic gel marks the first appearance of an infinite network. Gelation typically begins between 55 and 80% conversion. Gelation does not inhibit the curing process.

Vitrification is another step in cure. This is the transformation from either a viscous liquid or an elastic gel to a glass state. Vitrification occurs when the glass transition temperature of the growing chains and networks approach the curing temperature. Vitrification also marks the shift from chemical controlled to diffusion controlled reaction and marks the end of rapid cure.

The curing reaction of most epoxies can be described by a simple kinetic model

$$d\alpha/dt = kf(\alpha).$$

Where $d\alpha/dt$ is the conversion rate, k is the rate constant and $f(\alpha)$ is the concentration of reactants. The temperature dependence is assumed to reside in the rate constant through an Arrhenius relationship

$$k = Ae^{(-E/RT)}.$$

Where E is the activation energy, R is the gas constant and A is the pre-exponential factor.

A usable relationship between the activation energy (E), the heating rate (ϕ, where $\phi = dT/dt$) and the peak exothermic temperature (T_p) based on a difference method was presented by T. Ozawa [2]

$$\int_0^{\alpha_p} \frac{d\alpha}{f(\alpha)} = A\int_{t_0}^{t_p} e^{-E/RT}\, dt = \frac{a}{\phi}\int_{T_0}^{T_p} e^{-E/RT}\, dT \approx \frac{AE}{\phi R} p(E/RT_p)$$

where, $p(E/RT_p)$ represents a function of E/RT_p.

Solutions for $p(ER/T_p)$ were tabulated by C. D. Doyle [3], where

$$\log p(E/RT_p) \approx -2.315 - 0.4567E/RT_p$$

for $20 < E/RT_p < 60$. The extent of reaction (α_p) at the peak exotherm is a constant and independent of heating rate. Therefore, the first integral in the equation above is a constant and E can be obtained from dynamic scanning calorimetry (DSC) data

$$E \approx \frac{-R}{0.4567} \frac{\Delta \log \phi}{\Delta(1/T_p)}.$$

Likewise a useful expression for the pre-exponential factor for nth-order reactions was derived [4]

$$A = \frac{\phi E e^{(E/RT_p)}}{RT_p^2[n(1-\alpha_p)^{n-1}]} \approx \frac{\phi E e^{(E/RT_p)}}{RT_p^2}$$

where $n(1-\alpha_p)^{n-1} \approx 1$ for first order reactions. This is useful for our case since nth-order epoxy cure reactions are only 2–4% greater than 1. Using ϕ, T_p and the resulting activation energy (E), the pre-exponential factor (A) can be obtained. From A and E the rate constant (k) can then be calculated.

Assuming nth-order kinetics, this is a good assumption for our epoxy systems, DSC scans with ramp rates of 6 and 10 °C/min are used to determine $E, A,$ and k at different

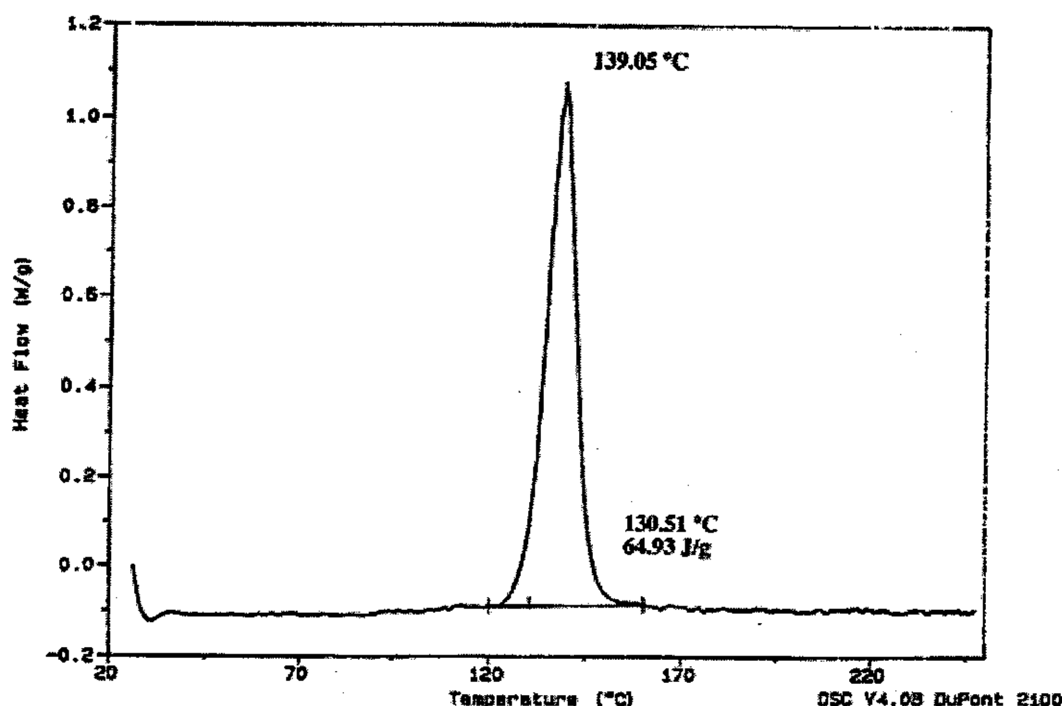

Fig. 2. DSC run at 10 °C/min for a silver filled epoxy.

TABLE I
DSC EXPERIMENTAL RESULTS WITH DIFFERENT RAMP RATES

	Ramp rate (ϕ) 6°C/min.	Ramp rate (ϕ) 10°C/min.
Onset Temp. (°C)	122.28 StDev = 0.078	130.31 StDev = 0.69
Peak Temp., T_p (°C)	130.15 StDev = 0..078	139.06 StDev = 0.31
Heat released (J/g)	76.9 StDev = 3.08	68.81 StDev = 3.61

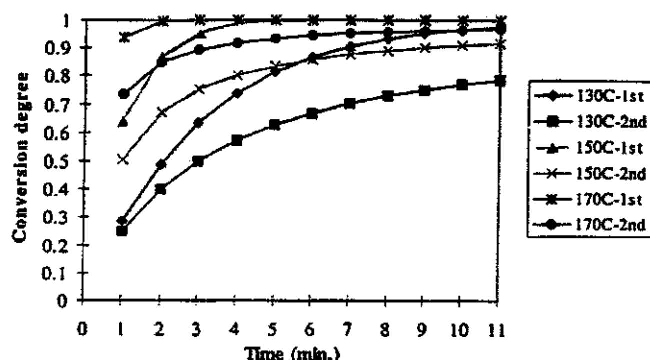

Fig. 3. Degree of cure versus cure time at different cure temperatures for both first and second-order reactions.

temperatures. One of the 10 °C/min DSC scans is shown in Fig. 2.

For this silver filled epoxy the following parameters were determined and tabulated in Table I.

The activation energy (E) pre-exponential (A) were calculated to be 78.41 kJ/mole and 82.2× 10^6/s, respectively. The rate constants at 120, 130, and 150 °C were then calculated to be 0.003 08/s, 0.005 58/s, and 0.0168/s, respectively.

Employing the 1st-order equation, $d\alpha/dt = k(1-\alpha)$, with boundary conditions $t = 0$ and $a = 0$, at a constant temperature, it is found that $\alpha = 1 - e^{-kt}$. When a 2nd-order of reaction is assumed the degree of conversion is found to be $\alpha = 1 - 1/(kt+1)$. Fig. 3 shows the degrees of conversion for the first and 2nd-order reaction assumptions.

From the graph in Fig. 3 it is observed that complete conversion is not achieved within 11 min for 2nd-order reactions, even when curing at 170 °C.

A similar result was obtained using a modified autocatalyzed cure rate equation that uses isothermal DSC data (Fig. 4) in-place of dynamic DSC data. The empirical model used in this study is given as

$$d\alpha/dt = (k_1 + k_2\alpha_n^m)(1-\alpha_n)^n$$

where $\alpha = H/H_{\text{ult}}$ and $\alpha_n = \alpha/\alpha_{\text{iso}}(T)$. H_{ult} is the ultimate heat of reaction in dynamic scanning. The curve fit using this approach is very good (Fig. 5). One of the conclusions from this approach is that the ICA's evaluated can not be fully cured with an isothermal cure schedule (Fig. 6).

With a thermal mechanical analyzer (TMA) the Tg is found to be 90 °C. The coefficient of thermal expansion (CTE) below and above Tg are found to be 61 and 168 ppm/°C, respectively. A 2% weight loss is detected below 100 °C with a thermal gravimetric analyzer (TGA) and the weight percent silver is found to be 87 (Fig. 7).

The weight loss prior to 100 °C is associated with solvent evaporation. This can lead to porosity in joints, which is undesirable.

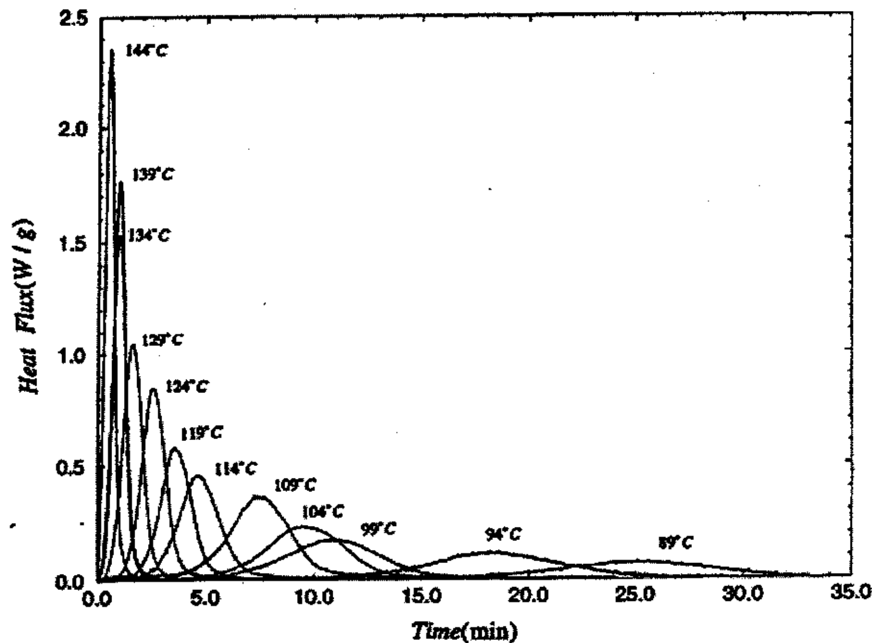

Fig. 4. DSC isothermal scan summary for a silver filled epoxy.

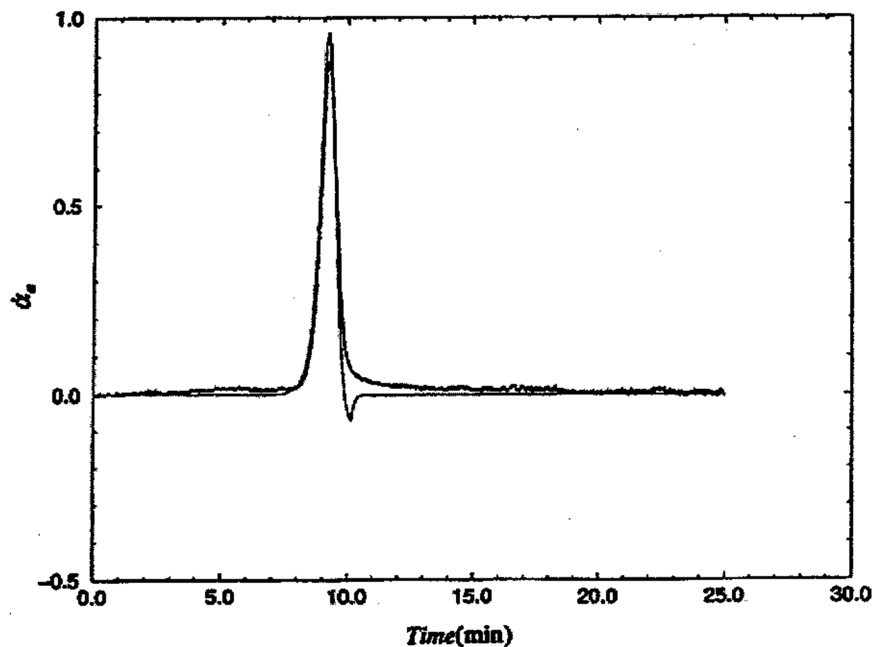

Fig. 5. Curve fit with DSC test data using a modified auto-catalyzed cure rate equation.

IV. Development of Conduction During Cure

A four point probe method for examining resistance was used to calculate resistivity and its change during cure (Fig. 8). Test leads from a HP 3458A Multimeter with a measurement range from 0.1 mΩ to 1 GΩ are soldered to terminals 1, 2, 3, and 5 on a FR-4 test vehicle. Any vehicle with 4 isolated terminals can be used [5].

A constant current was applied between terminals 1 and 5 to avoid interfacial effects between the current and voltage terminals. The voltage is then measured across adjacent terminals 2 and 3 and converted to resistance. Adjacent terminals must be used to make ℓ and A meaningful. If adjacent terminal are not used the volume of the middle terminal and its network effect must be taken into account. Resistivity is determined as $R{\cdot}\ell/A$ where R is the measured resistance, ℓ is the distance between terminals, and A is the cross section area of the ICA strip. Using this apparatus it is possible for us to monitor resistance or resistivity during cure.

The development of conduction during a typical cure schedule is shown Fig. 9.

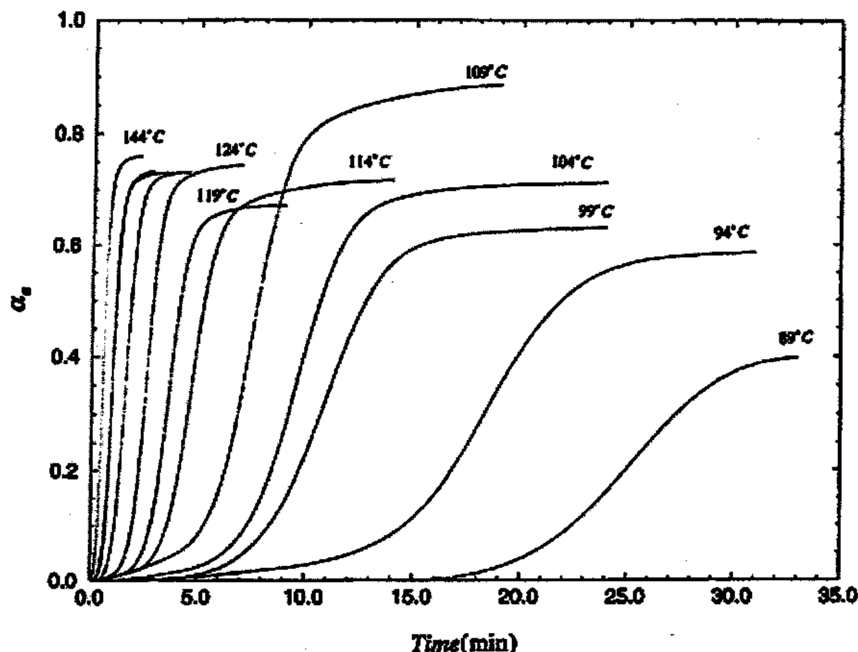

Fig. 6. Degree of cure versus cure time at different isothermal cure temperatures.

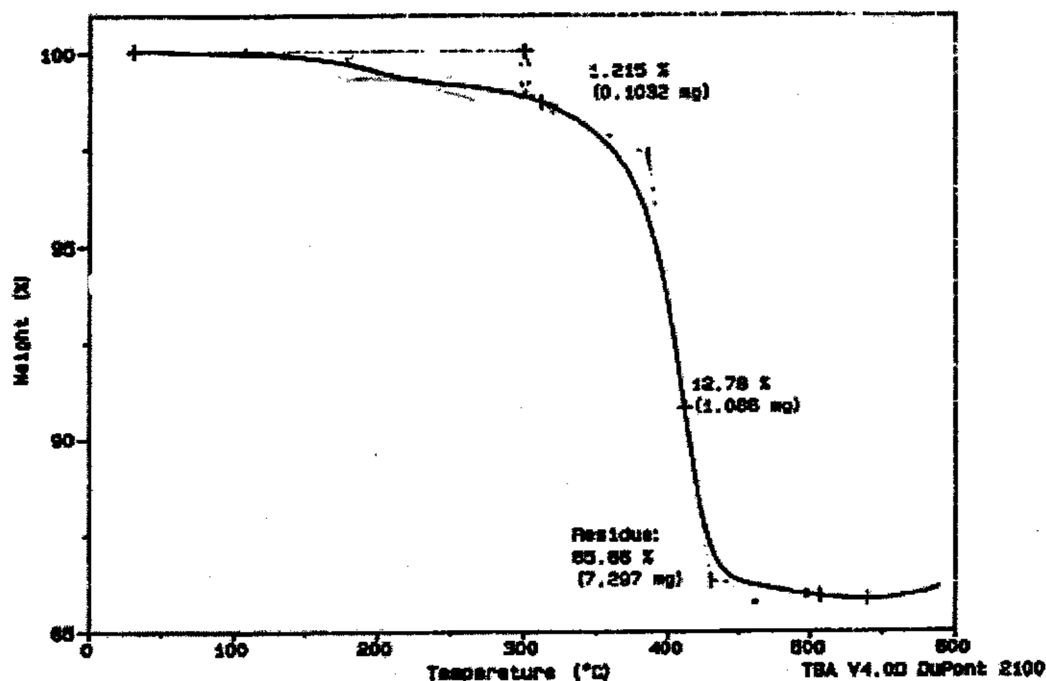

Fig. 7. TGA scan of a silver filled epoxy.

Before cure the resistivity is measured to be 1×10^5 $\Omega \cdot$cm. It starts to decrease with the application of heat. This sample was heated at 7 °C/min to 150 °C followed by a 5 min dwell at 150 °C. At approximately 80 °C the resistivity begins to drop off faster. At 100 °C it begins to decrease at a still faster rate. After reaching approximately 105 °C (10^{-2} $\Omega \cdot$ cm) the rate of change begins to decline. It then continues to decrease as the temperature increases to the isothermal cure temperature of 150 °C. The resistivity continues to decrease, but at a much slower rate, during isothermal cure and then drops off still further during cooling to 1×10^{-4} $\Omega \cdot$ cm. It is hypothesized that initial drop off in resistance is associated with silver packing as the viscosity falls. The large resistivity transition from 10–10^{-2} $\Omega \cdot$ cm is associated with gelation. The subsequent decrease in resistivity is then associated with vitrification (glassy state) and the further development of cure.

V. Joint Electrical Stability After Cure

After cure the same samples were subjected to sequential heating and cooling cycles to evaluate the resistivity dependence on temperature. Irreversible changes in resistivity are observed upon repeated cycling (Fig. 10).

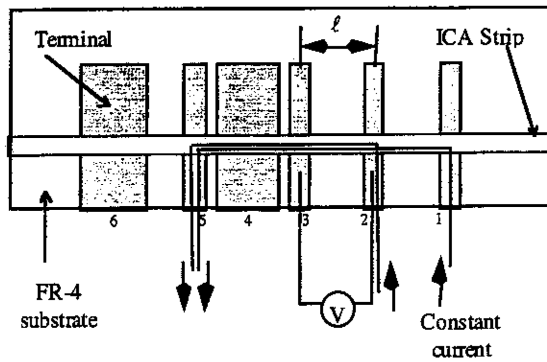

Fig. 8. Test vehicle.

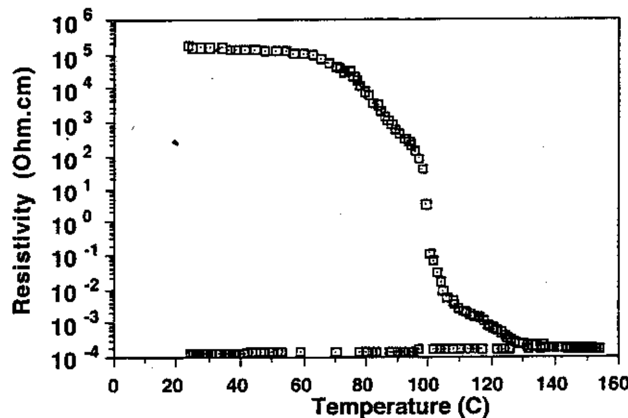

Fig. 9. Resistivity change during cure.

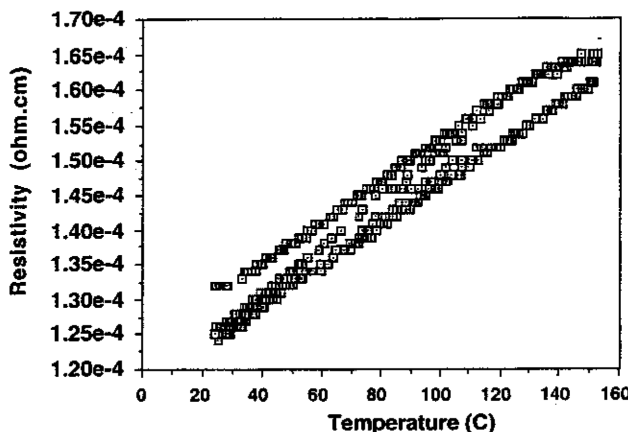

Fig. 10. Resistivity change with thermal cycles on an ICA cured for 5 min at 150 °C.

The degree of irreversible change in resistivity decreases with additional cycling, which is detected as a reduction in hysteresis. This indicates that the material did not develop its ultimate properties during the initial isothermal cure. After two cycles the change in resistivity with temperature becomes nearly linear. The other ICA's tested showed a much more pronounced hysteresis and required multiple cycles for the resistivity to become reversible with temperature (Fig. 11). The thermal coefficient of resistance (TCR) for this ICA is 2.4×10^{-3}/°C as measured during the second cycle. This is

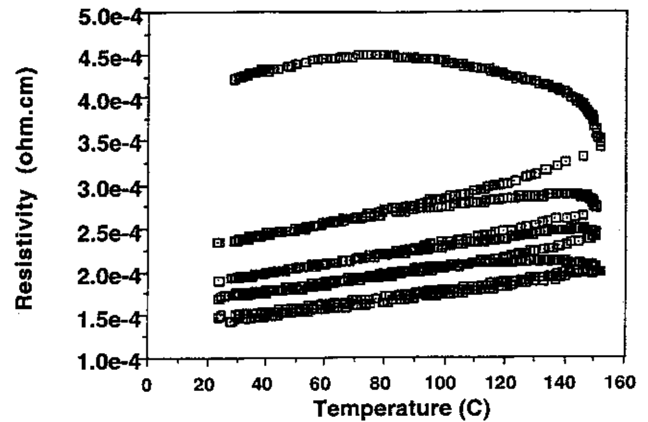

Fig. 11. Silver filled epoxy with a larger hysteresis in resistivity.

TABLE II
CURE SCHEDULES USED FOR THE RELIABILITY STUDY

Symbols	Soak temp. & time
B3	150 °C, 3 min.
B6	150 °C, 6 min.
B10	150 °C, 10 min.
B130	130 °C, 6 min.
B170	170 °C, 6 min.

less than silver which has a TCR of silver 3.8×10^{-3}/°C. It is hypothesized that the reason the ICA has a lower TCR than silver is because it is a composite and conduction is influenced both by bulk metallic effects and contact or constriction effects. Contact effects are also the reason that an ICA's resistivity can not reach that of bulk silver.

VI. VOLUME RESISTIVITY AND INTERFACIAL RESISTANCE IN 85 °C/85% R.H. HUMIDITY

Five different cure schedules were selected for the ICA's based on the vendor recommended cure schedules and initial DSC results. Table II shows the cure schedules used for one of the materials. Three test boards were used for each cure schedule (two with bare copper finishes and one with a Au finish). The boards were cured by placing them in a preheated oven for the isothermal cure times indicated. Two to four minutes were required for the samples to heat up to their isothermal cure temperatures.

Three volume resistivity measurement were made on each test board using terminals 1 and 2, 3, and 4, and 5 and 6 as depicted in Fig. 8. The average resistivities and their standard deviations were obtained from the nine resistance measurements taken from the three boards in each group. The interfacial resistance was obtained with two measurements by placing either one or both of the constant current probes on the same terminals as the voltage probe as depicted in Fig. 8

$$V12/I12 = R'_{12} = Rv + R_{I1} + R_{I2}$$
$$V12/I15 = R_{12} = Rv + R_{I2}.$$

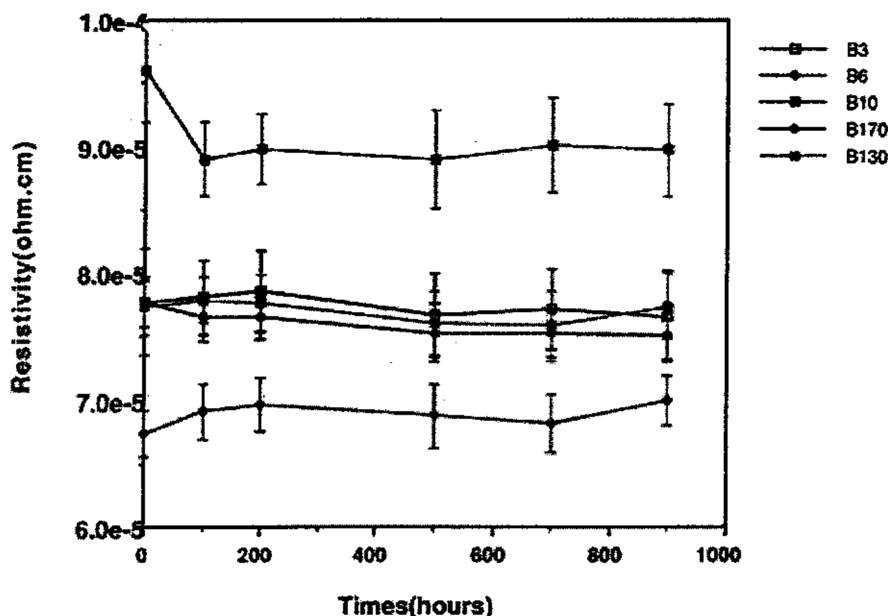

Fig. 12. Resistivity of an ICA exposed to 85 °C/85% RH.

The interfacial resistance was calculated by subtracting the two resistances

$$R'_{12} - R_{12} = R_{I2}.$$

The volume resistance could also be determined by substituting R_{I2} back into the first equation and assuming $R_{I2} = R_{I1}$.

Five interfacial resistance measurements were taken on each board using the six available terminals. The volume resistivity and interfacial resistance were measured initially and after every 100–300 h of exposure to 85 °C/85% R.H. up to 900 h.

The initial resistivity was observed to be dependent on the degree of cure (Fig. 12). The most important factor was the cure temperature. The under cured material's resistivity drops initially and then stabilizes. The lower the degree of cure the higher the resistivity drop upon exposure to 85 °C and 85% relative humidity. The cure time does not have nearly the effect that temperature does on the development of electrical properties and their stability.

The interfacial resistance for other ICA's (not previously used as an example) were observed to increase on both Cu and Au finishes; more so on the Cu finish (Fig. 13). This was different than the volume resistivity behavior. This behavior would be expected if the underlying Cu was oxidized, hydrolyzed or that the Cu/ICA interface delaminated.

In comparison, the same increase in resistance was not observed on the ICA used as the primary example so far in this paper (Figs. 14 and 15). This suggests that this ICA has either better adhesion or that it presents a barrier to humid air diffusion or both.

VII. Percolation and Contact Resistance Theory

By using metal particles (most commonly silver flakes) [6], a network of interconnections is made within the adhesive allowing electrical conduction throughout the material. As metal

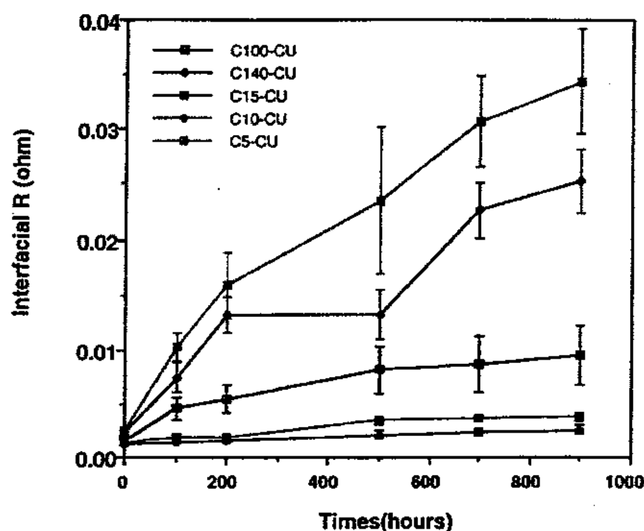

Fig. 13. Interfacial resistance versus 85 °C/85% RH exposure for a silver filled epoxy bonded to copper.

particles are added to the mixture, conductive pathways will increase. At the critical volume fraction, percolation theory and experience shows that resistance decreases dramatically (Fig. 16) [7].

The critical volume fraction, as calculated by Springett, should be between 15 and 20% metal by volume [8]. The model used to determine a 15–20% critical volume fraction was based on spheres. Other investigators have incorporated shape factors and packing density numbers to more accurately reproduce the observed phenomenon. Experience has shown that the critical volume fraction is actually 30–35% [9]. Therefore, any significant resistance would be due to a source other than a lack of metal flakes.

All of the silver filled adhesives evaluated in this study have filler volume fractions that exceed the critical volume

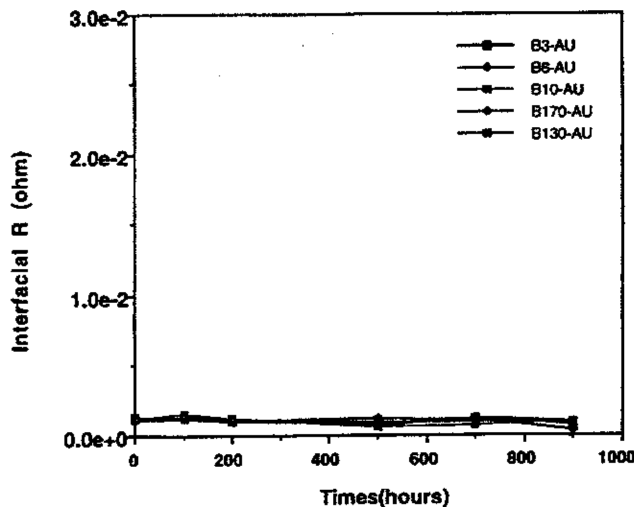

Fig. 14. Interfacial resistance versus 85 °C/85% RH exposure for an ICA bonded to gold.

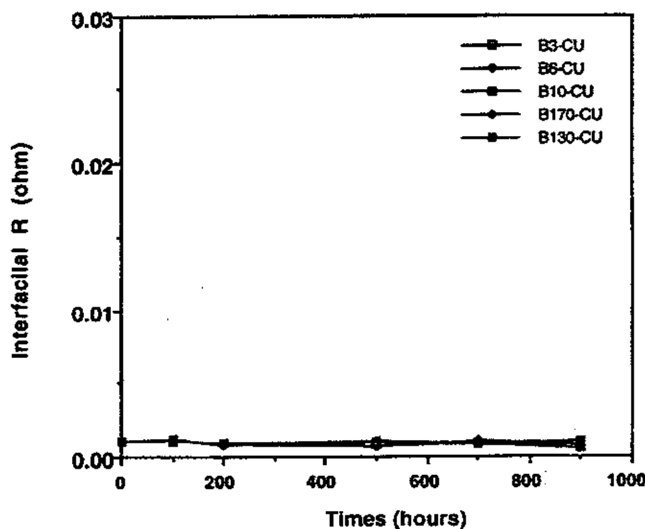

Fig. 15. Interfacial resistance versus 85 °C/85% RH exposure for an ICA bonded to copper.

fraction. Therefore, to further understand the conductive nature of these materials it is necessary to understand the conduction characteristics at their interfaces. Such interfaces occur at the silver and substrate interfaces. Current flowing through the contacts developed between the silver particles and the substrate will be constricted because of the small contact area developed between them. The bending of the current-flow paths requires an added voltage called the constriction voltage. Furthermore, additional voltage may be required to force current through a high-resistance film that may be separating two conductors, such as an oxide film.

For our case the resistance across a "point" contact region for a current, I, is simply

$$R_{12} = V_{12}/I$$

where V_{12} is the voltage drop between points 1 and 2 that are on either side of a contact.

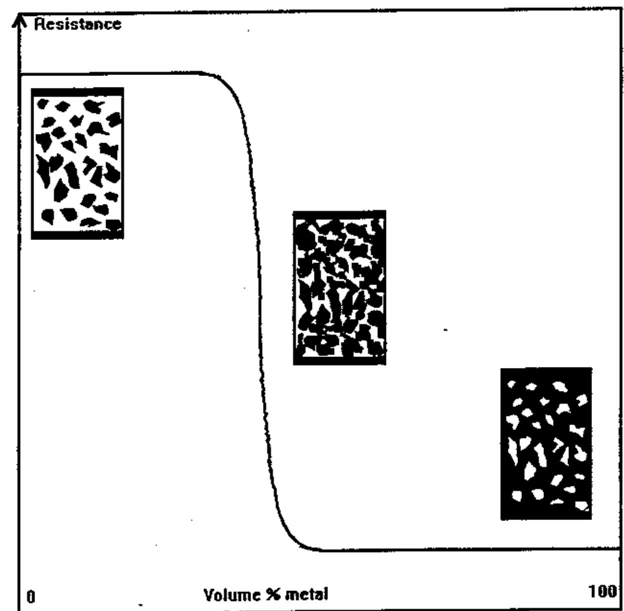

Fig. 16. Percolation theory showing decrease in resistivity at critical volume fraction.

The contact resistance, R_c, between conductor A and B is defined as the difference between the measured resistance, R_{12}, and the ideal resistance, R_{12}^{o}. Therefore

$$R_c = R_{CR} + R_f$$

where $R_{|mbiC}R$ is the resistance due to constriction and R_f is the film resistance.

The constriction resistance for $D/d > 3$ has been shown [10] to be equal to

$$R_{CR} = (r_a + r_b)/2d$$

where r is the resistivity of the component materials, d is the diameter of the constriction or "point" contact and D is the diameter of the overall contact.

For contacting materials that form metal to metal contacts and that do not oxidize R_f is zero. One source of a resistance higher than expected could be an oxide film on the metal surface. Another source could be organic film remaining between conducting surfaces. One group of experimenters [11] evaluated as-prepared (unaged) metal filled adhesives under varying A.C. conditions and did observed ohmic, only, effects. This result would be expected if film resistance was not a dominant factor. This observation may not hold for all systems and may actually vary with use and aging. It could be a function of metal surface contamination and the adhesive used. Neither of these factors have been explored to date.

VIII. Conclusion

The thermo-electrical and enviro-electrical tests performed help establish suitable cure schedules for the ICA's used in electronics applications. It was found that it may be possible to improve the resistance stability by dynamically curing (repeated heating and cooling) the ICA. The thermal analysis

work completed support these findings. All together the results from these studies support the basic contact resistance model of these joints.

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