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Reliability Considerations of Electrically Conductive Adhesives

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Isotropic conductive adhesives are typically silver filled epoxy resins. Electronics assemblers have evaluated these materials for a variety of unique interconnect applications. The goal is a conductive polymer that exhibits similar reliability and performance to traditional solder while offering the benefits of a polymer structure such as low temperature processing and good thermal stability as well as the ability to bond a variety of substrates. The challenge has been to develop materials that exhibit higher impact resistance and stable junction resistance. These materials offer the electronics assembler an interesting alternative to solder for creating an electronic interconnect. However, the long-term reliability of these adhesive systems must be carefully tested.

The National Center for Manufacturing Sciences (NCMS), in conjunction with seven industry collaborators, established a series of criteria for a successful SMCA replacement for metallic solder. The minima include: a volume resistivity not greater than 1 milliohm-centimeter (0.001 ohm-cm), less than 20% shift in contact resistance after 500 hours at 85oC/85% RH, and adequate impact resistance. 2.

The goal of this study was to compare and contrast the volume resistivity, shear adhesion, and impact resistance of 4 different types of silver filled epoxy resins.

Background:

Isotropic epoxies offer all-directional (uniform) conductivity by incorporating metallic particles such as silver, nickel, or gold within the epoxy resin. The most popular filler material is silver due to its moderate cost, high conductivity, and wide availability. There are greater than 100 different grades of silver flake and powder available on the market. The particle size is controlled by the screen mesh used to sort the filler; resulting in a typical size of less than 40 microns, with tightly controlled distribution. The aspect ratio of silver flake vs. powder form has a significant effect on the high-speed dispensability of these conductive adhesive resins. The epoxy resins are typically heat- or room temperature curing, single- or two-component formulations. The electrical conductivity of these materials is achieved by incorporating a high percentage of conductive filler within the dielectric epoxy matrix until reaching "isotropicity." Essentially, the amount of silver is so high that the particles come into contact

Experimental Method:

Electrically conductive adhesive systems must perform two basic functions; bond to the substrate and provide an electrical connection. The purpose of this effort was to evaluate the adhesion and electrical stability performance of 4 different types of silver filled isotropic epoxy formulations. The following 3 test programs were conducted:

1. PCB drop test, using a standard test board and PLCC-28 dummy components.

2. Shear adhesion on aluminum lapshear specimens in accordance with ASTM D-1002.

3. Volume resistivity on glass lapshears in accordance with MIL STD 883.

Reliability was characterized by establishing baseline performance values and comparing to changes due to environmental conditioning as follows:

A. Thermal shock, 250 cycles from –40°C to +150°C.
B. Heat / humidity (80°C / 95%RH) exposure for 500 hours.

Note: The above conditions for heat / humidity exposure could be considered more severe due to the increased humidity level, when compared to the industry standard of "85/85".

Products Tested:

The following isotropic epoxy adhesives were included in this program:

1. Repair / rework grade - Rapid setting, room temp cure, short pot life, rigid material.

2. High adhesion grade - Primarily for gold substrates, rigid, heat cure only material.

3. Die Attach grade - High purity, long work life, heat cure material.

4. Flexible grade - Low modulus, moderate work life, heat or room temp curable material.

PCB Drop Test:

Impact resistance of the materials was evaluated by bonding PLCC-28 dummy components to the Loctite Chipbonder Testboard V1.3 A-side with 3 of the 4 adhesive products:

1. Repair grade
2. High adhesion grade
3. Flexible grade

The adhesive was applied to the test board locations at a film thickness of 0.006 to 0.009 inches. The PLCC's were then manually placed and cured as required. The effect of heat vs. room temp cure was observed by preparing both heat and room temp cured assemblies with each adhesive.

The assemblies were then drop tested from a height of 5' (60"). There were two-drop techniques:

1. Flat drop = The pcb impacts the floor evenly, i.e. flat against the floor.

2. Angled drop = The pcb impacts the floor at the opposite corner to the PLCC component location. This was believed to create a more severe impact / shock load on the adhesive bond.

The # of drops required to make the PLCC separate from the board were recorded. Three assemblies were tested for each set of conditions with the following results...
Table #1 - PCB Drop Test

Average # of Drops to Bond Failure

Cure & Drop Method	PRODUCT		
	Repair Grade	Flexible Grade	High Adhesion
Room Temp - Flat	4	8	1
Room Temp - Angled	1	4	1
Heat Cure -Flat	1	8	4
Heat Cure - Angled	1	4	4

Notes:

1. One (1) drop = PLCC "popped off" on the 1st drop.
2. Multiple drops typically exhibited ±1 from average for the three replicates

The primary conclusions that can be drawn from this data include:

1. The angled drop is a more severe method of subjecting the assembly to an impact load.

2. The flexible material offers superior impact resistance to the rigid formulations due to the dampening effect of the low modulus adhesive matrix. Even after subjecting the material to a heat cure process, the adhesive is not embrittled.

3. The high adhesion grade offers acceptable performance if cured properly (heat.)

4. The repair grade material is not impact resistant**.**

Shear Adhesion:

Bond strength of the adhesive materials was evaluated in accordance with ASTM D-1002 on standard aluminum lapshear (1" X 4" x 1/16") assemblies with an Instron 4204 Mechanical Tester at a crosshead speed of 0.050 in/min. All four adhesive candidates were evaluated. In addition, cure method (room temp vs. heat) was included as a variable for the Repair and Flexible grades. Finally, the effect of bond gap thickness (zero vs. 0.005" induced) was measured.

Typically, a structural epoxy adhesive exhibits shear adhesion values of 3,000 psi or greater. We theorized that the high filler (non-adhesive) content in the isotropic materials would reduce the adhesion significantly. Essentially; the amount of surface area "wetted" by the epoxy matrix is reduced due to the presence of the silver required for electrical conductivity.

The first step in this test program was to generate baseline adhesion data. In order to evaluate bond strength reliability, additional assemblies were prepared and exposed to environmental extremes; thermal shock and heat/humidity aging as described earlier. Please refer to the following table.

Table #2 - Shear Adhesion; Initial vs. After Environmental Exposure

Average LapShear Adhesion, psi

Product	**Initial – Zero Gap**	**Initial – Induced Gap**	**After 250 cycles Thermal Shock Exposure Zero Gap**	**After 250 cycles Thermal Shock Exposure Induced Gap**	**After 500 hours Heat / Humidity Exposure Zero Gap**	**After 500 hours Heat / Humidity Exposure Induced Gap**
Repair grade – RT cure	900 psi	1,000 psi	700 psi	700 psi	*250 psi	400 psi
Repair grade – heat cure	1,000 psi	1,000 psi	650 psi	700 psi	failed	200 psi
High Adhesion – heat cure	900 psi	1,000 psi	500 psi	700 psi	*300 psi	*100 psi
Die Attach – heat cure	900 psi	1,000 psi	600 psi	700 psi	failed	*150 psi
Flexible - RT cure	800 psi	600 psi	500 psi	350 psi	failed	Failed
Flexible - heat cure	600 psi	400 psi	500 psi	200 psi	failed	Failed

Note: * = only 1 of 3 assemblies remained intact for testing.

A series of simple experiments were conducted during the initial stages of this project in an effort to understand the effect of *High Heat Exposure* on bond strength. Aluminum lapshear specimens were aged for 1 week at 200°C and 260°C. Result: When exposed to 200°C, the average bond strength increased to approx. 1,200 psi for all products, except the high adhesion grade which dropped to approx. 800 psi. When exposed to 260°C, bond strength was significantly decreased to <300 psi for all products.

The primary conclusions that can be drawn from this data include:

1. The 3 rigid grade materials exhibited typical baseline values of 900 to 1,000 psi while the flexible material exhibited lower adhesion values, ca. 400-600 psi.

2. Thermal shock reduced adhesive strength up to 50%.

3. Short-term heat aging increased bond strength by 10-20%.

4. Heat / humidity exposure significantly reduced the bond strength of all assemblies.
   Note: Multiple test specimens were placed "on the shelf" in the heat / humidity chamber and actually "fell off" during the 500 hour exposure cycle. The impact of falling off the shelf could have compromised bond integrity but does not invalidate the conclusion.

5. Aluminum was a poor choice as the test substrate. Severe oxidation of the lapshears was observed on all assemblies subjected to heat / humidity exposure.

Volume Resistivity:

The electrical conductivity of these materials was measured in accordance with MIL STD-883, which is more commonly known as the "Four Point Probe" test. Section 3.8.11.1.1 defines paste material test specimens ... "shall be prepared using a standard 1 inch X 3 inch glass slide... 2 scribed lines 100 mil apart and parallel to the length...2 strips of tape... Using a single edge razor blade maintaining a 30-degree angle between the slide surface and the razor blade, the material shall be squeezed between the tape strips... The length shall be at least 2.5 inches."

Further, section 3.8.11.1.3 defines Resistance measurements... "shall be made using a milliohm meter in conjunction with a special four-point probe test fixture... can be made of an acrylic material with 4 spring loaded contacts... must be set into the acrylic so that the current contacts are 2 inches apart, the voltage contacts are between the two current contacts, and the voltage contacts are separated from each current contact by 0.5 inch. The fixture shall be placed on the strip of conductive polymer... The measured resistance shall be recorded in ohms, and the resistivity shall be determined from the following formula...

$P = R (w X t) / L$

Where:

P = Volume Resistivity (ohm-cm)
R = measured resistance in ohms
w = width of strip (note: 100 mils = .100 inch = 2.54 mm = .254 cm)
t = thickness of strip (micrometer measurement, typ. 0.005", approx. .13 mm)
L = length between the inner pair of probes (note: 1 inch = 25.4 mm = 2.54 cm)

All measurements recorded in this project were taken at room temperature.

Baseline measurements were recorded for each specimen; which were then subjected to environmental conditioning as described earlier. Please refer to the following table...
Table #3 - Volume Resistivity, Initial vs. After Environmental Exposure

Typical Volume Resistivity, ohm-cm.

Product	Initial Volume Resistivity	After 250 cycles Thermal Shock Exposure	After 500 hours Heat / Humidity Exposure
Repair - RT cure	0.0008 ohm-cm	0.0003 ohm-cm	0.0003 ohm-cm
Repair - heat cure	0.0001 ohm-cm	0.0001 ohm-cm	0.0001 ohm-cm
High Adhesion – heat cure	0.0001 ohm-cm	0.0001 ohm-cm	0.0001 ohm-cm
Die Attach - heat cure	0.0001 ohm-cm	0.0001 ohm-cm	0.0001 ohm-cm
Flexible - RT cure	0.0010 ohm-cm	0.0008 ohm-cm	0.0004 ohm-cm
Flexible - heat cure	0.0008 ohm-cm	0.0006 ohm-cm	0.0003 ohm-cm

The primary learning experience in this phase of the project was proper technique in preparing the film on glass specimens. Careful attention was required to produce a film of uniform width and thickness. In addition, the four-point test probe was redesigned - heavier and easier to manipulate. Multiple test specimens were discarded due to variations in the surface which produced anomalous readings on the milliohm meter.

A series of simple experiments were conducted during the initial stages of this project in an effort to understand the principles of the test method...

A.) *Larger* strip specimens; up to 1/4" wide (vs. 0.100" mil spec requirement) and up to 0.010" thick. Result: Yielded significantly different resistance measurements on the milliohm meter, yet virtually identical volume resistivity values once calculated to ohm-cm.

B.) *Alternate substrate* specimens; prepared on epoxy glass (FR4) lapshears (vs. glass mil spec requirement.) Result: slightly increased difficulty in preparing the strip, yet no significant difference in resistance measurements or volume resistivity values.

C.) *High Heat Exposure*; in which both glass and FR4 specimens were aged for 1 week at 175°C, 200°C, 230°C, and 260°C. Result: Although some of the FR4 substrate specimens actually burned and severe discoloration was observed on some of the glass specimen strip; those strips which were measurable yielded resistance measurements that were virtually unchanged.

The primary conclusions that can be drawn from this data include:

1. Careful attention must be applied to the preparation of the specimen strip. Although the actual width, thickness, and substrate choice are less important due to the mathematical calculation of volume resistivity - variations in surface texture must be minimized as they can have a significant effect on the measured resistance of the strip.

2. All formulations exhibit consistent values, less than 1 milliohm-cm.

3. Thermal exposure improved volume resistivity values of the room temp cured specimens.

4. Heat / humidity exposure had virtually no effect on volume resistivity except for the room temp cured specimens as noted previously.

<u>Summary Comments:</u>

1. The PCB drop test indicates that the flexible conductive offers impact resistance superior to the rigid formulations. Even the high adhesion grade when properly heat cured does not offer the same level of "drop test resistance." This is consistent with Vona, Tong, Kuder, and Shenfield2 conclusion regarding lower modulus, lower Tg materials which yield improved drop test performance.

2. Shear Adhesion strength on aluminum laps is quite consistent for all of these highly filled conductive epoxies. Exception: The flexible does not form bonds which are as rigid, therefore exhibiting lower shear adhesion values. The data for induced gap reinforces this concept by exhibiting values slightly lower as the bondline thickness was increased.

3. Shear adhesion after thermal shock exposure is decreased across the entire product line up to 50%; but still offers acceptable performance. Short term heat aging typically increases average bond strength by 10-20%.

4. Heat / Humidity exposure had a dramatic effect on bond strength. Severe oxidation of the aluminum lapshear substrate was the dominant failure mode of the assembly.

5. Volume Resistivity testing via MIL STD 883 was remarkably consistent for all products tested, even when altering the strip width and thickness as well as the application substrate. In addition, VR is significantly improved by thermal exposure. Thermal shock and heat / humidity exposure had virtually no effect, except for the room temp cured specimens which were slightly improved (lowered resistance values.) Post-cure heat exposure may provide a more thorough cure of the adhesive matrix; helping to "pull" the silver filler particles closer together.

6. The shear adhesion data on aluminum substrate indicates that bond strength is compromised by heat / humidity exposure. Also, the volume resistivity data indicates that this material property is quite stable, even after heat aging, thermal shock, and heat / humidity exposure. However, loss of adhesion between the conductive epoxy and the substrate due to heat / humidity exposure in an electronic interconnect application will result in increased circuit resistance. These conclusions are consistent with Zwolinski, et al 1 in which their study

revealed increased junction resistance after heat/humidity exposure of SMT devices bonded with isotropic conductive adhesives. Oxidation of the aluminum substrate employed for this bonding study was the dominant failure mode of the assemblies subjected to heat / humidity exposure.

Isotropic (silver-filled) epoxy adhesives are available to the electronics assembler as an interesting alternative to solder. The primary benefits of a polymer system include low temperature processing options and good thermal cycling performance. In addition, flexible (low modulus, low Tg) epoxy materials offer improved impact (drop test) performance. Volume Resistivity is very stable due to the high silver content of these materials. However, heat / humidity exposure reduces adhesive bond strength, which can cause an increase in junction resistance of the interconnect site. The long-term reliability of these adhesive systems must be carefully tested for potential applications.

END.

Sources:

1. Electrically Conductive Adhesives for Surface Mount Solder Replacement; Zwolinski, M.; et al. IEEE Transactions on Components, Packaging, and Manufacturing Technology; Part C; Vol. 19; No. 4; October 1996.

2. Surface Mount Conductive Adhesives with Superior Impact Resistance; Vona, S.; Tong, Q.; Kuder, R.; and Shenfield, D.; 1998 International Symposium on Advanced Packaging Materials.

3. Conductive Adhesives for Surface Mount Devices; Iwasa, Y., EP&P Magazine, November 1997.

4. MIL STD 883E, Method 5011.4, EVALUATION AND ACCEPTANCE PROCEDURES FOR POLYMERIC MATERIALS. [Type 1 being electrically conductive]