Novel Conductive Adhesives for Surface Mount Applications

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ABSTRACT: Electrically conductive adhesives (ECAs) have been explored as a tin/lead (Sn/Pb) solder alternative for attaching encapsulated surface mount components on rigid and flexible printed circuits. However, limited practical use of conductive adhesives in surface mount applications is found because of the limitations and concerns of current commercial ECAs. One critical limitation is the significant increase of joint resistance with Sn/Pb finished components under 85°C/85% relative humidity (RH) aging. Conductive adhesives with stable joint resistance are especially desirable. In this study, a novel conductive adhesive system that is based on epoxy resins has been developed. Conductive adhesives from this system show very stable joint resistance with Sn/Pb-finished components during 85°C/85% RH aging. One ECA selected from this system has been tested here and compared with two popular commercial surface mount conductive adhesives. ECA properties studied included cure profile, glass transition temperature (T_g), bulk resistivity, moisture absorption, die shear adhesion strength, and shift of joint resistance with Sn/Pb metallization under 85°C/85% RH aging. It was found that, compared to the commercial conductive adhesives, our in-house conductive adhesive had higher T_g, comparable bulk resistivity, lower moisture absorption, comparable adhesion strength, and most importantly, much more stable joint resistance. Therefore, this conductive adhesive system should have better performance for surface mount applications than current commercial surface mount conductive adhesives. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 399–406, 1999

Key words: electrically conductive adhesives; stable joint resistance; tin/lead-finished components; surface mount applications

INTRODUCTION

The continued evolution of the electronics industry has created a need for environment and user-friendly alternatives to tin/lead (Sn/Pb) solders. For many years, special efforts were made to replace lead-containing solder materials with conductive adhesives in surface mount technology. Conductive adhesives can simultaneously establish mechanical and electrical joints between printed circuit board and the surface mount components. Conductive fillers in the adhesive are responsible for the electrical interconnection and the resin mainly provides the mechanical interconnection (Fig. 1).

Besides the environmental issue, conductive adhesives as one of the alternatives to solder have the following potential advantages: (i) lower sensitivity to thermomechanical stresses, due to higher flexibility than solder; (ii) lower curing temperatures enabling the use of heat sensitive or nonsolderable materials (chip on glass or surface mount device on polyester flex substrates); (iii) high-resolution capability for fine-pitch interconnects due to smaller particle size than solder

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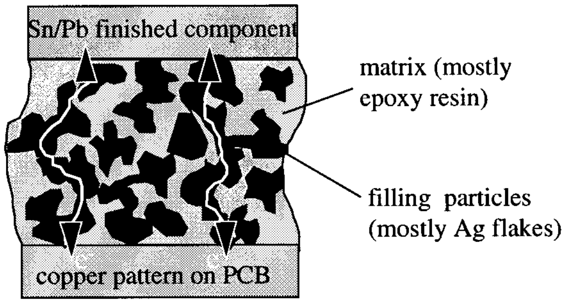

Figure 1 Conductance of conductive adhesives in a joint.

pastes; and (iv) simple processing if compared to wave soldering (less process steps).[1–5]

On the other hand, compared to traditional soldering technology, concerns and limitations about conductive adhesive technology are also present. One major limitation is that joint resistance of conductive adhesive with Sn/Pb finished components increased dramatically under 85°C/85% relative humidity (RH) aging. Although Sn/Pb finishing of the components is not necessary for using conductive adhesives, nevertheless, in the short term, Sn/Pb compatibility is a desirable quality for compatibility of this technology with the existing component supply infrastructure. Therefore, conductive adhesives with stable joint resistance are especially needed.[3] Besides stable joint resistance, a desirable conductive adhesive also should have the following properties: higher impact resistance, low moisture pickup, low bulk resistivity, and high adhesion strength.[4]

In this study, a conductive adhesive system based on epoxy resins has been developed. Shift of joint resistance with Sn/Pb metallization under 85°C/85% RH aging, and other properties including curing profile, glass transition temperature, bulk resistivity, moisture absorption, and die shear adhesion strength of one electrically conductive adhesives (ECA) selected from this system have been tested and compared with those of two popular commercial surface mount conductive adhesives.

EXPERIMENTAL

Materials

Epoxy resins used in this study were purchased from Shell Chemical Company. Hardeners were supplied by Aldrich Chemical Company. Ag flakes used in conductive adhesive formulations were obtained from Degussa Corporation. An adhesion promoter was purchased from Dow Corning. All the chemicals were used as received. Eutectic Sn/Pb wires (0.25 mm diameter) were provided by Hisco Company. Two commercial conductive adhesives, ECA-A and ECA-B, were provided by the same manufacturer.

Cure Study

Curing profiles of all adhesives were studied by using a differential scanning calorimeter (DSC) from TA Instruments, model 2923. An adhesive sample of about 10 mg was placed into an aluminum hermetic DSC pan. All samples were studied by both dynamic cure and isothermal cure. In the dynamic cure, the sample was heated in the DSC cell from 25 to 250°C at a heating rate of 5°C/min. In the isothermal cure studies, the sample was quickly placed into the DSC cell, which had been preheated to a prescribed temperature and the DSC data was collected thereafter.

Measurements of Glass Transition Temperatures (T_g)

T_gs were measured with a thermomechanical analyzer (TMA) from TA Instruments, model 2940. Preparation of TMA specimens was based on the following procedures: (a) placed an adhesive sample in an aluminum pan (1.5 in. diameter); (b) cured the sample in a convection oven; (c) removed the aluminum pan away after the cured sample cooled down to room temperature; and (d) cut the specimen into squares with dimensions of about 6 × 6 × 1.5 mm. A macroexpansion probe was used here and the static force applied on the probe was set to 0.050 Newton. Temperature was ramped from 25 to 250°C at a heating rate of 5°C/min. The dimension change with temperature was recorded. T_gs were obtained from the TMA curves.

Measurements of Bulk Resistivity

Resistivity of an ECA was calculated from the bulk resistance of the ECA specimen with specific dimensions. Two strips of an adhesive tape were applied onto a precleaned glass slide with a gap of 0.1 in. (0.254 cm) between these two strips. A conductive adhesive paste was then spread within the space by means of a doctor blade, and then the tapes were removed. After cure, the bulk resistance of this ECA strip was measured by

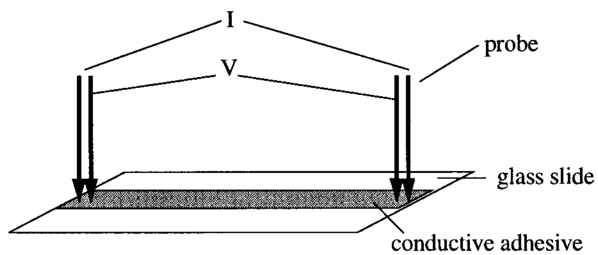

Figure 2 Layout of bulk resistance measurement setup.

using a Keithley 2000 multimeter with a four-point probe. The layout of the measurement setup is shown in Figure 2. The length of the specimen l is length of the glass slide (75.60 cm); its thickness h is that of the adhesive tape (0.007 cm), and its width w is that of the gap between the two adhesive strips (0.254 cm). Resistivity was calculated from bulk resistance R by using following equation:

$$\text{Resistivity (ohm-cm)} = R \times \frac{w \times h}{l}$$

Five specimens for each ECA sample were tested. An average bulk resistivity and a standard deviation for each sample were calculated and reported.

Measurements of Moisture Absorption

Moisture absorption of all the cured ECAs were tested using a dynamic vapor sorption system from Surface Measurement System, model DVS 1000. Dimensions of all the specimens used in this study were 150 μm thick, 1.5 cm wide, and 15 cm long. The dimensions of the specimens were closely controlled by the following procedures: (a) placed two strips of an adhesive tape (150 μm thick) on a Teflon coated aluminum plate with a 1.5 cm space between them; (b) applied an conductive adhesive paste on the plate between the two adhesive strips with a doctor blade; (c) removed the tape strips, and (d) cured the ECA samples. Then the specimens were aged under a 85°C/85% RH condition in the DVS instrument and their mass changes with time were recorded continuously.

Die Shear Adhesion Strength

Die shear adhesion strength was measured at 25°C by using an adhesion tester from Royce Instruments, model 552. The size of the die was 2 $\times$ 2 mm. The die and substrate were both passivated with Silicon Nitride (Si_3N_4). Ten specimens were tested for each ECA sample. The average adhesion strength and standard deviation for each ECA sample were reported. The adhesion strength data was not included in the calculation of the average adhesion strength if the die was broken or fractured during die shear adhesion test.

Joint Resistance Variation

Joint resistance variations were tested by using an in-house test device which is depicted in Figure 3.[6] This device consists of metal wire segments (1 cm long) that were separated by small gaps (1 mm). Conductive adhesives were applied to the gaps between the wire segments with 1 mL syringe and connected the metal wires. After the specimen was cured, joint resistance was measured from the two wire ends with a Keithley 2000 mutlimeter. Eutectic Sn/Pb wire was used here to simulate Sn/Pb finished components. The test devices were aged under 85°C/85% RH in a temperature and humidity chamber from Lunaire Environmental, model no. CEO932W-4. Joint resistance data were collected periodically during aging.

RESULTS AND DISCUSSION

Conductive Adhesive Formulations

Our in-house conductive adhesive formulations were based on epoxy systems. The epoxy could be either Bisphenol-F or Bisphenol-A type epoxies. A typical ECA formulation includes an epoxy resin, a hardener, a catalyst, an adhesion promoter, and Ag flake fillers. Filler loading of these two commercial ECAs were measured by dissolving resin parts with an acetone solvent. It was found that

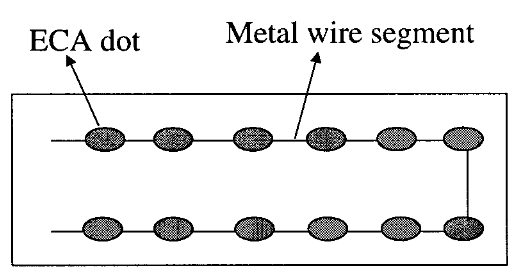

Figure 3 In-house joint resistance test device.

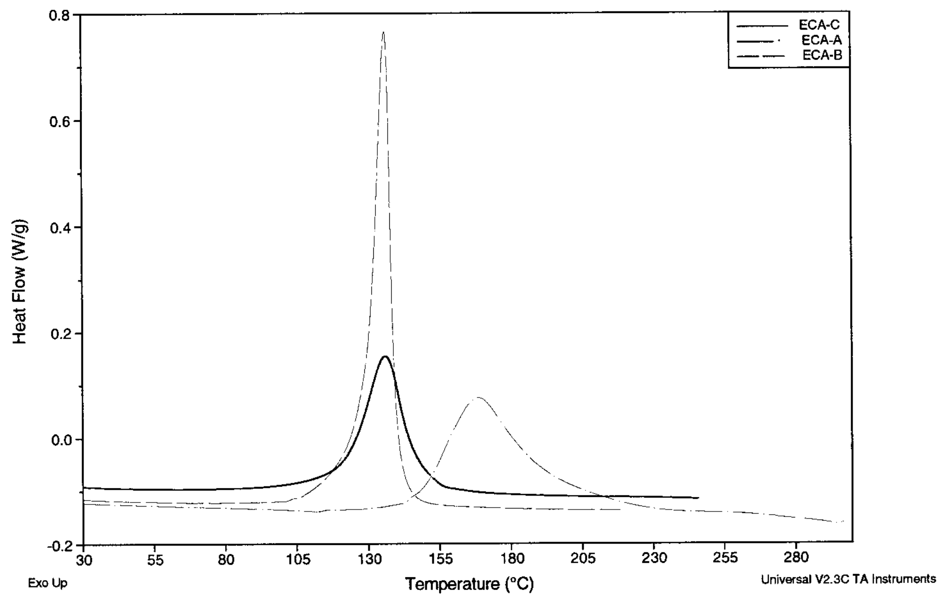

Figure 4 DSC curves of ECAs during a dynamic cure.

filler loading of both commercial adhesives was 80 wt %. To ensure comparability, the filler loading of in-house formulation ECA-C was also kept 80%.

Cure Study

One of the outstanding features of conductive adhesives is that they can cure at much lower temperatures than Sn/Pb solder reflow temperature. Therefore, ECAs are especially valuable when attaching heat-sensitive components and low-cost substrates. Another desirable property is that ECAs can be cured rapidly, which can save time and lower cost.

The cure behaviors of the in-house formulation (ECA-C) during both dynamic cure and isothermal cures were studied by using a DSC and compared to those of ECA-A and ECA-B. The cure profiles of all the samples during dynamic and isothermal cures are given in Figures 4 and 5, respectively. As can be seen in Figure 4, the ECA-A shows a broader cure peak at a higher temperature, compared to ECA-C and ECA-B. The in-house adhesive, ECA-C, had similar cure profile as ECA-B. ECA-A and ECA-B were both recommended by the manufacturers to cure at 150°C, as such isothermal cure profiles at 150°C of these adhesives were studied and compared with our in-house ECA-C (Figure 5). At 150°C, ECA-C had similar cure kinetic as ECA-B but it was cured much faster than ECA-A.

Measurements of Glass Transition Temperatures (T_g)

Adhesives ECA-A, ECA-B, and ECA-C were cured at 150°C for 40, 20, and 20 min, respectively, based on our DSC isothermal cure study results. The cured samples were studied by a TMA and results are given in Figure 6. As can be seen from Figure 6, the in-house formulation ECA-C had a higher T_g (105.67°C) than both commercial ECAs, ECA-A (63.61°C) and ECA-B (72.15°C). High T_gs are desirable for conductive adhesives.[4] ECAs with higher T_gs generally are less susceptible to creep, which is one of the possible mechanisms for the unstable joint resistance during 85°C/85% RH aging.[4]

Bulk Resistivity

Current commercial surface mount conductive adhesives generally have bulk resistivity in the range of 10^{-4} ohm-cm, which is higher than that of Sn/Pb solder, 10^{-5} ohm-cm, in surface mount applications.[7] The high resistivity is one of the limitations of current commercial ECAs. The resistivity of the three ECAs is shown in Figure 7. The in-house ECA-C had a lower bulk resistivity than ECA-B but with a similar bulk resistivity to ECA-A.

Moisture Absorption

Moisture absorption is one of very important parameters of conductive adhesives. Condensed wa-

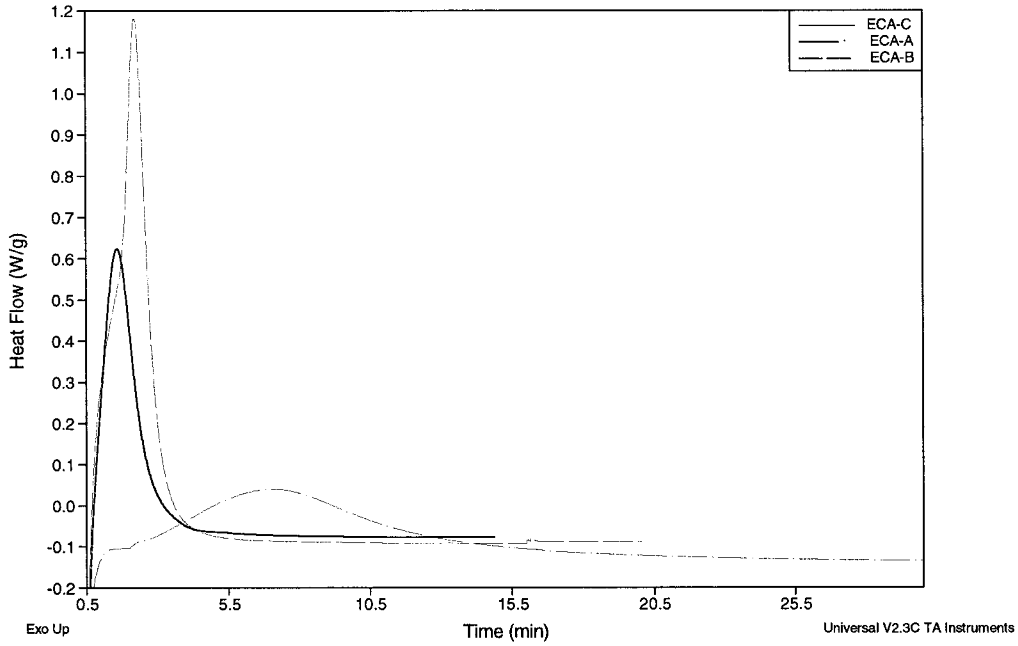

Figure 5 DSC curves of ECAs during an isothermal cure (at 150°C).

ter from moisture can degrade mechanical properties through depression of the T_g, giving rise to swelling stresses in the system, and creating voids or promoting the catastrophic growth of voids already present in the system.[7] Water also might affect electrical properties of ECAs by inducing the formation of oxide layers on pad metal resulting from corrosion and oxidation reactions.[7] Low moisture pickup is a particularly desirable property of a surface mount conductive adhesive.

Moisture absorption data, both dynamic and kinetic, of these three adhesives are given in Figures 8 and 9, respectively. As can be seen from the figures, the in-house formulation ECA-C reached an equilibrium moisture absorption faster than the commercial ECAs and it showed much lower

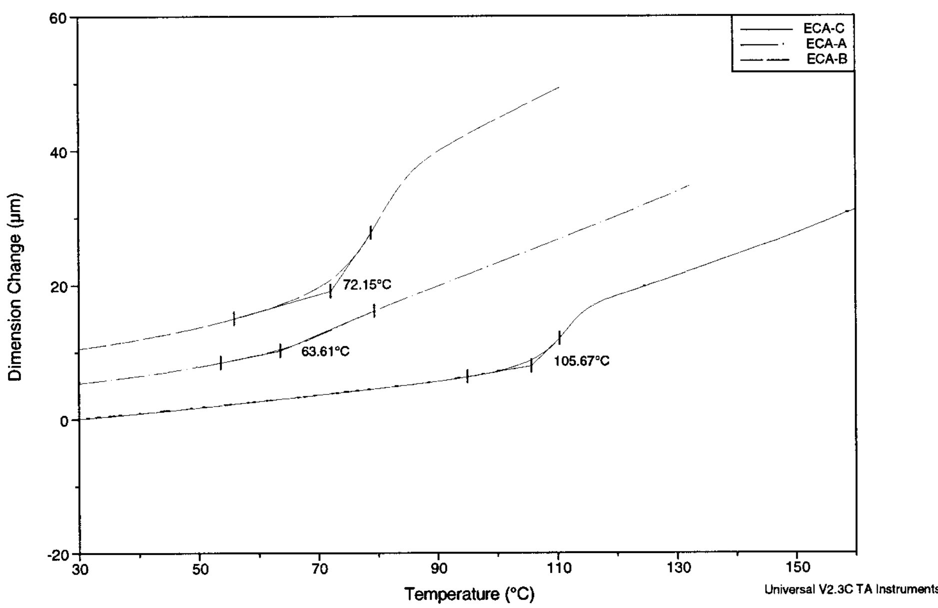

Figure 6 TMA curves of the conductive adhesives.

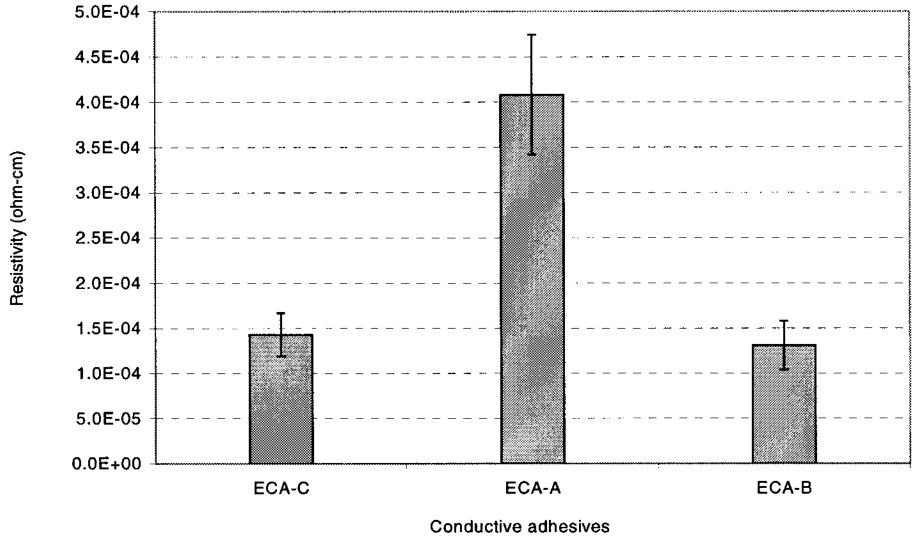

Figure 7 Bulk resistivity of the conductive adhesives.

moisture absorption, 0.25%, than both commercial materials (0.60 and 0.75%).

Die Shear Adhesion Strength

Die shear adhesion strength (at 25°C) of all the ECAs before and after 500-h 85°C/85% RH aging were tested, and results are given in Figure 10. As can be seen from the figure, all of the three ECAs showed comparable adhesion strengths both before and after aging.

Joint Resistance Variation

At present, compatibility of ECAs with Sn/Pb finished surface mount components is an important property although Sn/Pb finishing eventually might not be necessary. Therefore, ECAs that have stable joint resistance with Sn/Pb finished components and comparable other properties are particularly needed. A convenient joint resistance test device was specially designed for this study. Eutectic Sn/Pb wire was selected and used in the

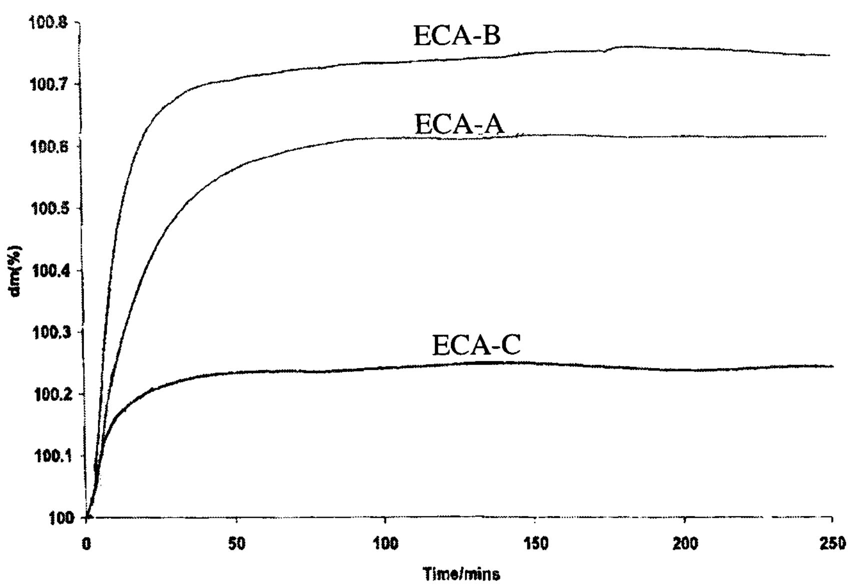

Figure 8 Dynamic moisture absorption of conductive adhesives.

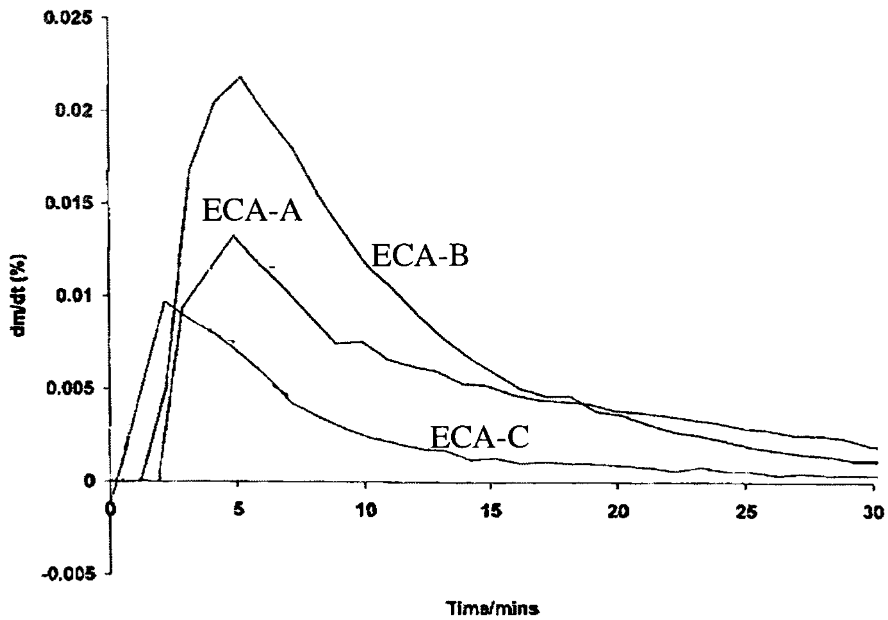

Figure 9 Kinetic moisture absorption of the conductive adhesives.

test device to simulate Sn/Pb finished surface mount components. Changes of joint resistance of these conductive adhesives with Sn/Pb solder wire during 85°C/85% RH aging are given in Figure 11. It was found that our in-house conductive adhesive showed no significant joint resistance change but the two commercial ECAs showed dramatic joint resistance increase after 500-h aging. Therefore, the in-house conductive adhesive had much better compatibility with Sn/Pb finished components.

CONCLUSIONS

An epoxy-based electrically conductive adhesive system that has improved compatibility with Sn/Pb finished components was developed. Com-

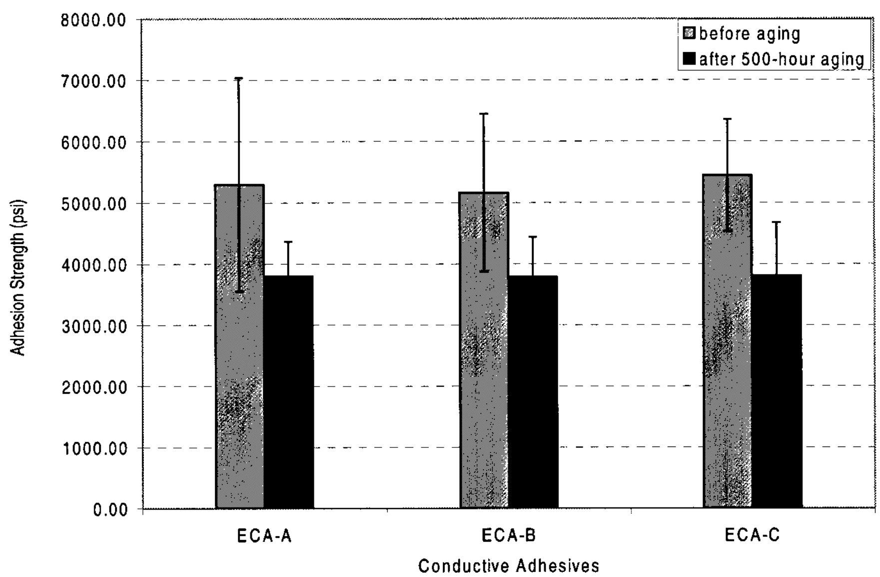

Figure 10 Adhesion strength of conductive adhesives before and after aging.

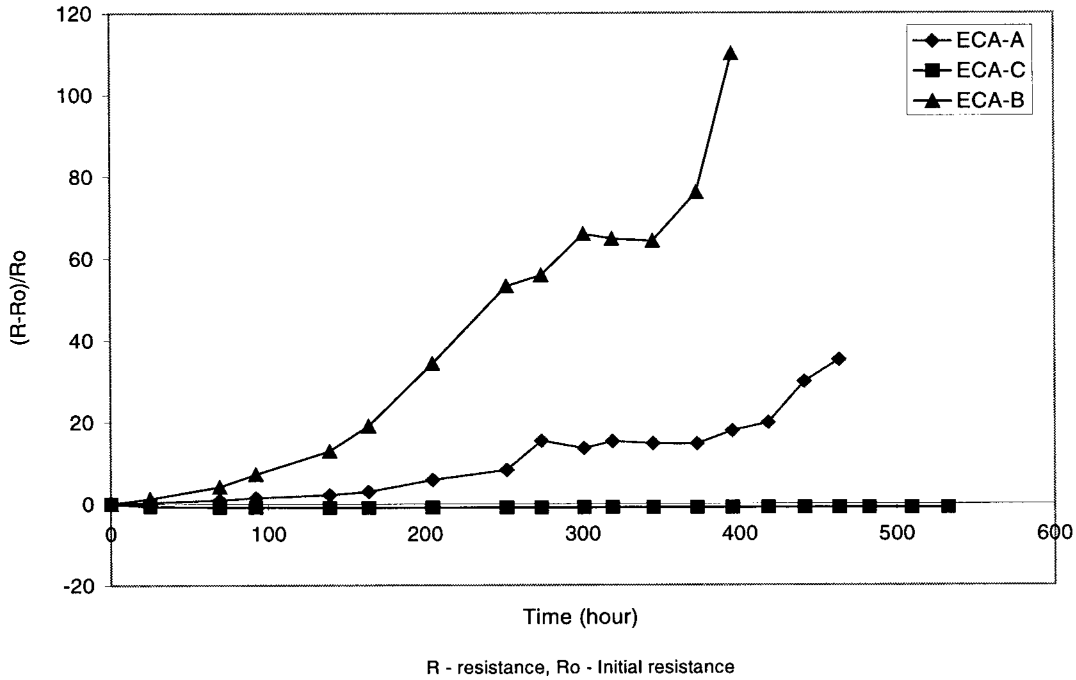

Figure 11 Shift of joint resistance of the ECAs during 85°C/85% RH aging.

pared to the two commercial surface mount conductive adhesives, this conductive adhesive has more stable joint resistance with Sn/Pb finished components, much lower moisture absorption, faster cure, comparable bulk resistivity, comparable adhesion strength, and higher glass transition temperature.

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