Development of Conductive Adhesives for Solder Replacement
Daoqiang Lu, Member, IEEE, and C. P. Wong, Fellow, IEEE

Abstract—With the phasing out of lead-bearing solders, electrically conductive adhesives (ECAs) have been identified as an environmentally friendly alternative to tin/lead (Sn/Pb) solders in electronics packaging applications. Compared to Sn/Pb solders, conductive adhesive technology offers numerous advantages. However, this new technology still has reliability limitations. Two critical limitations are unstable contact resistance on non-noble metals and poor impact performance. Our previous study proved that galvanic corrosion is the dominant mechanism for the unstable contact resistance during elevated temperature and humidity aging. The ultimate goal of this study is to develop conductive adhesives with stable contact resistance and desirable impact performance. In this study, effects of purity of the resins and moisture absorption on contact resistance are investigated. Several different additives (oxygen scavengers and corrosion inhibitors) on contact resistance stability during elevated temperature and humidity aging are studied, and effective additives are identified based on this study. Then, several rubber-modified epoxy resins and two synthesized epoxide-terminated polyurethane resins are introduced into ECA formulations to determine their effects on impact strength. The loss factor, tan δ, of each formulation is measured using a dynamic mechanical analyzer (DMA) and impact strength is evaluated using the National Center for Manufacturing Science (NCMS) standard drop test procedure. Finally, high performance conductive adhesives are formulated by combining the modified resins and the effective additives. It is found that 1) purity of the resins and moisture absorption of the formulation affect the contact resistance stability of an ECA; 2) the oxygen scavengers and corrosion inhibitors can delay contact resistance shift; 3) one of the corrosion inhibitors is very effective in stabilizing the contact resistance; 4) some rubber-modified epoxy resins and the epoxide-terminated polyurethane resins can provide the conductive adhesives with superior impact performance; and 5) conductive adhesives with stable contact resistance and desirable impact performance are developed.

Index Terms—Conductive adhesives, contact resistance shift, corrosion inhibitors, electronics packaging, impact performance, oxygen scavengers, solder replacement.

I. INTRODUCTION

SOLDERING technology using tin/lead (Sn/Pb) solders plays an important role in electronic packaging, such as flip-chip, solder-ball connections in ball grid arrays (BGA), and integrated circuit (IC) package assembly to a printed circuit board [1]. With advances in microelectronics, some issues associated with Sn/Pb solders have become noticeable. From the environmental point of view, lead-containing solders are harmful to the environment and human beings [2]. Lead is highly toxic to human beings and has been eliminated from gasoline and paint. Eliminating lead from electronic packages is underway [3]. Another limitation of solder paste exists in its use for fine pitch components. The current solder paste technology used in surface mount technology (SMT) cannot handle this very fine pitch interconnection due to the soldering defects such as bridging or soldering balling [2]–[4]. In the electronic industry, two groups of materials are being investigated currently as possible alternatives for lead-containing solders: lead-free solders [5], [6] and electrically conductive adhesives [7]–[9], [25].

Compared to the mature soldering technology, conductive adhesive technology is still in its infancy. Concerns and issues do exist. Two critical issues of conductive adhesives for surface mount applications are contact resistance shift and poor impact performance. Contact resistance of ECAs on non-noble metals increases dramatically when the ECA joints are exposed to elevated temperature and humidity environments [10]–[13]. Our previous study indicated that galvanic corrosion was the dominant mechanism for the increase of contact resistance [12]. Also, current conductive adhesives have poor impact performance [14], [15]. The components joined by ECAs separated from the printed circuit board (PCB) when the assemblies experience significant shocks during assembly, handling, and throughout product life. Impact performance of ECAs can be tested using a standard drop test [11]. A simple approach is to decrease the filler loading to improve the impact strength. However, such a process reduces the electrical properties of the conductive adhesives [11]. It was reported recently that conductive adhesives were developed using resins with low modulus so that this class of conductive adhesives was able to absorb the impact energy developed during the drop [16]. However, these developed materials lacked mechanical strength. Also, conformal coating of the surface mount devices was used to improve mechanical strength. It was demonstrated that conformal coating could improve the impact strength of conductive adhesives joints [17]. In this study, conductive adhesives with stable contact resistance and superior impact performance were developed.

II. EXPERIMENTAL

A. Materials

A bisphenol-F type epoxy resin, Epon 862, was obtained from the Shell Chemical Company. A cycloaliphatic epoxy resin, ERL4299, was supplied by Union Carbide. Epoxy hardeners including methylhexahydrophthalic anhydride...
(MHHPA), 2-ethyl-4-methyl imidazole (2E4MZ), oxygen scavengers, corrosion inhibitors and sodium chloride were all purchased from the Aldrich Chemical Company and used without further purification. Two commercial rubber-modified epoxy resins were purchased from Shell Chemical Company and Dainippon Ink and Chemicals, Incorporated. The silver flakes used were purchased from Degussa Corporation.

B. Study of Contact Resistance Shifts

Contact resistance of an ECA on a metal was measured using the test device in Fig. 1. The device consists of metal patterns printed on a PCB. Conductive adhesives were dispensed on the gaps between every two metal patterns. After the adhesive was cured, the resistance of a circuit was measured from two ends of the pattern using a multimeter from Keithley, model 2000, with a four-point probe. Three specimens were prepared for each sample. The specimens were exposed to 85 °C/85% relative humidity (RH) in a temperature and humidity chamber from Luanrai Environmental, model CEO932W-4. Contact resistance of each specimen was measured periodically. The average contact resistance of the three specimens was reported.

C. Study of the Effects of Oxygen Scavengers and Corrosion Inhibitors

A small amount (5 part per hundred part resin) of an additive (an oxygen scavenger or a corrosion inhibitor) was added to a base ECA formulation. Shifts of the contact resistance (on Sn/Pb surface) of conductive adhesives with and without the additives during 85 °C/85%RH aging were measured and compared.

D. Electrochemical Study on Corrosion Inhibitors

The experiments were carried out with Sn/Pb electrodes which were made using 99.9% Sn/Pb ribbon. Measurements were taken at a conventional electrolytic cell with a platinum counter electrode using a saturated calomel electrode as the reference electrode. The electrolyte was 0.2 mol/liter sodium chloride (NaCl) without and with the addition of the investigated organic corrosion inhibitors at a concentration of 0.001 mol/liter. Before each measurement, the electrode was kept in the electrolyte solution for 18 hours. The surface of the Sn/Pb electrode was refreshed using very fine sand paper before each measurement. The protecting characteristics of the inhibitors were examined by potentiostatic polarization method. Steady-state current voltage measurements were used to obtain information about reactions of adsorption of inhibitors. Polarization resistance $R_p$ was determined as the slope ($dE/di$) plot was measured in the vicinity of the corrosion potential starting from cathodic potential ($E = E_{corr} - 2$ mV) to the anodic potential ($E = E_{corr} + 2$ mV). The measurements procedures assured good reproducibility of results. The electrochemical measurements (potentiostatic polarization and determination of polarization resistance) were performed using a Potentiostat/Galvanostat, model 272, from Princeton Applied Research. The experiments were carried out at room temperature (25 °C).

E. Dynamic Mechanical Analysis of ECAs

Dynamic mechanical properties of cured conductive adhesives were investigated using a dynamic mechanical analyzer (DMA) from TA Instruments, model 2980, with a film tension clamp. The samples were prepared based on the following procedures:

1) spray some mold releasing agent inside a die with dimensions of 40 mm long, 8 mm wide, and 1.5 mm thick;
2) dispense a conductive adhesive paste into the die;
3) cure the adhesive samples in an oven;
4) remove the cured sample from the die;
5) polish the cured samples until smooth surfaces are obtained.

In a DMA dynamic scan study, after a sample was mounted on the clamp, the temperature was raised from 25–250 °C at a heating rate of 3 °C per min. In a frequency sweep study, the frequency was raised from 0.1–180 Hz at room temperature. $\tan \delta$ value versus frequency was recorded.

F. Study of Impact Performance of ECAs

Drop tests were conducted based on the standard established by the National Center of Manufacturing Science (NCMS). 44 I/O plastic leaded chip carriers, PLCC, were used in drop tests to evaluate the impact performance of the conductive adhesives. The drop test procedure could be found elsewhere [18].

III. RESULTS AND DISCUSSION

A. Effects of Resin Purity and Moisture Absorption on Contact Resistance Shifts

Our previous study strongly indicated that galvanic corrosion is the main mechanism for the unstable contact resistance of conductive adhesives on nonnoble metals. Electrolyte solution is one of the requirements for galvanic corrosion. Electrolytes increase the electrical conductivity of the solution, accelerate galvanic corrosion, and cause larger contact resistance increase.

The effects of four electrolytes, sodium chloride (NaCl), sodium acetate (NaOAc), ammonium chloride (NH$_4$Cl), and ammonium sulfate ((NH$_4$)$_2$SO$_4$), on contact resistance shifts of an ECA on Sn/Pb metal were investigated. The concentration of each electrolyte was 0.5 part per 100 parts of the resin of the ECA. The contact resistance of the ECAs on Sn/Pb with and without the electrolytes was measured periodically during 85°C/85%RH aging. The results are shown in Fig. 2.

As can be seen from Fig. 2, the ECAs with the added electrolytes showed faster increase of contact resistance than the...
TABLE I
COMPOSITIONS OF THREE ECAS

<table>
<thead>
<tr>
<th>ECA</th>
<th>Epon-862</th>
<th>ERL-4299</th>
<th>MHHPA</th>
<th>2E4MZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECA-I</td>
<td>5.0</td>
<td>0.0</td>
<td>4.18</td>
<td>0.090</td>
</tr>
<tr>
<td>ECA-II</td>
<td>3.0</td>
<td>3.0</td>
<td>4.7</td>
<td>0.11</td>
</tr>
<tr>
<td>ECA-III</td>
<td>0.0</td>
<td>6.0</td>
<td>4.2</td>
<td>0.10</td>
</tr>
</tbody>
</table>

ECA without the added electrolytes. This is because the electrolytes accelerated galvanic corrosion and thus caused faster increase of contact resistance. It can be concluded from this study that, in order to stabilize contact resistance during aging, resins with high purity should be used to formulate ECAs.

The water condensed from the absorbed moisture at the interface between an ECA and the metal formed the electrolyte solution which was required for galvanic corrosion. Therefore, an ECA with lower moisture absorption is expected to show slower contact resistance shift during aging due to its slower corrosion rate at the interface.

Three ECA (ECA-I, ECA-II, and ECA-III) formulations which consisted of different epoxy resins but the same hardener and catalyst were studied. The detailed compositions of the resins of these ECAs are shown in Table I. These three ECAs had similar properties but different moisture absorption. The moisture absorption of the cured resins of these ECAs is shown in Fig. 3. As can be seen from this Figure, ECA-III had the highest moisture absorption and ECA-I showed the lowest moisture absorption.

The contact resistance shifts of these ECAs on Sn/Pb were compared and are shown in Fig. 4. Comparing Figs. 4 and 3, it was found that the ECA with the highest moisture absorption (ECA-III) showed the fastest contact resistance shift and the ECA with the lowest moisture absorption (ECA-I) showed the slowest contact resistance shift during aging. There is a correlation between moisture absorption and contact resistance shift. Therefore, one of the approaches to formulate an ECA with more stable contact resistance is to select epoxy and hardener combinations which can provide ECAs with lowest moisture absorption.
B. Effects of Oxygen Scavengers and Corrosion Inhibitors on Contact Resistance

1) Effects of Oxygen Scavengers: Our previous study indicated that metal oxide formation resulting from galvanic corrosion was responsible for the increase of contact resistance of an ECA on nonnoble metals [12]. The cathodic reaction of the galvanic corrosion is:

\[
2\mathrm{H}_2\mathrm{O} + \mathrm{O}_2 + 4e^- = 4\mathrm{OH}^-.
\]

The rate of the reaction is controlled by the rate at which oxygen reaches the adhesive-metal interface [19], [21]. Since oxygen scavengers can react with dissolved oxygen in aqueous solution, they can consume the oxygen diffused into the ECA joints and thus delay the galvanic corrosion [20].

Three oxygen scavengers (OS1, OS2, OS3) were used in this study. Shifts of contact resistance of the ECAs with and without the added scavengers are shown in Fig. 5. As can be observed from Fig. 5, the ECAs with the oxygen scavengers showed slower increase of contact resistance than the ECA without scavengers, and OS1 was the most effective among the three scavengers. The detailed chemical structures of these oxygen scavengers will be found in a U.S. patent [22].

2) Effects of Corrosion Inhibitors:

Effects on corrosion inhibitors on contact resistance: Corrosion inhibitors are specific chemical agents that significantly reduce the corrosion rate that is observed in the absence of the inhibitor. In general, the mechanism of corrosion inhibition by organic corrosion inhibitors is considered to be primarily by adsorption of the organic compound and separation of the metal from the environment [19], [21].

The effects of two corrosion inhibitors (Inh1 and Inh2) on contact resistance were investigated. The detailed chemical structures of these oxygen scavengers will be found in a U.S. patent [22]. The shifts of contact resistance of ECAs with and without corrosion inhibitors during 85 °C/85%RH aging were measured and compared. The results are shown in Fig. 6. The ECAs with corrosion inhibitors showed smaller increase of contact resistance than the ECA without inhibitors, and OS1 was the most effective among the three scavengers. The detailed chemical structures of these oxygen scavengers will be found in a U.S. patent [22].

Therefore, only Inh1 will be used in high performance ECA materials.

Electrochemical study on corrosion inhibitors: The purpose of this electrochemical study was to elucidate the effects of corrosion inhibitors on decreasing the corrosion rate and stabilizing contact resistance. The potentiostatic polarization curves of Sn/Pb in the electrolyte solutions without and with the corrosion inhibitors are shown in Fig. 7. Polarization resistance (\(R_p\)) was determined as the slope plot was measured in the vicinity of the zero current. The polarization conductance (\(1/R_p\)), which are directly proportional to the corrosion current, was measured on Sn/Pb electrodes in the solutions. Therefore, if the Sn/Pb shows a higher polarization conductance in a solution, it is more susceptible to corrode in that solution. The polarization resistance and polarization conductance of the Sn/Pb in the electrolyte solutions without or with the inhibitors are shown in Table II. As can be seen from the Table, Sn/Pb had a much lower polarization conductance in the electrolyte solution with Inh1 than the one without inhibitor. But Sn/Pb showed slightly lower polarization conductance in Inh2 electrolyte solution than in the electrolyte solution without inhibitor. The results clearly indicated that Sn/Pb showed a much slower corrosion rate in NaCl solution with Inh1 than Inh2. Therefore, Inh1 could stabilize contact resistance of ECAs on Sn/Pb much more effectively than Inh2.

C. Improvement of Impact Performance of ECAs

High impact strength is a critical parameter of a high performance conductive adhesive. Without adequate impact strength, ECA joints cannot survive the significant shocks encountered during assembly, handling and throughout the product life [11]. Impact strength of a material is closely related to its damping property, the capability to dissipate energy which is represented by the loss factor, \(\tan \delta\), of a material. In general, a material with a high \(\tan \delta\) should have higher impact strength and better impact performance.

The impact performance of an ECA was determined using a drop test following the standard procedure established by the NCMS [11]. If the test sample survived 6 drops from a height...
Fig. 7. Potentiostatic polarization curves of (a) Sn/Pb in 0.2 M NaCl without the addition of an inhibitor, (b) curve 0.2 M NaCl with 0.001 M Inh1, and (c) curve 0.2 M NaCl with 0.001 M Inh2.

of 60 in without the 44 I/O PLCC popping off, then this material “passed the drop test” exhibiting acceptable impact strength as a solder replacement adhesive.

In this study, two rubber-modified epoxy resins, and two synthesized epoxide-terminated polyurethane resins were used as the base resins in ECA formulations. In these formulations, an anhydride was selected as the curing agent because anhydrides were found to provide ECA formulations with low moisture absorption and relatively stable contact resistance [23]. Also liquid anhydride was helpful to decrease the viscosity of the formulations because most rubber-modified epoxy resins had a high viscosity. For comparison, an ECA which was formulated with a bisphenol-F type epoxy resin was used as a control in this study.

1) ECAs Based on Rubber-Modified Epoxy Resins: Two rubber-modified epoxy resins were used to formulate three ECAs (ECA-1 and ECA-2). Thermal cure behavior, damping property, and impact strength were studied.

Fig. 8 shows the tan δ value changes with different frequency at the frequency range from 0.1–180 Hz. It can be seen that both ECA-1 and ECA-2 had a much higher tan δ value than the control over the entire frequency range tested. Therefore, both ECAs are expected to have better impact performance than the control in this frequency range. Drop tests on these three ECAs indicated that ECA-1 and ECA-2 passed 6 drops from a 60-in height but the control failed the drop test. This result was consistent with the tan δ results.

2) ECAs Based on Epoxide-Terminated Polyurethane Resins: Two epoxide-terminated polyurethane resins were synthesized in our lab and were used to formulate ECAs (ECA-3 and ECA-4) [24].

Fig. 9 shows the tan δ changes with frequency in the frequency range from 0.1–180 Hz. As can be seen from Fig. 8, both ECAs formulated with the epoxide-terminated
polyurethane resins had higher $\tan \delta$ values than the control. Therefore, these materials should have good impact strength in the frequency range. The impact strengths of these materials were evaluated by the NCMS drop test. It was found that both ECA materials passed drop test and showed desirable impact performance.

D. Development of ECAs with Stable Contact Resistance and Superior Impact Performance

As a solder replacement, conductive adhesives must have desirable impact performance, stable contact resistance on nonnoble metal surfaces, and low resistivity (less than $10^{-3}$ ohm-cm) [11]. Based on the results in the previous sections, conductive adhesives with desirable impact performance and stable contact resistance were formulated by combining a rubber-modified epoxy resin or an epoxide-terminated polyurethane resin and an additive used in the previous section. Inh1 was chosen as the additive because it could stabilize contact resistance effectively. Four ECAs (ECA-A, ECA-B, ECA-C, and ECA-D) were formulated using above four resins and the anhydride. The contact resistance shifts on a nonnoble metal (Sn/Pb) and impact performance of the formulated conductive adhesive were studied. The shifts of contact resistance are shown in Fig. 10. From Fig. 10, shifts of the contact resistance of these ECA on Sn/Pb after 500-hour aging were less than 20%, which met the NCMS requirement on contact resistance shifts for solder replacement adhesives [11]. Also, drop test results indicated that these ECAs passed 6 drops from a 60-inch height. As such, these ECA also met the NCMS drop test requirement and had desirable impact strength. In addition, the resistivity of all these ECAs was in the range of $10^{-4}$ Ω·cm. Therefore, these conductive adhesives met all of the NCMS requirements for solder replacement conductive adhesives.

IV. CONCLUSION

ECAs formulated with resins of higher purity show more stable contact resistance. Also, ECAs with lower moisture absorption tend to have more stable contact resistance. Both oxygen scavengers and corrosion inhibitor can somewhat delay the increase of contact resistance of ECAs on nonnoble metals. However, the corrosion inhibitors are more effective than the oxygen scavengers in term of stabilizing contact resistance. Inh1 can stabilize contact resistance of ECAs on a nonnoble metal (Sn/Pb in this case) most effectively because Sn/Pb had lowest polarization conductance with the presence of Inh1.

ECAs based on some rubber-modified epoxy resins and epoxide-terminated polyurethane resins show much higher $\tan \delta$ values and improved impact strength. Conductive adhesives with stable contact resistance and desirable impact performance are developed by combining a rubber-modified epoxy resin or an epoxide-terminated polyurethane resin and a corrosion inhibitor (Inh1). The formulated ECA meet all the NCMS requirements for surface mount solder replacement conductive adhesives.
REFERENCES


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