Enhancement of Electrical Properties of Electrically Conductive Adhesives (ECAs) by Using Novel Aldehydes

Yi Li, *Member, IEEE*, Kyoung-Sik Moon, Andrew Whitman, and C. P. Wong, *Fellow, IEEE*

***Abstract*—To improve the electrical properties of electrically conductive adhesives (ECAs), different types of aldehydes, salicylaldehyde and transcinnamaldehyde, were introduced into ECA formulations. During the curing process, the aldehydes acted as a reducing agent and reduced metal oxide in ECAs. At the same time, aldehydes could consume ambient oxygen and prevent the oxidation of the metal fillers in the ECA. The oxidation product of aldehydes, carboxylic acids with shorter molecular chains, could partially replace or remove the long chain stearic acid (C_{18}) surfactant on the lubricated Ag flakes and enhance the electrons tunneling between the Ag flakes in the ECAs. As such, the multiple effects of aldehydes in ECAs improved the conductivity significantly. Dynamic mechanical analysis and thermomechanical analysis studies indicated the improved performance for mechanical and physical properties of ECAs as well.**

***Index Terms*—Electrically conductive adhesives (ECAs), electrical properties improvement, electronic packaging, *in-situ* replacement.**

I. Introduction

SOLDERING processes with tin–lead solders (Sn–Pb) have been the main interconnection technologies in most areas of electronic packaging, including interconnection technologies such as pin through hole (PTH), surface mount technology (SMT), ball grid array (BGA), chip scale package (CSP), flip chip and so on [1], [2]. With advances in microelectronics, some issues associated with Sn–Pb solders have become noticeable. The use of lead in the elctronic devices is becoming a more and more serious concern for the comsumers and the manufacturing industry due to the alloy's arguably harmful impact on the environment. Recently, the elimination of lead-containing materials from electronics industry has become important and will soon become a legislative regulation [3]–[5]. As part of the effort to achieve "green electronics manufacturing," many research activities are now focused on the alternative interconnection materials to tin–lead solder in the elctronic packaging industry. Electrically conductive adhesives (ECAs) have been identified as a major alternative to the traditional tin–lead solder due to numerous advantages, such as fewer processing steps which reduce processing cost, lower processing temperature which makes use of heat-sensitive and low cost components and substrates possible, and fine pitch capability [6]–[9]. However, compared to the mature soldering technology, there are several limitations for conductive adhesives, such as relatively lower conductivity and unstable contact resistance [10]–[14].

Isotropic conductive adhesives (ICAs), the major type of ECA, are composites of polymer matrix and conductive fillers. In an ICA interconnect junction, the polymer resin provides mechanical interconnection and the conductive filler provides electrical conductivity. In order to maximize the electrical conductivity, high filler loadings are needed in the ICA formulation. However, too high filler loadings deteriorate the mechanical property of the ECA. Therefore, the challenge in formulating an ICA is to achieve a high electrical conductivity without adversely affecting the mechanical properties.

Silver flakes coated with stearic acid (C-18 carboxylic acid, the structure is shown in Table I) surfactant are widely used as the conductive fillers in most ICA formulations [15]. The presence of such organic lubricants can reduce the viscosity of conductive adhesive paste and prevent agglomeration of silver flakes, but it can also decrease the conductivity of the ICAs due to the insulative property of the surfactant. A possible solution to this problem is the introduction of short chain carboxylic acids to the Ag flakes. Our previous study showed that by *in-situ* replacing the stearic acid with short chain dicarboxylic acids, the conductivity of the ECAs could be improved [16]. For the short chain carboxylic acid, it is much easier for the electrons to tunnel/transport because of the more intimate contact between Ag flakes. Therefore, the electrons could more easily transport through the organic acid and enhance the electrical conductivity. However, there are still some issues to be addressed. The carboxylic acids are solid in state, thus they are not easily dissolved into the epoxy resin. After the addition of short chain carboxylic acid, the viscosity of ECA increased due to some premature reaction of the acid with the epoxy. Furthermore, with the higher loading of the acid in the ECA formulation, the resulted higher viscosity introduced some processing problems. In the present study, different types of aldehydes rather than carboxylic acids are introduced in a commercially available ECA. The effects of the aldehydes on the electrical performance and mechanical and physical properties of the ECAs are investigated.

II. Experimental

A commercially available ECA (XCE3050 from Emerson and Cumming) was used as a base formulation. Two different

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Color versions of Figs. 3–6, 9, and 10 are available at http://ieeexplore.ieee.org.

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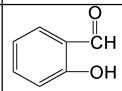
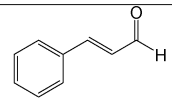
TABLE I
CHEMICAL STRUCTURES OF THE ACIDS

Chemical Name	Chemical Structure	Molecular Weight	Oxidation product	PKa of acids at room temperature
Stearic acid	$CH_3(CH_2)_{16}COOH$	284.48		5.3
Salicylaldehyde (ALD1)		122.12	Salycylic acid	2.97
Trans-cinnamaldehyde (ALD2)		132.16	Trans-cinnamalic acid	4.5

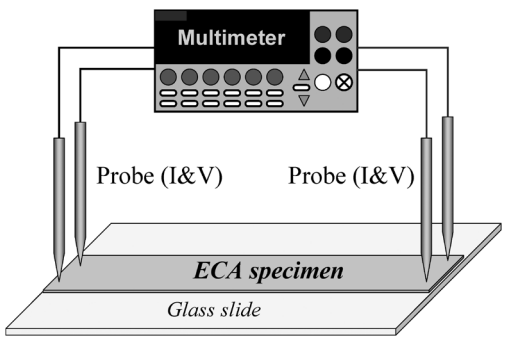


Fig. 1. Schematic illustration of a bulk resistivity test coupon.

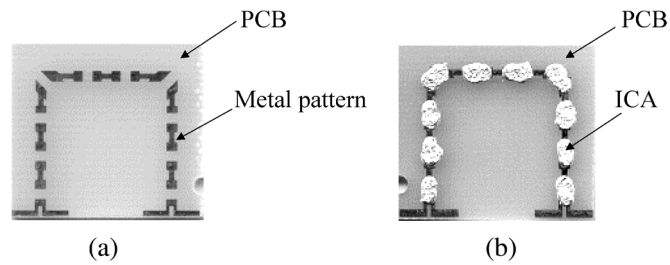


Fig. 2. Contact resistance test device (a) before ECA deposition and (b) after ECA deposition.

types of aldehydes, salicylaldehyde (ALD1) and trans-cinnamaldehyde (ALD2), were added into the ECA (structures and molecular weights of the aldehydes are shown in Table I) and mixed, respectively. After preparing the samples, the curing behaviors were determined using a modulated differential scanning calorimeter (MDSC) from TA Instruments, model 2970. The dynamic scans were made on the samples in nitrogen at a heating rate of 5 °C/min, usually from 25 °C to 250 °C.

Resistivity of the ECAs was calculated from the bulk resistance of the specimen with specific dimensions. Two strips of an adhesive tape were applied on to a precleaned glass slide with a gap width of 6.62 mm between these two strips. The conductive adhesive paste was then doctor-bladed within the gap space, and then the tapes were removed. After cure, the bulk resistance (R) of the ICA strips was measured as well as the size of the specimen. A schematic of the bulk resistivity coupons is shown in Fig. 1. The bulk resistivity, ρ, and conductivity, σ were calculated using following equations:

$$\rho = \frac{t \times w}{l} \times R$$
$$\sigma = \frac{1}{\rho} = \frac{l}{t \times w} \times \frac{1}{R}$$

where l, w, and t are the length, width, and thickness of sample, respectively.

Contact resistance of an ECA on Sn surface is measured using the test device illustrated in Fig. 2. The device consists of metal patterns (e.g., Sn finish) printed on a printed circuit board (PCB). Conductive adhesives are dispensed on the gaps between every two metal patterns. After the adhesive is cured, the resistance of a circuit is measured from two ends of the pattern using a multimeter with a four-point probe. The specimens are exposed to 85 °C/85% relative humidity (RH) in a temperature/humidity chamber (Lunaire Environmental, model CEO932W-4). Contact resistance of each specimen is measured periodically for 500 h and reported.

To characterize the reaction between aldehydes and Ag flakes during the heating process, the weight loss of silver flakes before and after treatment in aldehyde solutions was measured using a thermogravimetry analyzer (TGA, TA Instruments, model 2050) in air. The temperature was raised from 25 °C to 500 °C at a heating rate of 10 °C/min. One mM aldehyde solutions were prepared to treat the Ag flakes and the treating time was 24 h. After treatment, the Ag flakes were removed from the solution and rinsed with ethanol in order to remove excess aldehyde. The solvent was then dried out under a controlled nitrigen atmosphere.

The rheological study of the ECA was conducted with a stress-controlled rheometer, from TA Instruments, model AR1000-N. A 4-cm steel parallel plate fixture was used in the study. The gap between two plates was set at 300 μm. The viscosity of the adhesive formulations was measured at room temperature under an oscillation mode.

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. After a sample was mounted on the clamp, the temperature was raised from 25 °C to 200 °C at a heating rate of 3 °C/min. The sample was studied under an oscillation mode with a frequency of 1 Hz. Storage modulus and tan delta versus temperature were recorded.

Coefficients of thermal expansion (CTEs) and glass transistion temperatures (Tgs) of ECA samples were measured with a thermomechnical analyzer (TMA) from TA Instruments, model 2940. An expansion probe was used and a static force applied on this probe was set to 0.050 Newton. Temperature was ramped from 25 °C to 200 °C at a heating rate of 5 °C/min. The dimension change with temperature was recorded. The slope of the straight line below the Tg was calculated as the CTE, $\alpha 1$, of the sample.

III. Results and Discussion

The weight loss of silver flakes before and after treatment in aldehyde solutions was studied using a thermogravimetry analyzer (TGA) (Fig. 3). For the untreated Ag flakes, obvious weight loss over 0.2% was observed at the temperature ranging from 150 to 250 °C, due to the presence of organic lubricants on the Ag flakes. After treated in aldehyde solutions, the Ag flakes firstly showed increased weight around 0.1%–0.2% at lower temperatures of 50 °C–100 °C. This indicates that the aldehyde has been coated on the Ag flake surfaces after treatment. At these temperatures, the coated aldehyde may be oxidized to carboxylic acid and therefore led to the increased weight

$$2\mathrm{R}-\mathrm{CHO}+\mathrm{O}_2 \xrightarrow{\Delta} 2\mathrm{R}-\mathrm{COOH}. \quad (1)$$

When it is assumed that an orgranic material forms a layer on the whole particle surface, the weight ratio of the organic layer to the particle can be calculated as following (2). For simplicity, the particles were considered as perfect spheres

$$\begin{aligned}\text{Weight ratio} &= \frac{\text{surface area} * t * D_{\text{aldehyde}}}{\text{volume of particles} * D_{\text{Ag}}} \\ &= \frac{4\pi r^2 * t * D_{\text{aldehyde}}}{\frac{4}{3}\pi r^3 * D_{\text{Ag}}} = \frac{3t * D_{\text{aldehyde}}}{r * D_{\text{Ag}}} \quad (2)\end{aligned}$$

where r and t refer to the radius of the particles and thickness of the organic layer, and $D_{\text{aldydehyde}}$ and D_{Ag} refer to the density of aldehydes and Ag flakes, respectively. The radius of particles used was around 1 μm and the molecular length for the organic layer was approximately 1 nm. $D_{\text{aldydehyde}}$ and D_{Ag} are 1.1 and 10.49 g/cm^3, respectively. Also, for the flakes and spheres with the same volume, the ratio of surface area of spheres to flakes is around 0.28 [17]. Therefore, the weight ratio for the organic layer could be deducted as (3). The calculated value of 0.1% was very much close to the weight change obtained from TGA result

$$\begin{aligned}\text{Weight ratio} &= \frac{3t * D_{\text{aldehyde}}}{r * D_{\text{Ag}}}/0.28 \\ &= \frac{3 * 1 * 10^{-7}\ \text{cm} * 1.1\ \text{g/cm}^3 *}{1 * 10^{-4}\ \text{cm} * 10.49\ \text{g/cm}^3}/0.28 \\ &\approx 0.1\%. \quad (3)\end{aligned}$$

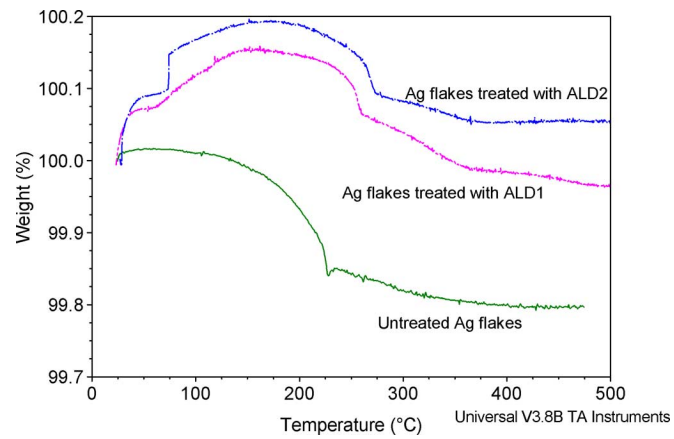


Fig. 3. Thermogravimetric analysis curves of Ag flakes before and after treating with aldehydes.

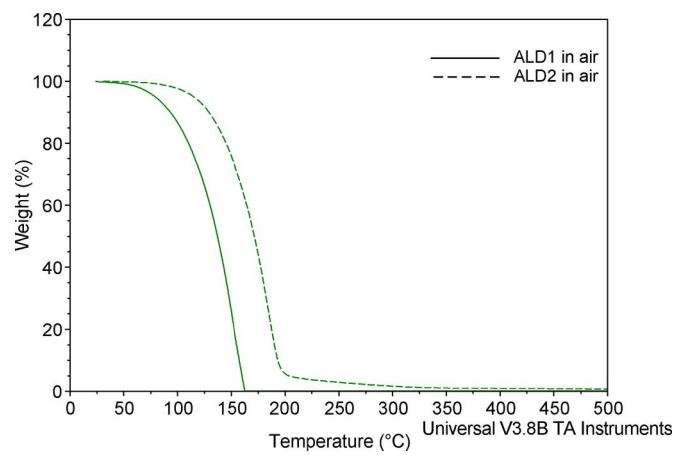


Fig. 4. Thermogravimetric analysis curves of aldehydes.

The treated Ag flakes, after increasing weight at lower temperature, showed around 0.1% weight loss at higher temperatures similar to those for untreated samples (150 °C–250 °C). However, the amount of weight loss was lower than that of untreated Ag flakes. Therefore, the surfactant on Ag flakes have been partially replaced or removed by the formed salycylic acid and trans-cinnamalic acid which have lower pKa values than stearic acid (Table I). Lower Pka value indicates stronger acidity and therefore better affinity to Ag flakes.

Although obvious weight increase was found for Ag flakes treated with aldehyde, similar phenomenon could not be observed for aldehyde itself (Fig. 4). The final weight loss at around 100 °C and 170 °C for the aldehydes corresponded to their evaporation/decomposition. Thus, the oxidation of aldehyde at relatively lower temperature might be catalyzed by Ag flakes.

Fig. 5 illustrates the curing profile of ECAs before and after the addition of aldehydes. All ECAs showed similar curing behaviors and had exothermic peak temperatures ranged from 150 °C to 200 °C. The total reaction heat of the curing of ECAs slightly decreased after the addition of aldehydes (Table II). The change was negligible compared to that observed for dicarboxylic acids [16], indicating there was no severe reaction

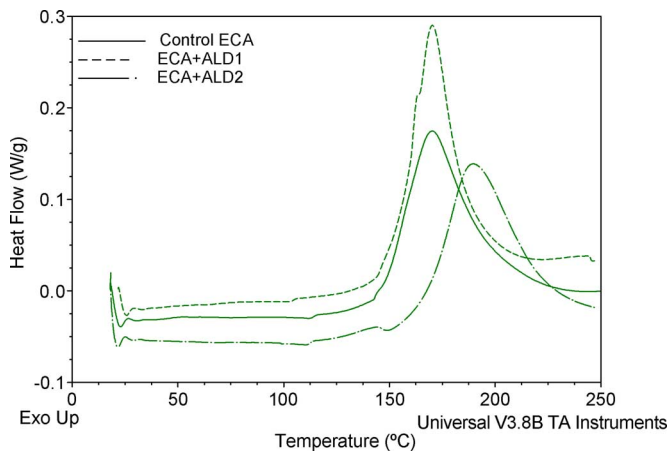


Fig. 5. Curing behavior of the ECAs with aldehydes.

TABLE II
CURING PROFILE OF ECA WITH ALDEHYDES

Formulations	Peak temperature (°C)	Reaction heat (J/g)
ECA control	170	92
ECA+ALD 1	170	85
ECA+ALD 2	188	83

between ECAs and aldehydes during the mixing process at room temperature and the prematured curing did not happen.

The bulk resistivity of ECAs with different loading levels of ALD1 and ALD2 is shown in Fig. 6. The resistivity of ECAs was dramatically decreased by incorporating aldehydes. The best results were achieved for ECAs with 1 wt% of aldehydes, for which the conductivity of ECAs has been improved over 40% and 30% for AlD1 and ALD2, respectively. By introducing aldehydes into ECAs, the bulk resistivity could be achieved as low as $6 \times 10^{-5}\ \Omega - \mathrm{cm}$, which is comparable to that of eutectic solders $(10^{-5} - 10^{-4}\ \Omega - \mathrm{cm})$. The possible mechanism for the improvement of conductivity is due to the reducing effects of aldehydes. The aldehydes could reduce the metal oxides that exist on the surface of metal fillers in ECAs during the curing process (4). Although silver oxide has been recognized as electrically conductive which is superior to other metal oxides, the conductivity is still much lower than silvers. Therefore, the oxidation of aldehydes and the subsequent reduction of the silver oxide to silver resulted in the conductivity improvement

$$\mathrm{R-CHO + Ag_2O \rightarrow R-COOH + 2Ag.} \tag{4}$$

Another contribution of aldehydes to the conductivity improvement is due to their consumption of oxygen during heating. From the TGA results [Fig. 3 and (1)], it was observed that the aldehydes could consume oxygen and be oxidized to carboxylic acid in the presence of Ag flakes. Thus, the metal fillers in ECAs were prevented from oxidation due to the low level of oxygen. The oxidation product of aldehydes, carboxylic acids, which are stronger acids and have shorter molecular length than C-18 stearic acid, can partially replace

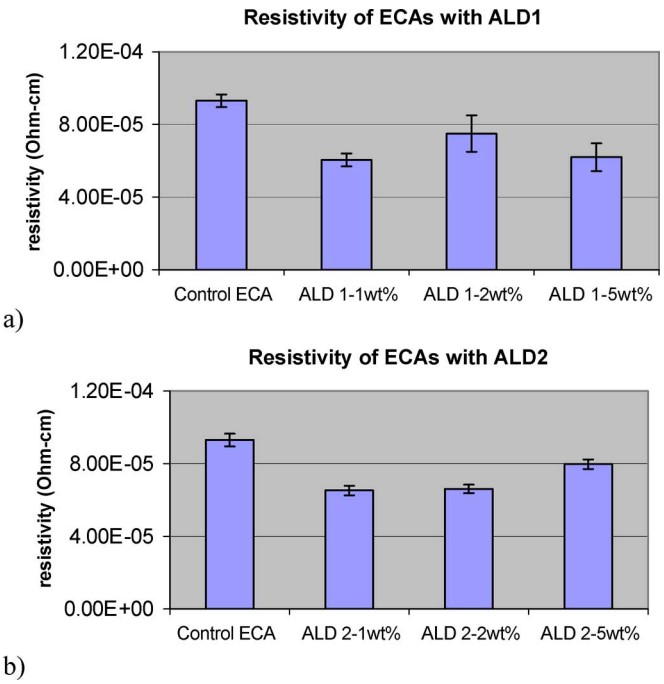


Fig. 6. Effects of aldehydes on the conductivity of ECA.

or remove the stearic acid on Ag flakes. The connection of silver flakes with short chain carboxylic acid facilitates electrons transport along the chain and helps electrons tunnelling. Furthermore, the resulted carboxylic acid can also act as a reducing agent and keep the metal filler from oxidation and maintain higher conductivity of the ECA. The multiple functions of aldehydes in ECAs thereby improved the electrical conductivity significantly.

The effects of the aldehydes on contact resistance were also investigated. The contact resistance shifts of ECAs on a Sn surface with and without aldehydes during 85 °C/85% RH aging are shown in Fig. 7. The Sn surface has been known to be most easily oxidized and corroded with aging, and consequently the dramatically increased contact resistance for all samples was observed. Nevertheless, with a longer aging time, the contact resistance of ECAs with aldehydes was slightly lower than that of a control sample. This may be due to the formed carboxylic acids which served as reducing agent to maintain good metallic contact and slow down the corrosion. But to get a satisfactory stabilized contact resistance, suitable corrosion inhibitors or sacrificial anodes have to be incorporated to achieve high reliability adhesives [9].

Viscosity of ECAs reflects the interaction between ingredients in the formulation and also the processibility of the composite materials. Our previous study on dicarboxylic acids in ECAs demonstrated the increased viscosity and significant processing issues after using the acids [16]. For the aldehyde added ECAs, however, the viscosity did not change much and even decreased slightly (Fig. 8). This is very important when considering the processibility of ECAs.

The mechanical properties after the addition of aldehydes were also investigated. Fig. 9 shows the storage modulus and $\tan\delta$ value changes as a function of temperature. The storage

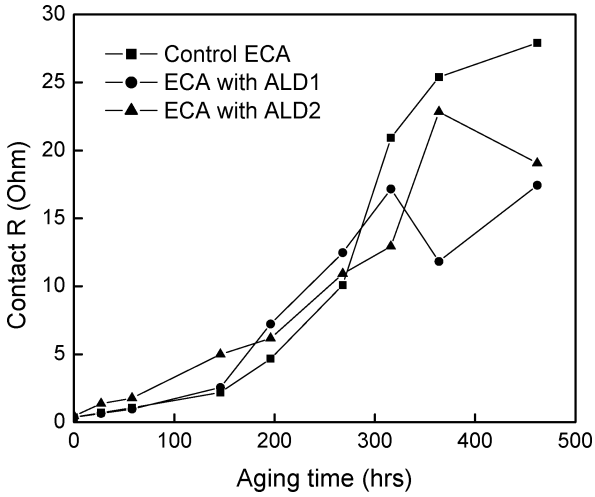


Fig. 7. Contact resistance shifts of ECAs with aldehydes.

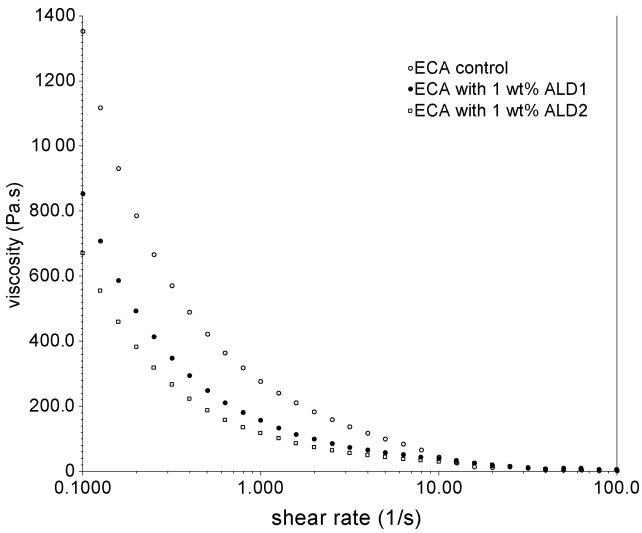


Fig. 8. Effect of aldehyde on the viscosity of ECA.

modulus decreased after using aldehyde and therefore an increased $\tan\delta$ value was obtained, which suggested a higher toughness and better impact performance of the ECA composite. Also, the higher storage modulus of the cured polymers at temperature 30 °C higher than Tg indicated a decreased cross-linking density.

Coefficient of thermal expansion (CTE) of the cured ECAs was measured using a thermomechanical analyzer (TMA). (Fig. 10) The CTE values before Tg $(\alpha 1)$ of ECAs without and with addition of aldehyde were 61 ppm/°C and 26 ppm/°C, respectively. The dramatically decreased in $\alpha 1$ is due to more interactions between Ag–Ag and between Ag-epoxy of the aldehyde added ECAs. The more filler-polymer interaction, the less free volume within the cured epoxy composite matrix material, and also less likely for the epoxy chain to slip by during the heating process and resulted in a lower CTE value with increasing temperatures. Furthermore, a lower CTE of the ECA will reduce the thermomechanical stress of the ECA to the PWB substrate (CTE ∼16–24 ppm/°C) interconnect structure. This lowered stress can enhance the temperature cycle

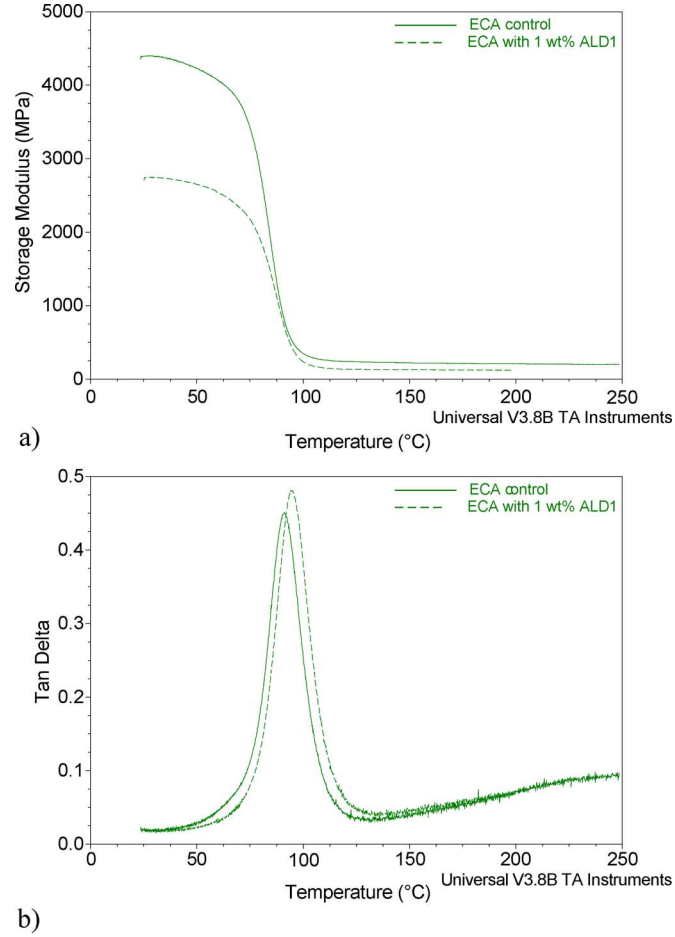


Fig. 9. Storage modulus (a) and tan delta (b) of cured ECAs without and with the aldehyde.

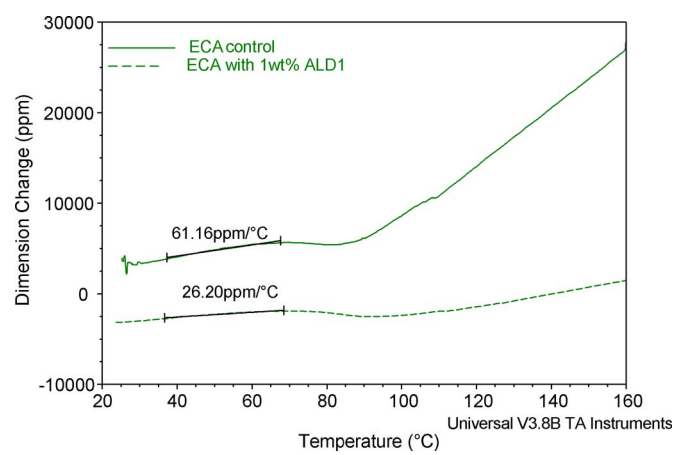


Fig. 10. Dimension changes of Cured ECAs without and with the aldehyde.

reliability of the interconnection. The details for the decreased CTE will be discussed elsewhere.

IV. Conclusion

Aldehydes could act as a reducing agent for metal oxide in ECAs and also consume oxygen and prevent the oxidation of the metal fillers during the curing process. The effect of the reducing

agent could lead to the improved electrical properties. The oxidation products of aldehydes, carboxylic acids, when partially replacing or removing the surfactant on Ag flakes, helped the electron tunneling and therefore further increased the conductivity of ECAs. Most importantly, the better electrical properties have been achieved together with the lower CTE and improved mechanical properties.

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