Electrical Property Improvement of Electrically Conductive Adhesives Through *In-Situ* Replacement by Short-Chain Difunctional Acids

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

***Abstract*—To improve the electrical properties of electrically conductive adhesives (ECAs), short-chain difunctional acids, such as malonic acid (acid M), adipic acid (acid A), and terephthalic acid (acid T) were introduced into a typical isotropic conductive adhesive formulation. By *in-situ* replacement of the commonly used surfactant-stearic acid in silver(Ag) flakes, such difunctional acids can increase the conductivity of ECAs. With the addition of malonic acid and adipic acid, which only have short chain single-bond hydrocarbon between the dicarboxylic groups, the conductivity of the typical conductive adhesives was improved significantly. Terephthalic acid, however, deteriorates the conductivity due to the rigid aromatic structure in the molecule. Dynamic mechanical analysis and thermomechanical study indicated the improved electrical properties with malonic and adipic acids were achieved without negatively affecting the mechanical and physical properties of ECAs.**

***Index Terms*—Conductivity improvement, dicarboxylic acid, electrically conductive adhesives (ECAs), *in-situ* replacement of silver flake surfactant.**

I. INTRODUCTION

SOLDERING processes with tin/lead solders (Sn/Pb) are standard 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. From the environmental point of view, lead-containing solders are harmful to the environment and human beings [3]. Eliminating lead from electronic packages is imperative to our society [4]. Another limitation of solder paste exists in its use for fine pitch components. The current solder paste technology used in SMT can not handle this very fine pitch interconnection due to the soldering defects such as bridging or soldering balling [3]–[5]. In the electronic industry, two groups of materials are being investigated at present as possible alternatives for lead-containing solders: lead-free solders such as Sn/Ag, Sn/Ag/Cu [6], [7] and electrically conductive adhesives [8]–[10]. However, the melting points of most lead-free metal alloys are 30 °–40 °C higher than the eutectic tin/lead solder. Such a high melting temperature introduces many issues, such as increased processing temperature, having to use more expensive substrates, higher components stress, pop-corning problem of the packages on the printed wiring board (PWB) assembly and so on. On the other hand, ECA technology can offer numerous advantages, such as fewer processing steps that eliminate the fluxing and cleaning of the components which reduce processing cost, lower processing temperature which makes use of heat-sensitive and low cost components and substrates possible, and fine pitch interconnect capability. However, compared to the mature soldering technology, there are several limitations for conductive adhesives, such as relatively lower conductivity and unstable contact resistance.

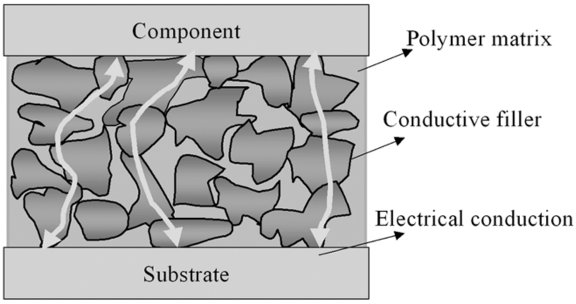

Fig. 1. Cross section of an ICA interconnect junction.

Isotropic conductive adhesives (ICAs), the major type of ECA, are composites of polymer matrix and conductive fillers. In an ICA interconnect junction (Fig. 1), the polymer resin provides mechanical interconnection and the conductive fillers provide electrical conductivity. In order to maximize the electrical conductivity, high conductive filler are needed in the ICA formulation. However, too high filler loadings deteriorate the mechanical property of the ECA. Therefore, improving the conductivity while maintaining the mechanical properties has been the key issue for the study of ICAs.

Silver flakes coated with surfactant stearic acid (C-18 carboxylic acids), are widely used as the conductive fillers in most ICA formulations [11]. The existence of such organic lubricants can affect the viscosity of conductive adhesive paste and prevent agglomeration of silver flake, but it can also decrease

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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 into the ICA formulations. By *in-situ* replacing the stearic acid with such short chain acids, it is much easier for the electrons to tunnel/transport between silver flakes, provided that the added acids can attach to the silver flakes. An important consideration for the selection of short chain acid is the affinity of functional groups to the silver. Since carboxylic functional group (−COOH) has a strong affinity to self-assemble into a silver surface, the *in-situ* replacement of C-18 lubricant layer by short chain dicarboxylic acids should have potential for the improvement of conductivity in the ICA [12].

In this study, three short-chain difunctional carboxylic acids, malonic acid (acid M), adipic acid (acid A) and terephthalic acid (acid T), were used in a typical ICA formulation. (the structure of all the acids are shown in Table I). The replacement of stearic acid was indicated by TGA, DSC, and rheology characterizations. Effects of different dicarboxylic acids on the electrical and mechanical properties of ICA have been studied. The improved conductivity has been achieved without adversely affecting the mechanical properties.

II. EXPERIMENTAL

A. *Materials Preparation*

A typical ICA formulation was prepared in which the epoxy, anhydride, and catalyst were used as the polymer binder and two kinds (bimodal) of silver flakes with different sizes were used as conductive fillers. After preparing the ICAs, small amounts of short chain acids were added into the formulations and mixed. All chemicals were used as received.

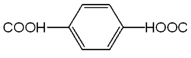
B. *Characterization*

The curing behaviors of the ICAs were determined using a modulated differential scanning calorimeter (MDSC) from TA Instruments, model 2970. Dynamic scans were made on the samples at a heating rate of 5 °C/min, usually from 25 °C to 250 °C.

The rheology study of the adhesive formulations was conducted with a stress-controlled rheometer, model AR1000-N, from TA Instruments. 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 oscillation mode.

Dicarboxylic acid solutions were prepared by dissolving the acids in ethanol. 15 ml of each solution was used to treat the pre-cleaned silver surfaces and silver flakes. After treatment for 1 h, the samples were removed from the solutions and rinsed with ethanol in order to remove un-adhered/excess acids. The silver surfaces were dried off with argon and then the contact angle of a deionized (DI) water drpolet on the silver surfaces was measured by a goniometer. To characterize the treatment with short chain acids, the weight loss of silver flakes before and after treatments with short chain acids was studied using a thermogravimetry analyzer (TGA) from TA Instruments, model 2050. The temperature was raised from 25 °C to 600 °C at a heating rate of 10 °C/min.

TABLE I
CHEMICAL STRUCTURES OF THE ACIDS

Acid name	**Chemical structure**	**Mol. wt.**	**Mol. Distance(Å)**
Stearic acid	$CH_3(CH_2)_{16}COOH$	284.48	27
Acid T		166.13	7.5
Acid A	$HOOC(CH_2)_4COOH$	146.14	9
Acid M	$HOOC\text{-}CH_2\text{-}COOH$	104.06	4.5

Resistivity of the ICAs was calculated from the bulk resistance of the specimen with specific dimensions. Two strips of an adhesive tape were applied onto a pre-cleaned glass slide with a gap of 6.62 mm between these two strips. The conductive adhesive paste was then coated within the gap space by means of a doctor blade, and then the tapes were removed. After cure, the bulk resistance (R) of this ICA strip was measured as well as the size of the specimen. The bulk resistivity, ρ, was calculated using following equation:

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

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

Contact resistance of a specimen was measured with a Keithley 2000 multimeter. The specimens were exposed to the condition of 85 °C/85% RH (in a temperature and humidity chamber from Lunaire Environmental, model CEO932W-4). The contact resistance of each specimen was measured periodically during aging.

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. Tan delta versus temperature was recorded.

Coefficients of thermal expansions (CTEs) and glass transistion temperatures(Tgs) of ICA 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 250 °C at a heating rate of 5 °C/min. The dimension change with temperature was recorded. The slope of the straight line before the Tg was the CTE, α_1, of the sample.

C. *Results and Discussion*

The curing profiles of these formulated ICAs with different dicarboxylic acids are illustrated in Fig. 2. From the figure, all

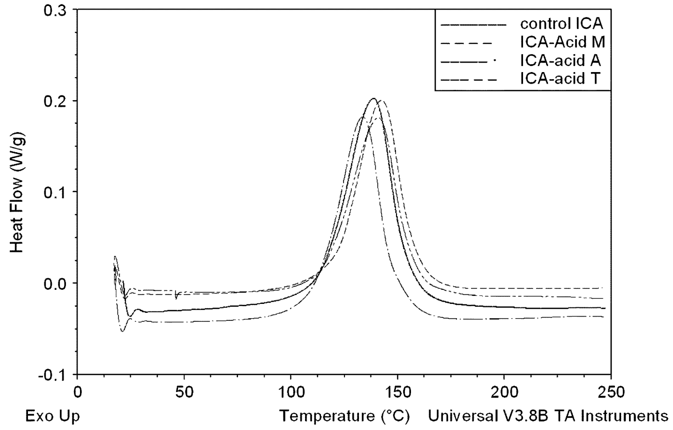


Fig. 2. Curing behavior of the ICAs with different acids.

TABLE II
CURING PROFILE OF ICA WITH ACIDS

Formulations	Peak temperature (°C)	Reaction heat (J/g)
ICA control	138.9	82
ICA with acid M	142.5	68
ICA with acid A	133.9	69
ICA with acid T	141.2	65

the formulations showed similar curing behaviors and had a curing peak in the temperature range from 100 to 165 °C. Measured by DSC, the total reaction heat of the curing of the ICAs decreased after the addition of dicarboxylic acids (Table II). These DSC results suggested that the silver flake lubricant in ICA formulations was partially reacted with the added acids.

Viscosity changes of the ECA formulation after addition of a small amount (0.5% wt.) of dicarboxylic acids were shown in Fig. 3. As can be seen from the figure, viscosity of the ECA formulation increased slightly with the addition of small amount of dicarboxylic acids. This phenomenon again suggested that these acids substituted the lubricant on silver flakes and consequently affected the interaction between the silver flakes and the resin and the interaction among silver flakes. Another possible reason is that the short chain dicarboxylic acids can work as a catalyst for crosslinking of the epoxy resin at room temperature, and therefore lead to the slightly increased viscosity.

To get a clear profile whether the short chain dicarboxylic acids can remove or replace the lubricant in silver flakes, the weight loss of silver flakes before and after the diacids treatment was measured and the result is shown in Fig. 4. Before the treatment, silver flakes showed weight loss of around 0.2% at the temperature ranging from 200 °C to 250 °C, indicating the existence of lubricants on the silver flakes. After treating with malonic acid and adipic acid, there was very little weight loss in the temperature range. This indicated the lubricant on silver flakes has been removed or replaced by the short chain acids. For the terephthalic acid treated silver flakes, however, the weight

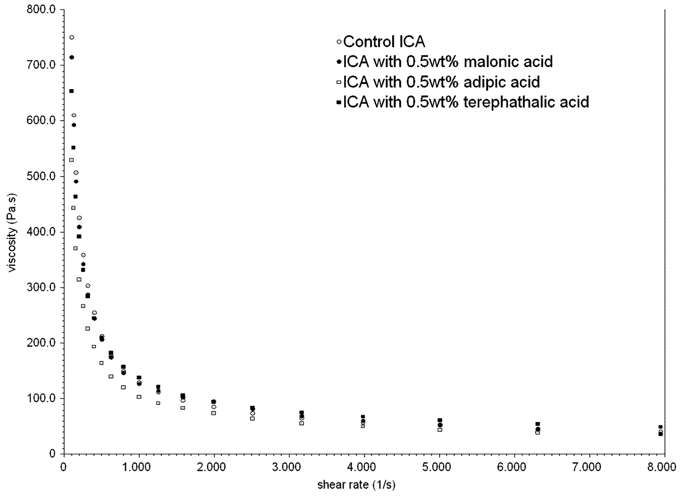
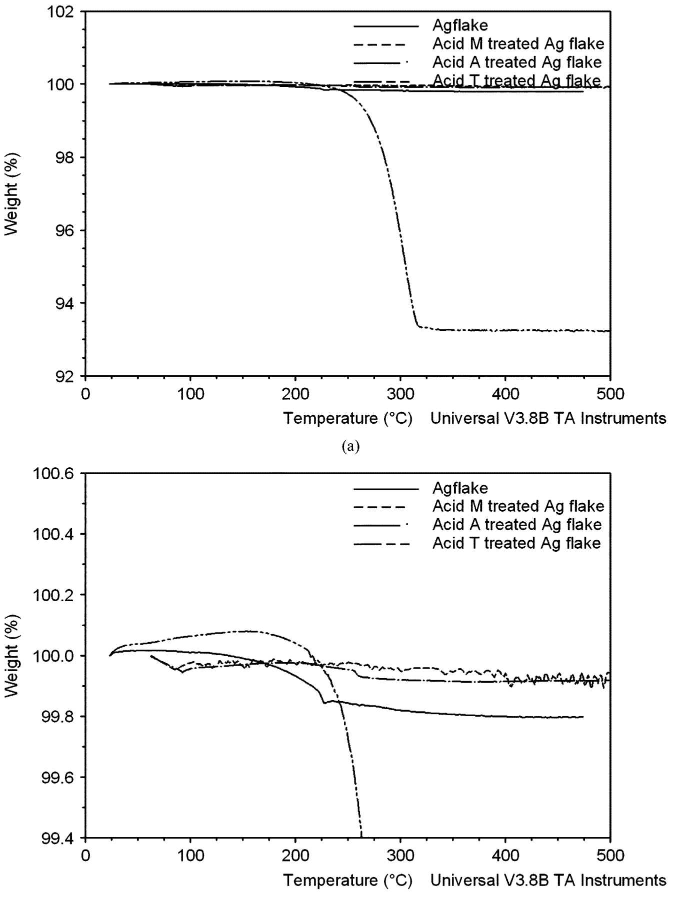


Fig. 3. Effect of acids on viscosity of the ECA formulation.



(a)

(b)

Fig. 4. Thermogravimetric analysis curves of silver flakes before and after treating with different short chain dicarboxylic acids: (a) full range for weight loss of all samples and (b) enlarged image for the weight loss.

loss was much higher (7%). This suggested the terephthalic acid has stronger bonding to the silver surface. During treatment, the acid can be coated heavily on the silver surface. Furthermore, some reaction or polymerization may happen during the treating process. The abnormal DSC profile for acid T treated silver flakes (Fig. 5) also indicated the possible reaction for the treating process.

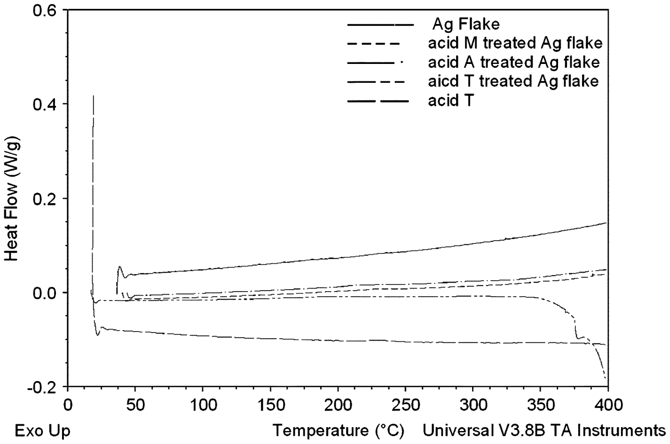


Fig. 5. DSC analysis of silver flakes before and after treating with different short chain dicarboxylic acids.

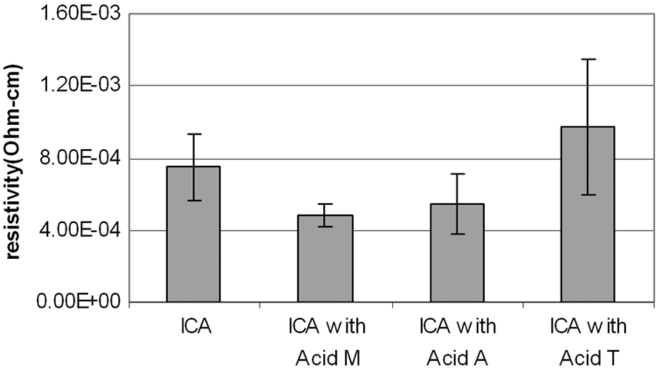


Fig. 6. Effects of different dicarboxylic acids on the conductivity of ICA.

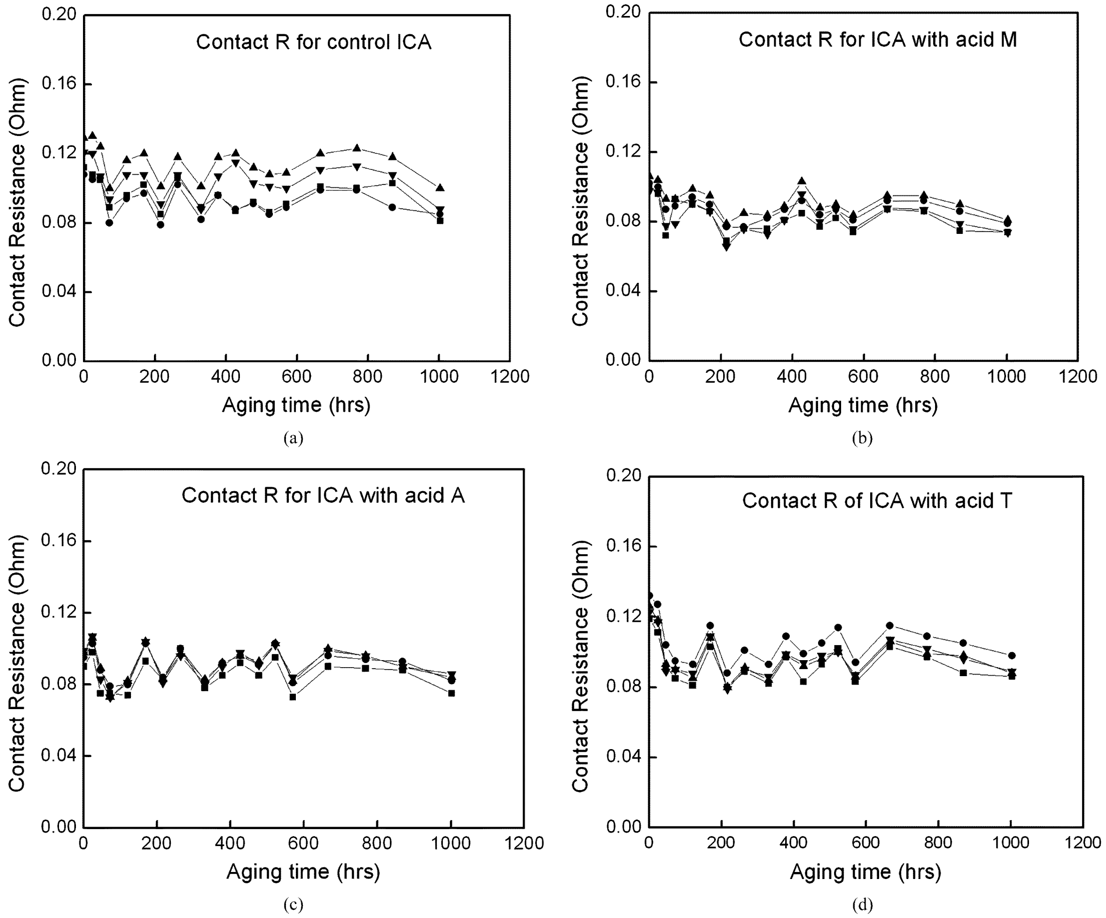
The bulk resistivity of ICAs without short chain acids, with malonic acid, with adipic acid, and with terephthalic acid was measured and compared (Fig. 6). The addition of only small amount (0.5 wt%) of malonic acid and adipic acid can increase the conductivity of ICA significantly and with malonic acid performed the best for the improvement of electrical conductivity of the ICA. However, for terephthalic acid added ICAs, the conductivity decreased. The various effects of dicarboxylic acids are due to their structure difference. For malonic acid and adipic acid, only short chain single-bond hydrocarbon exists between the dicarboxylic groups. The molecular distance is much shorter than the stearic acid, as such, it facilitates the electronic tunneling in the ECA, resulting in a lower resistivity. In removing or replacing the stearic acid in ECAs, the carboxylic groups on both ends of the added acid may form carboxylic ions (COO^-), which delocalize the charge of the anion and coordinate themselves with the silver flakes. The strong attraction between silver flakes and the added acid is because the carboxlyic anion has a strong affinity to silver. The connection of silver flake with short-chain dicarboxylic acid facilitates electrons transport along the chain and thereby improves the electrical conductivity. For malonic acid, there is only one carbon between the dicarboxlylic groups, therefore, the transportation of electrons is much easier. At the same time, compared with the TGA result (Fig. 4), the replacement was more complete (least weight loss after treatment). Therefore, the highest conductivity was achieved. As for the terephthalic acid, although the molecular distance is still shorter than C-18 stearic acid, there is a rigid benzene ring between the dicarboxlylic groups and some unfavorable reaction has happened. The self-polymerization of the terephthalic acid with the silver may explain the high (7 wt %).weight loss in the TGA measurement. Such reaction forms an insulative coating of the silver flake which leads to the deterioration of conductivity of the ICA.

The effects of the three dicarboxylic acids on contact resistance were also investigated. The contact resistance shifts of ICAs with and without dicarboxylic acids during 85 °C/85% RH aging were measured and compared. As shown in Fig. 7, all the ICA formulations showed relatively stable contact resistance after aging around 1000 h, especially for the adipic acid and malonic acid treated samples, the contact resistance showed the most stable values. It is important to notice that these samples also corresponded to the improved conductivity. The possible reason is that such short chain acids may form a layer of thin film on the pad surface and slow down or prevent the corrosion of the substrate surface. The detailed mechanism deserves further investigation.

The strong affinity of dicarboxylic group to silver is the main reason for the improvement of conductivity for the present research. To get a better understanding of the affinity and alignment configuration for different acids, the contact angle data of a DI water droplet on silver surfaces after treated in various acid solutions were measured and compared (Fig. 8). The contact angles decreased dramatically on acid-treated silver surfaces, suggesting that dicarboxylic acids, with hydrophic carboxylic groups, coat well on these silver surfaces. For malonic acid and adipic acid, the decrease of contact angle values was less than those for terephthalic acid. This difference may be attributed to the different structure and reactivity of the acids and subsequently the different modes of alignment. For acid M and acid A, the two carboxylic groups in the molecule (difunctional groups) could both adhere to the silver surface, due to the short chain length and relatively flexible hydrocarbon linkage that is in between two carboxylic groups. Then there is enough physical space for the molecule to lie flat with the surface, as shown in Fig. 9(a). On the other hand, due to the rigidity of the benzene ring in acid T, one of carboxylic groups seemed to anchor or react with the silver surface and the other −COOH in the molecule might be aligned with a tilt angle as shown in Fig. 9(b).

Some characterizations related to mechanical properties after the addition of acid were also studied. Fig. 10 shows the loss modulus value changes with different temperatures at the temperature range from 25 ^oC to 200 ^oC. It can be seen that there was no big difference for loss modulus after the addition of acid. Therefore, the addition of short chain dicarboxylic acid, did not adversely affect the mechanical property.

Coefficient of thermal expansion (CTE) of the cured ICAs was measured using a thermomechanical analyzer (TMA) (see Fig. 11). The CTE before Tg of ICAs with and without adipic acid are 19.5 ppm/K and 22.3 ppm/K, respectively. This is due



(a) (b) (c) (d)

Fig. 7. Contact resistance Shifts of ECAs with and without dicarboxylic acids.

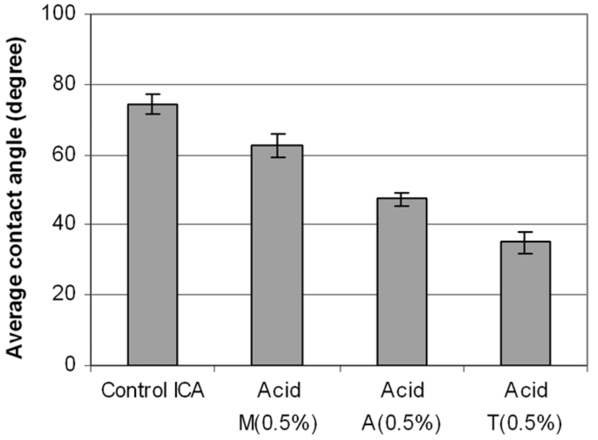
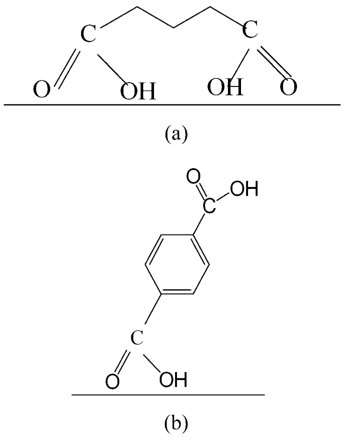


Fig. 8. Contact angle values of DI water droplets on silver surfaces treated in different Acids.



(a) (b)

Fig. 9. Possible alignment configurations of dicarboxylic acids on silver surfaces.

to more filler (Ag)−filler(Ag) and filler(Ag)-polymer (epoxy) interactions with the added dicarboxylic acids ICAs. 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 change with temperature. Furthermore, a lower CTE of the ICA will reduce the thermomechanical stress of the ICA to the PWB substrate(TCE ∼18 ppm) interconnect structure which can enhance the temperature cycle reliability of the interconnection.

III. CONCLUSION

Short chain dicarboxylic acids can effectively *in-situ* remove or replace the C-18 stearic acid in silver flakes for ICA formulations. Such replacement affects the electrical properties of ICAs dramatically. Malonic acid and adipic acid, which have

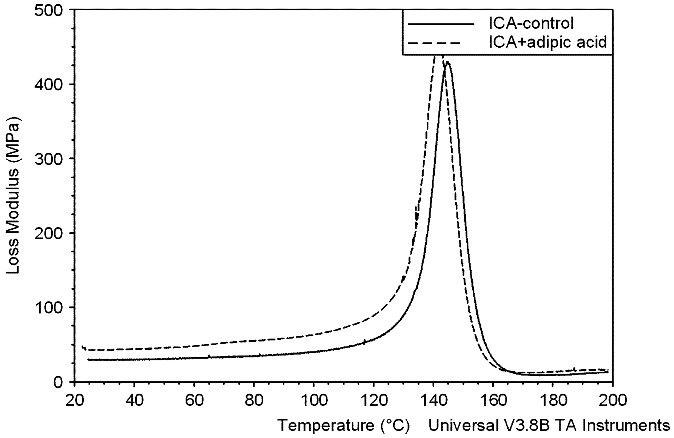


Fig. 10. Loss moduli of Cured ICAs without and with the carboxylic acid.

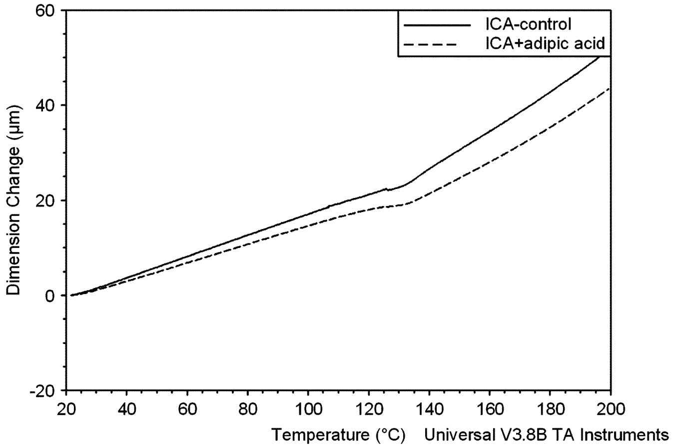


Fig. 11. Dimension changes of cured ICAs without and with the carboxylic acid.

single-bond short chain in between the dicarboxylic groups, increase the conductivity of conductive adhesives greatly. Terephthalic acid, however, deteriorates the conductivity due to the rigid benzene functional group in the molecule and the unfavorable reaction with silver. The stabilized contact resistance has also been achieved with the introduction of such dicarboxylic acids. The significant improvement of electrical properties of ICAs was achieved without adversely affecting the physical and mechanical properties of the ICAs.

REFERENCES

[1] R. R. Tummala and E. J. Rymaszewski, Eds., *Microelectronics Packaging Handbook*. New York: Van Norstrand Reinhold, 1989, p. 361.

[2] F. N. Sinnadurai, Ed., *Handbook of Microelectronics Packaging and Interconnection Technologies*. Isle of Man, U.K.: Electrochemical Publ., 1985.

[3] B. T. Alpert and A. J. Schoenberg, "Conductive adhesives as a soldering alternative," *Electron. Packag. Prod.*, pp. 130–132, 1991.

[4] S. K. Kang, R. S. Rai, and S. Purushothaman, "Development of high conductivity lead (Pb)-free conducting adhesives," *IEEE Trans. Comp. Packag. Manufact. Technol. A*, vol. 21, no. 1, pp. 18–22, Mar. 1998.

[5] J. Hwang, *Solder Joint Reliability*, J. Lau, Ed. New Yrok: Van Nostrand Reinhold, 1991, p. 38.

[6] B. Trumble, "Get the lead out," *IEEE Spectrum*, pp. 55–60, May 1998.

[7] S. K. Kang and A. Sarkel, "Lead (Pb)-free solders for electronic packaging," *J. Electron. Mater.*, vol. 23, p. 701, 1994.

[8] K. Gilleo, "Evaluating polymer solders for Pb-free assembly," *Circuits Assembly*, pp. 52–50, Jan./Feb. 1994.

[9] D. J. Small, B. Eisenach, A. Lewis, and A. Babiarz, "Electrically conductive adhesives as an alternative to solder," *Adv. Packag.*, pp. 38–42, Jan. 1999.

[10] S. Corbett and M. J. Domiano, "Processing with polymer solders," *Surface Mount Technol.*, pp. 48–52, Jun. 1997.

[11] D. Lu, Q. K. Tong, and C. P. Wong, "A study of lubricants on silver flakes for microelectronic conductive adhesives," *IEEE Trans. Comp. Packag. Technol.*, vol. 22, no. 4, pp. 365–371, Dec. 1999.

[12] D. Lu and C. P. Wong, "Novel conductive adhesives for surface mount applications," *J. Appl. Polymer Sci.*, vol. 74, pp. 399–406, 1999.

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