# Development of Novel, Flexible, Electrically Conductive Adhesives for Next-Generation Microelectronics Interconnect Applications

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**Abstract**

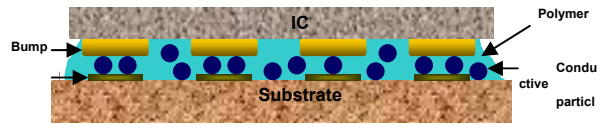
In this paper, a novel flexible electrically conductive adhesive (FECA) has been designed for electronic interconnect applications that require high flexibility at the interconnects, such as assembly and repair of flexible circuits on flexible substrates and connectors. The physical properties of the resulting FECAs such as the elastic moduli, glass transition temperatures, adhesion strength and electrical properties were characterized by differential scanning calorimetry (DSC), dynamic mechanical analyzer (DMA), thermomechanical analyzer (TMA), die shear tester and multimeter electrical measurement. A high performance FECA with tunable modulus, flowability, glass transition temperature, electrical conductivity and adhesion strength was developed for the next-generation large scale flexible flat panel displays applications.

## Introduction

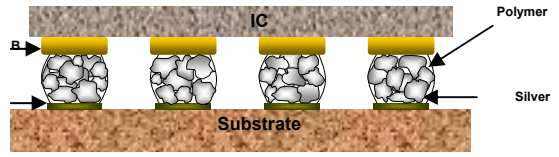
Microelectronics requirements are driven toward smaller, higher density, and lower cost solutions. Polymer-based electrically conductive adhesives (ECAs) have drawn much attention as an environmentally friendly solution for lead-free interconnects due to the advantages of environmental friendliness, mild processing conditions, fewer processing steps, and especially, the fine pitch interconnect capability due to the availability of small-sized conductive fillers. Therefore, ECAs have been widely used in bonding the flex circuit of a glass liquid crystal display(LCD) to the mating of conducting electrode traces onto a printed circuit board(PCB), or attaching a component lead to a matching contact substrate pad on a thermally-sensitive PCB, etc [1-5].

Conductive adhesives can be categorized into isotropically conductive adhesives (ICA with 2~5 μm conductive fillers) and anisotropically conductive adhesives (ACA with 5~7 μm sized conductive fillers) as shown in Figure 1. Different adhesive types are being adapted as interconnect materials for surface mount technology(SMT) processes, such as chip on glass (COG), chip on flex (COF) and flip-chip bonding technologies in electronic packaging industries

Traditionally, rigid epoxy resins are used as polymer matrix for ECA to provide chemical bonding, excellent mechanical and adhesion strengths. However, with the popularity of flex circuits or flexible substrates in particular for large scale flexible flat panel displays, there are some limitations when attaching the traditional ECAs materials to the flex due to poor flexibility of the ECA interconnect, especially under highly mechanical bending conditions of printed electronics. In addition, the internal stress generated by rigid ECA tends to result in the interconnect failure and affects the contact reliability. If the resulting ECAs can readily release the thermal stress or absorb the stress efficiently, the joint failure due to thermomechanical stresses could be dramatically reduced. To achieve flexibility, thin film polyimide or polyurethane has been used. However, the poor adhesion strength and high electrical resistance have restricted their applications in ECAs.




(a)




(b)

Figure 1 Schematic illustrations of (a) ACA and (b) ICA in flip-chip bondings.

In this paper, a flexible epoxy with good adhesion and reasonable shrinkage is introduced into an ECA formulation. A mixture of a flexible epoxy and a typical rigid epoxy is employed as the matrix for flexible ECAs with silver flakes as conductive fillers. Various ratios of epoxies were studied to combine the advantages of flexibility, mechanical strength, adhesion, shrinkage of different epoxies and to optimize the materials properties. By tuning the ratios of epoxies and fillers, the elastic moduli, glass transition temperatures, adhesion strength, electrical conductivity, and impact strength can be modified accordingly to satisfy requirements for different applications.

## Experimental

A diglycidyl ether of bisphenol-F (DGEBF) EPON 862 epoxy resin and a flexible epoxy (E.R.L. 732) were used as matrix resins. An anhydride type hardener of methylhexa-hydrophthalic anhydride (MHHPA) was employed as crosslinker. The catalyst is 1-cyanoethyl-2-ethyl-4-ethylimidazole (2E4MZCN) and the concentration of the catalyst was 1 part per hundred parts resin (phr). Two types of silver flakes, with particle sizes of 1.5–5 and 0.8–2.0 μm were donated by Ferro Co. and incorporated by 80wt% with 1:1 ratio in the ECA formulations.

The resistivity of the ECAs 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 printed on the glass slide, and then the tapes were removed. After cure, the bulk resistance (R) of this ECA strip was measured as well as the size of the specimen. The bulk resistivity, ρ, was calculated using Equation 1:

$$\rho = \frac{t \times w}{l} \times R \qquad (1)$$

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

The specimens were exposed to the condition of 85°C/85% RH (in a temperature and humidity chamber from Lunaire Environmental, model EO932W-4). The contact resistance of each specimen on test coupons 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.

For adhesion test, a die shear test configuration and a die shear tester (Dage series 400) were utilized. The die shear test configuration is shown in Figure 2. The size of the die was 2 mm by 2 mm.

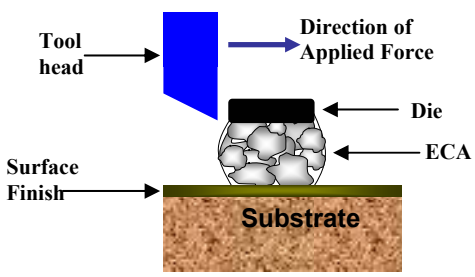
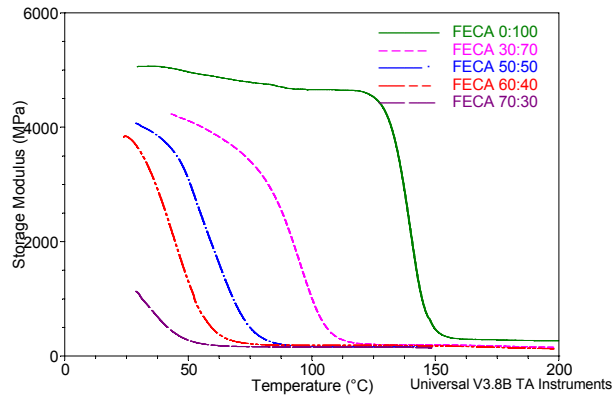



Figure 2 Schematic illustration of die shear test of FECA

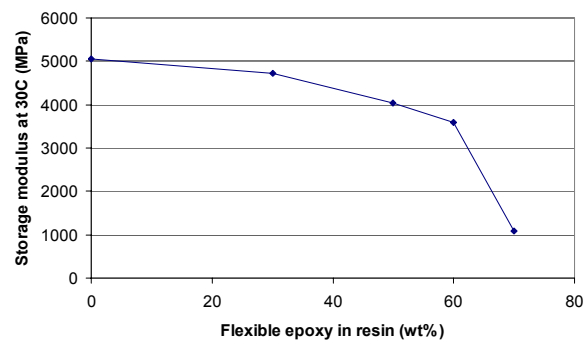
**Results and Discussion**

Mechanical Properties of FECAs

To study the effects of flexible epoxy on the performance of ECA, the flexible epoxy was mixed with the typical rigid epoxy with various ratios before adding the silver flakes fillers. The storage modulus with temperature of the different mixtures of flexible and rigid ECAs is shown in Figure 3 (a). With increasing the ratio of flexible epoxy in ECA resins, the storage modulus of the resulting ECA at room temperature decreases from 5000 MPa to 1000 MPa (see Figure 3 (b)), indicating a more flexible structure. The glass transition temperature (Tg) of the FECA decreased obviously with increasing the amount of flexible epoxy in the polymer resin, as shown in Figure 4. Moreover, only a single Tg was observed for each formulation, indicating that the resulting ECA was a single homogeneous phase. Furthermore, the loss modulus at room temperature could also be tuned from 100 MPa to 450 MPa with increasing the ratio of flexible to rigid epoxy, as illustrated in Figure 5. Typically, a higher loss modulus indicated a better damping property, as such, higher flexible epoxy amount is beneficial to achieve higher impact performance. However, more flexible epoxy also resulted in lower storage modulus and Tg which led to poor mechanical properties. In order to achieve the balanced mechanical properties, the formulation needs to be optimized.




(a)




(b)

Figure 3 (a) Changes of Storage moduli of ECAs with different ratios of flexible epoxy to rigid epoxy; (b) Storage moduli of ECAs with different ratios of flexible epoxy to rigid epoxy at 30C.

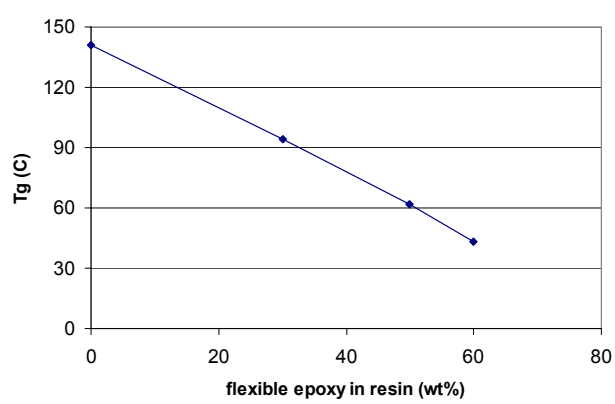
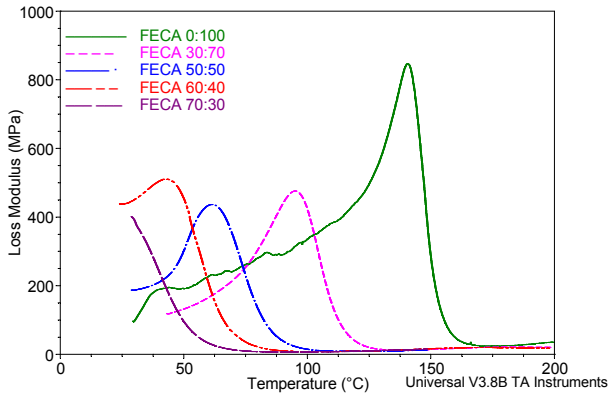



Figure 4 Glass transition temperatures (Tgs) of FECAs with different ratios of flexible epoxy to rigid epoxy

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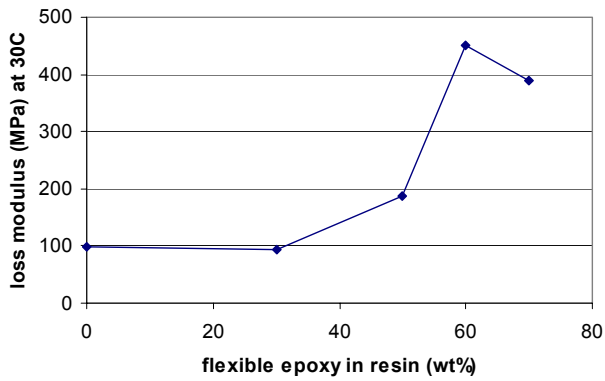



(b)

Figure 5 (a) Changes of loss moduli of ECAs with different ratios of flexible epoxy to rigid epoxy; (b) Loss moduli of FECAs with different ratios of flexible epoxy to rigid epoxy at 30C.

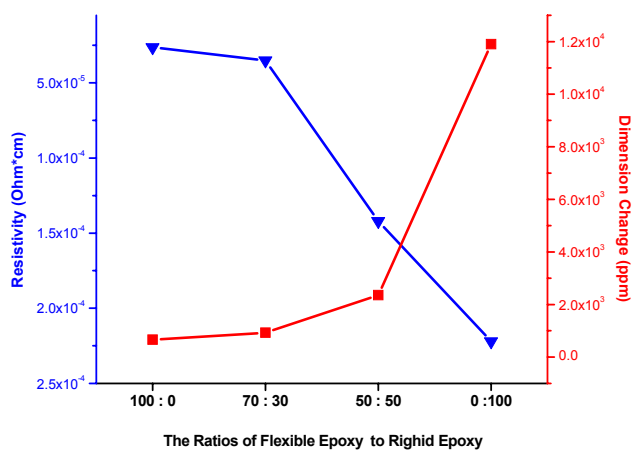



Figure 6 Electrical properties and dimension change of ICAs (80 wt% Ag flakes) with different ratios of flexible epoxy to rigid epoxy

Electrical conductivity of FECA

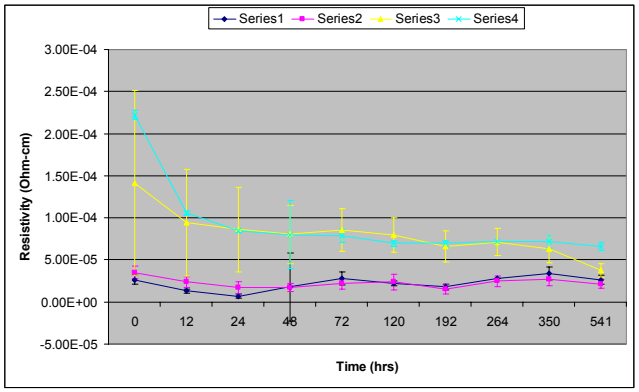
Generally, an ECA has low conductivity before cure, but the conductivity increases dramatically after the ECA is cured, provided the filler loading exceeds the percolation threshold of the composite. The ECA achieves conductivity during the cure process, mainly through more intimate contact between Ag flakes caused by cure shrinkage of polymer binder [6, 7]. Previous research work in our group has demonstrated that resin cure shrinkage plays a very important role during conductivity establishment of a conductive adhesive. It has been discovered that an ICA with higher cure shrinkage generally shows better conductivity. However, for flexible ECA, it was found that with increasing the amount of flexible epoxy in the ECA formulations, there was less shrinkage after cure while the electrical conductivity was higher with more flexible ECA (Figure 6).

Fundamental understanding of the mechanism is crucial for the investigation and development of high performance ECA (such as flexible, high conductivity and high reliability) for the wide applications ranging from consumer printed electronic products, medical device to aerospace. Two possible reasons may account for the intriguing phenomena: (a) Removal of silver oxide on Ag flakes surface and prevention of further oxidation of silver with –OH and –COOH groups in the epoxy resin. Although stoichiometric ratios of diglycidyl ether of polypropylene glycol to anhydride (curing agent) were used, the relatively high viscosity of the resulting mixture with 80wt% silver flakes may hinder the complete reaction of epoxy resins with anhydride. Consequently, there may be more –OH and –COOH groups left in the epoxy system since less cross-links are formed Our previous research work demonstrated that incorporation of reducing agents [8] and short-chain acids [9] would improve the electrical conductivity of ICA. First, after curing, the residual –COOH in the polymer matrix will react with silver oxide and remove the silver oxide from Ag flake surface. (b) Improvement of interface among silver flakes by flexible epoxy resin. The enhanced interface property could reduce the contact resistance between silver flakes and silver/epoxy by reducing both constriction resistance and the tunneling resistance due to more intimate contact between silver flakes and silver/epoxy. As such, the bulk resistivity can be obviously improved. As shown in Equation 2, the total contact resistance between joints is the sum of constriction resistance ($R_c$) and tunnel resistance ($R_t$).

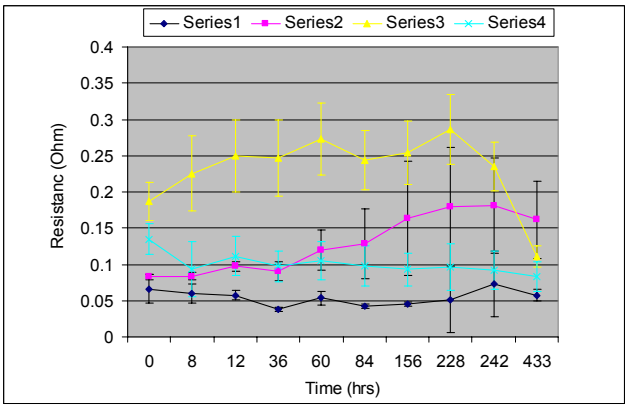
$$R = R_c + R_t = \frac{\rho}{2a} + \frac{\sigma}{\pi a^2} \qquad (2)$$

Where ρ is the bulk resistivity of the material, $a$ is the radius of the circular conducting area and σ is the tunnel resistivity [10].

The changes of mean bulk resistivity and mean contact resistance with 2 times standard deviation as the error bar of the ICA with different ratios of flexible epoxy to rigid epoxy during 85 °C/85% RH aging are shown in Figures 7. All the ECA formulations show relatively stable bulk resistivity (Figure 7 (a)) and contact resistance (Figure 7 (b)) after aging around 500 hrs. It should be noted that the bulk resistivity decreased in the first 24 hrs may be due to the post curing of epoxy resins (see Figure 7 (a)).




(a)



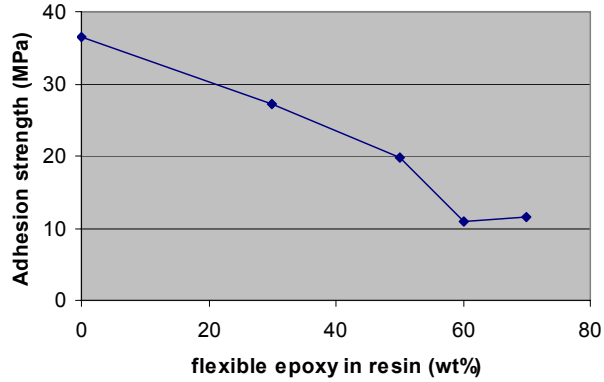

(b)

Figure 7 The mean bulk resistivity (a) and mean contact resistance (b) on Au with different ratios of flexible epoxy to rigid epoxy during 85 $^{o}$C/85% RH aging.

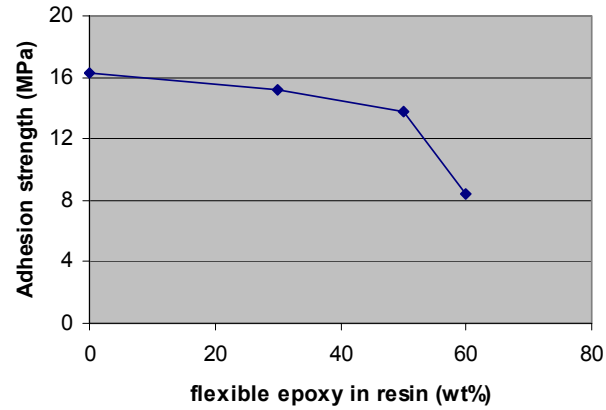
Adhesion strength

In order to study the influence of flexible epoxy on the adhesion of the resulting FECAs, FECAs with different ratios of flexible epoxy and rigid epoxy were formulated and the die shear strength of the FECAs on glass, polyimide and gold substrate were measured, respectively. As shown in Figure 8, with the addition of flexible epoxy, the adhesion strength generally reduced. Continuous decrease of adhesion strength was observed for FECA on glass substrate. However, for polyimide and gold substrate, no significant decrease in the adhesion strength was observed for the ECA with up to 50 wt% flexible epoxy. Comparing the adhesion strength of FECAs on various substrates, the adhesion strength of FECAs on Au was the lowest with the same resin formulation.

High adhesion strength is a critical parameter in fine pitch interconnection that is fragile to shocks encountered during assembly, handling and lifetime reliability. In order to enhance the adhesion strength of FECA on Au surface, di-functional self-assembled monolayer (SAM) was used to treat the Au surface before the die shear test. Our previous study has demonstrated that SAMs with various functional groups tend to have strong affinity on specific metal surfaces and form the strong connection with the metal particles or surfaces [11, 12]. In particular, conjugated molecules which have a smaller band gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and possess delocalized conjugated π-electrons that can contribute to conduction. In semiconductors, self-assembled molecular wires have seen importance in tuning the metal work function (Φ) and electrical conduction of metal-molecule contact [13-18].




(a)

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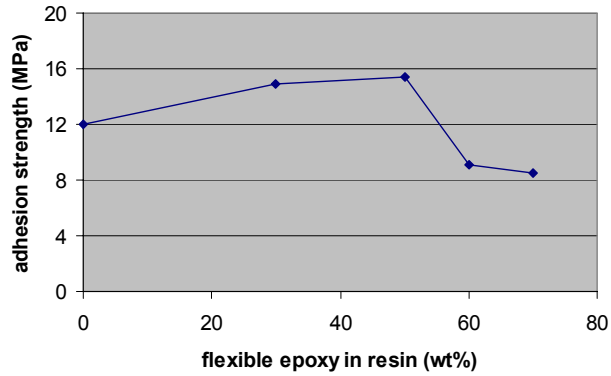


(c)

Figure 8 Adhesion strength of FECAs on (a) glass substrate; (b) polyimide substrate and (c) Au substrate.

The adhesion strength of FECA on Au surface with di-functional conjugated SAM treatment was measured for the formulation of 50wt% and 70wt% flexible epoxy, respectively. As shown in Figure 8, with the SAM treatment, the adhesion strength of FECA on Au substrates were significantly enhanced. Typically, for the di-functional SAM molecule used, one functional group could strongly adhere to the Au surface, while the other end of the SAM molecule attached to the epoxy. As such, a strong bridging/coupling was formed between the FECA and Au substrate and increased the adhesion strength. The added-SAM functionalization on silver flake is similar to a coupling agent. However, typical coupling agents such as silane may sacrifice the electrical conductivity of FECA. The short chain di-functional SAM molecules, usually can further improve the electrical conductivity, as reported by the previous study [19].

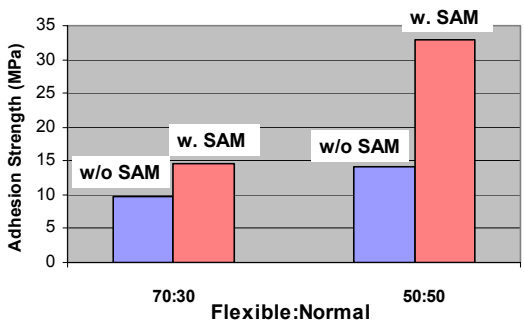


Figure 9 Adhesion strength of FECA with SAMs

**Conclusions**

A variety of FECAs have been formulated to provide a wide range of electrical and mechanical properties. By tuning the ratios of flexible and rigid epoxies, the electrical and mechanical properties can be modified accordingly to satisfy requirements for different applications. In particular, good flexibility, high electrical conductivity, and good interconnect reliability could be achieved. Adhesion strength of FECA can be significantly enhanced with treatment of di-functional SAM molecules. The high-performance flexible ECAs developed will have a promising application in large scale flexible printed electronics such as flat panel displays, solar cells, etc.

**Acknowledgments**

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