Fabrication and Characterization of Silver-Polyaniline-Epoxy Electrical Conductive Adhesive

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Electrically conductive adhesives (ECAs) are an integral part of the microelectronic packaging assembly. ECAs perform two principal roles, providing a physical bond between two surfaces and establishing an electrical interconnection between two bonded surfaces. This dual functionality is achieved by dispersing electrically conductive fillers in the adhesive matrix. Adhesive matrix imparts the mechanical strength to the composite and conductive fillers decrease the electrical resistance of the adhesive matrix. In the process of achieving enhanced electrical conductivity, it is important to retain the mechanical properties of the composite. Often, it is observed that filler material negatively affects the mechanical properties of the matrix and also such composite becomes economically unfeasible due to its increased volume fraction and high cost. In order to overcome this problem, attempts have been made to use different size and shape of fillers. ECAs are the systems which are usually filled with Cu, Ni, Au and Ag filler materials of different size and shapes.

In the present work, we address the problem of upholding the mechanical and electrical properties, along with cost effectiveness. Our approach involves utilization of hybrid filler systems and process for the effective dispersion of fillers in adhesive matrix. The system under study consists of epoxy as an adhesive matrix and, Ag and polyaniline (PANI) as electrically conductive filler materials. It is worth to mention that PANI acts as co-filler which is cost effective material compared to Ag. Two different experiments were performed; one without PANI and another with PANI, to study effect of incorporation of PANI. Primary steps in the experimentation include uniform dispersion of filler material in the adhesive matrix and fabrication of a specimen for electrical and mechanical characterization. Liquid epoxy (DER 331) was used as used as an adhesive matrix which exhibit the volume resistivity of $1.7*10^{15}$ ohm-cm and viscosity 2250 cps at 25^0C. Silver filler was characterized for its shape and size which found to be flakes shape of 10 micrometers. Epoxy was diluted with isopropyl alcohol (IPA) for the ease of processing and dispersion of fillers. As IPA is compatible with both epoxy and Ag, Ag was dispersed in IPA and sonicated for de-agglomeration of the flakes. Colloidal solution of Ag flakes was dispersed in diluted epoxy using high energy vortex mixing process. As-prepared mixture was cross-linked with 13 PHR triethylene tetraamine (TETA). Resultant mixture was spin-coated on copper substrate to obtain the film of uniform thickness with known dimensions.

Novel *in-situ* electro-mechanical characterization system is employed to study the properties of the conductive adhesives. It involves indentation of the specimen with electrically conducting probe which logs real-time data of the applied force, corresponding displacement and electrical contact resistance (ECR). Force, displacement and ECR response of the specimen were obtained to gain insights of the filler dispersion and subsequent formation of interpenetrating network of conductive paths. These results were confirmed with SEM micrographs. Mechanical properties (elastic modulus and stiffness) were determined from force-displacement curve (figure 1). Force

dependency of resistance and electrical resistance hysteresis was studied from resistance-force relationship (figure 2).

Results obtained from the above study are essential to understand inter-dependency of mechanical and electrical properties of the conductive adhesives. Stiffness and elastic modulus of the epoxy+Ag and epoxy+Ag+PANI was calculated under the preload of 400g and 800g. For the calculation of the both mechanical properties, force-displacement relationship was used. Change in the initial unloading force with respect to change in displacement gives stiffness of the specimen. Elastic modulus of the specimen was calculated by fitting the experimental data of force-displacement with the Hertz model. Both the specimens showed comparable stiffness under same given loading conditions. Stiffness was observed to be more pronounced under 800g preload. This observation signifies that 10 wt% replacement of Ag by PANI maintains the stiffness of the composite. On the other note, elastic modulus was found to be decreased by 50% after 10 wt% replacement of Ag by PANI. This observation implies that PANI co-filler facilitate more elastic deformation of the specimen compared to individual epoxy+Ag composite under the given force. It is mainly because Ag metal has considerably higher elastic modulus than PANI. Decrement in the weight fraction of Ag and replacement by PANI causes reduction in effective elastic modulus. Reduction in engineering strain was also observed on the addition of PANI. We attribute this reduction to enhanced facilitation of the force transfer inside the matrix.

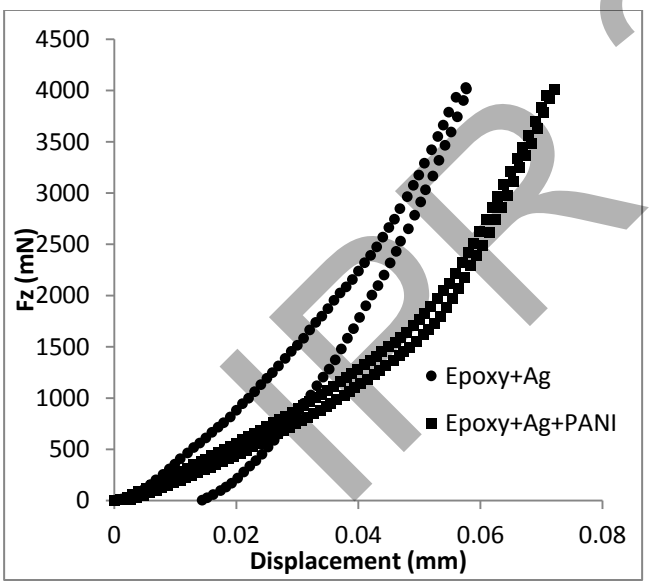

Fig.1: Force-displacement curve of the composites

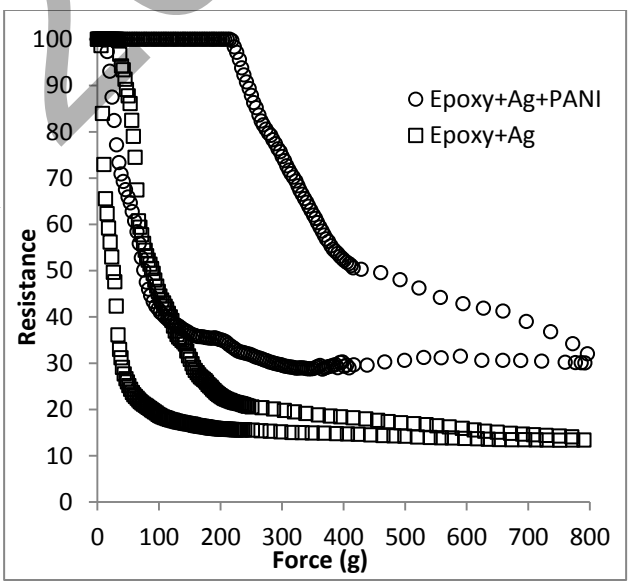

Fig.2: Force dependency of the resistance

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Electrical Conductive Adhesives


Conductive tapes for SEM


Electrical contact paste


Micro-electronic packaging

- Electrically Conductive
- Type of application: Temporary adhesive
  Liquid underfill
  Rigid thermoset

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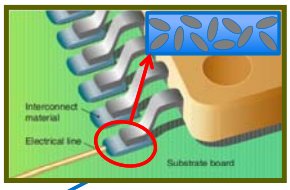
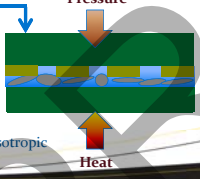
Application to micro-electronic packaging


Li et al. *Science* (2005)




Isotropic



Anisotropic

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- ***Typical characteristics of conductive adhesives***
- Polymeric binder
  - ✓ Thermoset polymer+Hardener
  - ✓ Viscous, higher mechanical strength
- Filler material
  - ✓ Electrically conductive
  - ✓ Dispersible in polymer
- Direction of conductivity
  - ✓ Isotropic
  - ✓ Anisotropic

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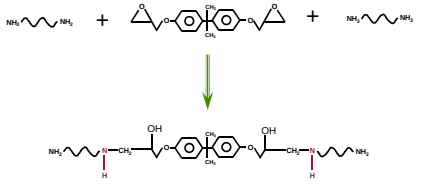
Experimental work

- ***Materials***
  - ✓ Epoxy + Tertiary amine
  - ✓ Ag filler: 10µm, flakes shape
  - ✓ Polyaniline: 10µm, flakes shape



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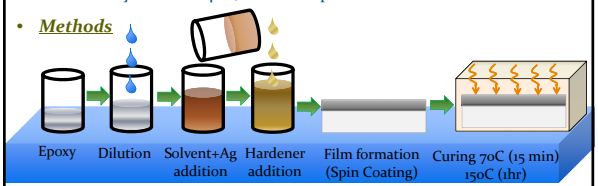
Synthesis

- ***Materials***
  - ✓ Epoxy + Tertiary amine
  - ✓ Ag filler: 10µm, flakes shape
  - ✓ Polyaniline: 10µm, flakes shape
- ***Methods***



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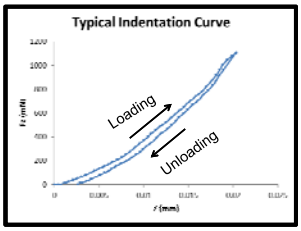
Characterization

- *Electro-mechanical testing*
  - ✓Force-displacement
  - ✓Resistance-force
  - ✓Resistance-displacement
- *Morphological characterization*
  - ✓Scanning Electron Microscopy



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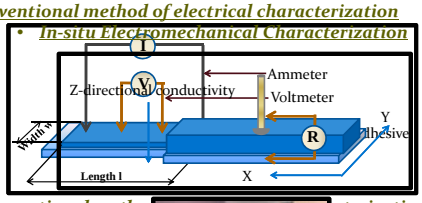
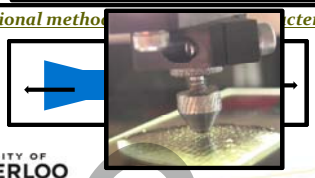
Electromechanical testing

- *Conventional method of electrical characterization*
- *In-situ Electromechanical Characterization*



- *Conventional method of electrical characterization*



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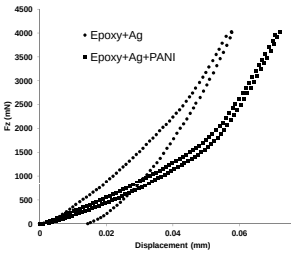
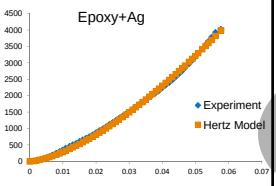
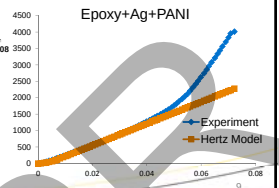
Results: Mechanical Property Analysis







Contact Stiffness=dP/dh

Elastic modulus $F = \frac{4}{3} E^* R^{1/2} d^{3/2}$

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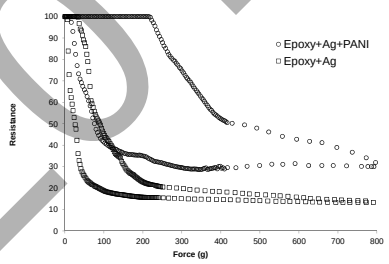
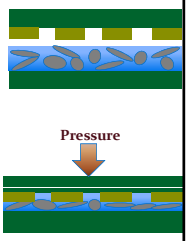
Results: Force-dependant Resistance





Tailoring the resistance in operating region

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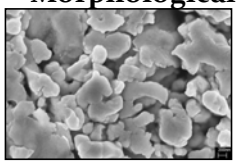
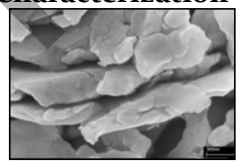
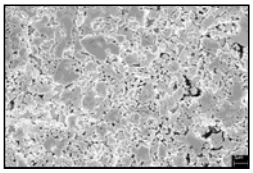
Morphological Characterization



Silver



Polyaniline



Composite

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Summary

- *Synergistic effect of silver and polyaniline*
- *Novel in-situ electro-mechanical analysis of ECAs.*
- *Tuning the electrical resistance in operating window*

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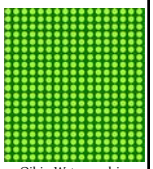
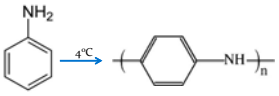
Future work: Polyaniline Synthesis

Direct Oil-in-Water Emulsion method

- Emulsion: Organized heterogeneous system with large interfacial area
- Water: continuous phase, Oil: dispersed phase
- Poymerization occurs in nano-dimensional channels created by nano-size oil droplets
- Polymer grows in continuous aqueous channel with fibrous morphology



Oil-in-Water emulsion
Rahy et al 2009



Aniline Polyaniline

Milky Emulsion

Dark green nano-sized Polyaniline

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Acknowledgement

- *Dr. Boxin Zhao*
- *Financial support from Natural Sciences and Engineering Research Council (NSERC) of Canada*
- *Industrial partners*

Celestica RIM microbonds

Thank You.

Questions??

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14