

Electrical and Mechanical Properties of Carbon Nanotube Filled Adhesives on Lead Free PCB Surface Finishes

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Abstract

Electrically conductive adhesives are attractive alternatives to solder and die attach materials in electronic assemblies particularly in the lead free era. Compared to metal filled conductive adhesives, multiwall carbon nanotube (MWCNT) filled adhesives are lightweight, corrosion resistant, high strength and resistant to metal migration. Previous studies of MWCNT filled epoxies on bare copper printed circuit boards identified contact resistance as a challenge for surface mount component attachment. The adhesive formulations under investigation are mixtures of epoxy Epon resin 862, Heloxy modifier 68, anhydride curing agent, catalyst and MWCNT. Loadings ranging from 2 to 14 wt% are tested to determine electrical and mechanical properties. Here we present contact resistance, volume resistivity and lap shear testing of MWCNT filled epoxy on printed circuit boards with various surface finishes on the copper pads. The surface finishes selected are immersion tin, immersion silver and electroless nickel immersion gold (ENIG).

I. Introduction

Carbon nanotubes (CNT) are allotropes of carbon with a nanostructure that can have a length-to-diameter ratio greater than 1,000,000:1. Multiwall carbon nanotubes (MWCNT) are metallic, whereas single wall carbon nanotubes (SWCNT) may be metallic or semiconducting depending on the chirality of the graphene walls. The measured electrical conductivity of metallic carbon nanotubes is on the order of 10^4 S/cm [1]. The thermal conductivity of carbon nanotubes at room temperature can be as high as 6600 W/mK [2]. Carbon nanotubes have a Young's modulus of approximately 1 TPa and a maximum tensile strength of nearly 30 GPa [3]. The density of MWCNT is 2.6 g/cm³ and the density of SWCNT range from 1.33 to 1.40 g/cm³ depending on the chirality [4]. Blending the extreme properties of carbon nanotubes into polymer matrix composites has tremendous potential for increasing strength, strength to weight ratio, thermal conductivity and electrical conductivity of the bulk polymer. For example, replacing lead-tin solder with MWCNT loaded electrically conductive adhesive would reduce the weight of the component attachment layer by approximately 80%.

Isotropic conductive adhesives (ICA), as an alternative to solder reflow processing, are widely used for die attach and surface mount assemblies. Traditional metal filled ICAs require 25% to 30% volume fraction (up to 80 wt%) to ensure electrical

conductivity [5]. Such a high volume fraction degrades the mechanical properties of the polymer matrices. With conventional metal filled conductive adhesives, only a small portion of shear strength of polymer matrix can be retained [6]. Since MWCNTs have very high aspect ratio, it is possible to reach the percolation threshold with small volume fraction [7]. Replacing metal fillers with MWCNT has the potential benefits of being lead free, low process temperature, corrosion resistant, high electrical conductivity, high mechanical strength and lightweight.

The selection of an appropriate surface finish plays an important role in printed circuit board manufacturing to ensure solderability, reliability and high yield assembly of through hole and surface mount products. Surface finish is applied to copper pads and exposed traces for protection during storage and transportation from the time of board manufactured to the time the circuit is assembled. Therefore, the surface finish must maintain the solderability of the board and protect the metal areas from contamination and oxidation, thus increasing its shelf-life. We considered the following surface finishes: hot air solder leveling (HASL), organic solderability preservatives (OSP), immersion tin, immersion silver, hard gold and electroless nickel-immersion gold (ENIG) [8]. Immersion tin, immersion silver and electroless nickel-immersion

gold have good wettability, coplanarity and reflow cycles. Although ENIG has the most desirable properties, it is also the most costly.

In previous reports [7], [9-11], we measured the electrical and mechanical properties for carbon nanotube filled adhesives applied to bare copper FR-4 printed circuit boards and alumina ceramic substrates. The adhesive formulations included various resin, curing agent and catalyst compositions without the Heloxy viscosity modifier. In this paper we discuss the results for the volume resistivity, contact resistance and lap shear strength to extend the previous results with the goal of developing an electrically conductive adhesive suitable for microelectronic applications.

I

II. Experimental

Materials:

The epoxy resin and viscosity modifier used for the experiments were diglycidyl ether bisphenol-F (Epon 862, Shell Chemical, USA) and neopentyl glycol diglycidyl ether (Miller-Stephenson Chemical, USA), respectively. The curing agent used is methyl hexahydro phthalic anhydride (MHHPA, Miller-Stephenson Chemical, USA). Cyanoethyl-2-ethyl-4 methylimidazole is used as a catalyst (2E4MZ-CN, Shikoku Chemical, Japan). Multiwall carbon nanotubes grown by chemical vapor deposition were obtained from University of Kentucky Center for Applied Energy (CAER). As grown MWCNT have an average length of 50 μm and diameter of 20 nm. Shatter milled MWCNT were processed at CAER by grinding for 10 minutes in a shatter mill. Figure 1 presents a scanning electron micrograph showing agglomerates of shatter milled MWCNT.

The tin, silver and gold coated FR-4 circuit board panels were obtained from Imagineering, Inc. Each panel consists of patterned subcircuits designed for volume resistivity, contact resistance or die shear tests. Lap shear tabs are milled from the remaining unpatterned areas of the panels. Surface mount resistors for contact resistance tests were purchased from DigiKey and are Panasonic 1206 zero Ohm thick film resistors. Alumina ceramic substrates were provided by CoorsTek.

MWCNT-Epoxy Composite Preparation:

The resin to curing agent to catalyst ratio is 100:85:0.5 for each batch of conductive adhesive. Each component in a 20 gram batch is added by weight to a polyethylene container and a Thinky AR-250 planetary mixer blends the adhesive. The planetary mixer generates large continuous centripetal forces (up to 400G) by compound motion of the revolving centrifuge and the counter-rotation

of the material container. The high shear mixing action achieves uniform distribution and removes air bubbles from the mixture. No blending tool is required and each batch is mixed in a new clean container to prevent cross contamination.

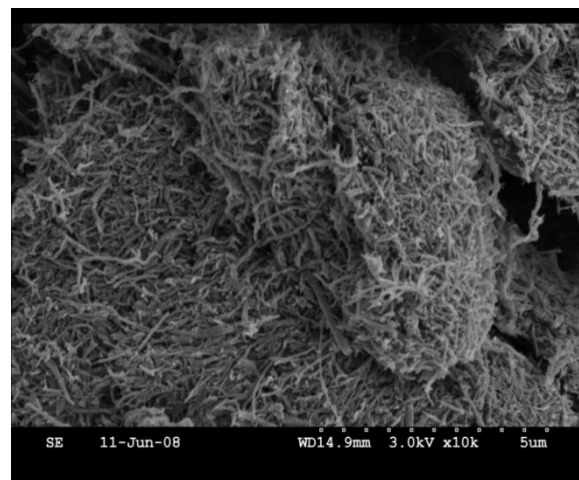


Figure 1. Scanning electron micrograph of shatter milled MWCNT.

First, the resin, curing agent and catalyst are added to the sample container and then the desired weight percent loading of MWCNT is added. Each mixing cycle includes five minutes at 800 rpm rotation and 2000 rpm revolution rates followed by a three minute defoaming cycle at 60 rpm rotation and 2200 rpm revolution rates. Batches are stored in a refrigerator at 40°C. At room temperature, the mixtures have a pot life of approximately 72 hours. Formulations are allowed to come to room temperature and remixed prior to sample fabrication using a 3 minute mix and 2 minute defoam cycle. Patterns for each test are stencil printed onto the corresponding patterned circuit boards using an Aremco 3230B screen printer.

All samples are held at 80 °C for 4 hours to evaporate the solvents in the epoxy and then cured at 150 °C for 30 minutes. Only the contact resistance samples are cured with an applied weight to press the zero ohm resistors onto the printed adhesive pads.

MWCNT-Epoxy:Heloxy Composite Preparation:

While the epoxy resin has a room temperature viscosity of 25-45 P, the Heloxy viscosity modifier has a viscosity of 13-18 cP. The resin portion of the formulation was varied to include Heloxy modifier at resin to Heloxy ratios of 3:7, 2:3, 1:1, 3:2 and 7:3. The blending sequence is the same as the formulations without Heloxy.

Volume Resistivity Measurement:

The volume resistivity of the samples is calculated by measuring the sheet resistance and the thickness of the measuring the sheet resistance and the thickness of the MWCNT filled conductive adhesive layer. A Signatone four point probe instrument is used to record the voltage drop for an injected current. The sheet resistance (R_s) is proportional to the ratio of the voltage, V to the current, I

$$R_s = C \cdot \frac{V}{I}$$

where $C = 4.53$ for an infinite film. A Tencor Alpha-step 500 stylus profilometer is used to measure the thickness, t of the layer. The sheet resistance was converted to volume resistivity, ρ_v by

$$\rho_v = 4.53 \times \frac{V}{I} \cdot t \text{ (ohm-cm)}.$$

For each adhesive formulation, six pads are stencil printed onto a ceramic substrate as shown in Figure 2. Two substrates are printed from each formulation for a total of twelve measurements per batch. The adhesive pads are cured and measured to obtain the average sheet resistance and thickness.

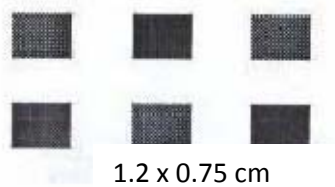


Figure 2: Volume resistivity stencil pattern.

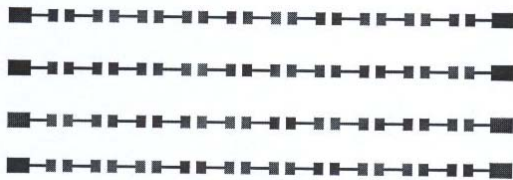


Figure 3: Contact resistance measurement test board.

Contact Resistance Measurement:

To measure the contact resistance of MWCNT filled adhesives, the formulation is stencil printed on to the pads of FR-4 printed circuit board and 1206 size zero ohm resistors are mounted in daisy chain patterns on the pads using a pick and place machine. Each daisy chain consists of 10 zero ohm resistors with 4 such

daisy chains on each test board as shown in Figure 3. After curing, a multimeter is used to measure the total resistance for each daisy chain which is divided by 20 to get an average contact resistance for each joint. The overall contact resistance is calculated by averaging the values from all four daisy chains.

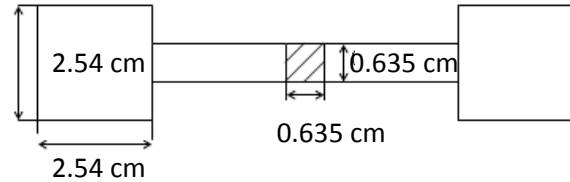


Figure 4: Lap shear test sample tab.

Lap Shear Strength Measurement:

To evaluate the mechanical degradation of the polymer matrix caused by adding MWCNT, a lap shear test was conducted by using an Instron 4442 tensile tester. The test sample was prepared by bonding two PWB strips face to face using the MWCNT filled ICAs. The lap area was $0.635 \times 0.635 \text{ cm}^2$. Shear strengths of samples made by pure epoxy and by epoxy with different MWCNT loadings were measured and compared. The dimensions of the test sample are shown in Figure 4.

III. Results and Discussion

Volume Resistivity Results:

The data in Figure 5 represent the average volume resistivity versus weight percentage of MWCNT in MWCNT-Epoxy mixtures. Increasing the weight percentage of MWCNT reduces the resistivity as expected. Contact between nanotubes form conductive paths through the composite structure. As more nanotubes are added the number of conductive paths increases. The variance also decreases with increased loading indicating that the resistivity measurement becomes more reliable with increased loading. The results are consistent with prior results on volume resistivity as a function of loading [JAST]. In those formulations an upper limit of approximately 12 wt% MWCNT was observed, beyond which the mixtures were too viscous to process by printing or dispensing.

Higher loadings and processable viscosities were obtained using shatter milled MWCNT. The shorter nanotubes disperse more readily in the epoxy to allow higher loadings.

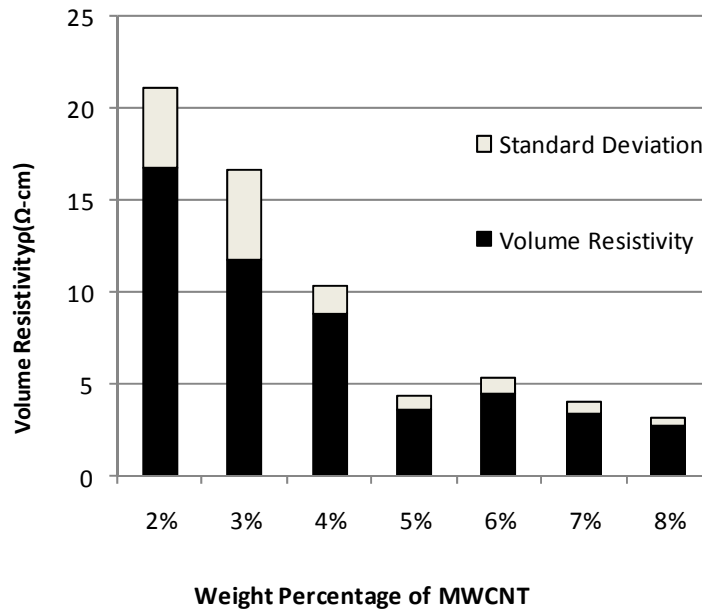


Figure 5: Average volume resistivity versus weight percentage of MWCNT in MWCNT-Epoxy mixtures.

However, the average volume resistivity results shown in Figure 6 indicate higher resistivity than mixtures containing as grown MWCNT even at loadings as high as 20 wt% shatter milled MWCNT. The shorter nanotubes form longer conductive networks in the composite with higher total resistance per path.

Figure 7 shows the dependence of the average volume resistivity on epoxy to Heloxy ratio for 8, 12 and 14 wt% MWCNT loadings. Data are presented for epoxy to Heloxy ratios of 2:3, 1:1 and 3:2. At the higher epoxy resin content of 7:3, the mixtures are too viscous to print uniformly. At the higher Heloxy content of 3:7, the low viscosity solution bleeds out from the printed pads leaving a rough dry agglomeration of nanotubes. The rough surfaces resulting from the 3:7 and 7:3 mixtures can not be reliably measured using the four point probe instrument. The 1:1 composition demonstrates a decreasing resistivity with increasing MWCNT loading, while the 2:3 and 3:2 ratios show minimum resistivities at 12 wt%.

Comparing Figures 5 and 7, the average volume resistivities for the epoxy-Heloxly formulations (Figure 7) are all lower than the values for the epoxy formulations (Figure 5). The 8 wt% loading is common to the formulations in both sets of experiments. The volume resistivity of the epoxy mixture is close to the volume resistivity of the higher epoxy to Heloxy ratio (3:2) at the same 8 wt% loading.

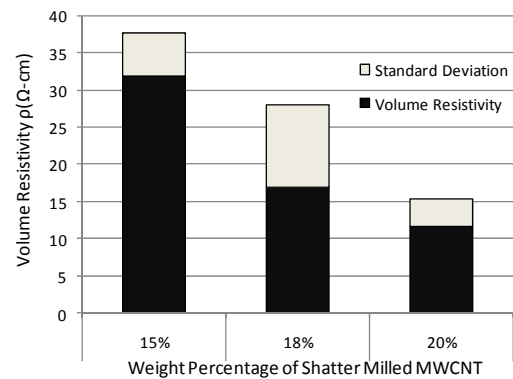


Figure 6: Average volume resistivity versus weight percentage of shatter milled MWCNT in MWCNT-Epoxy mixtures.

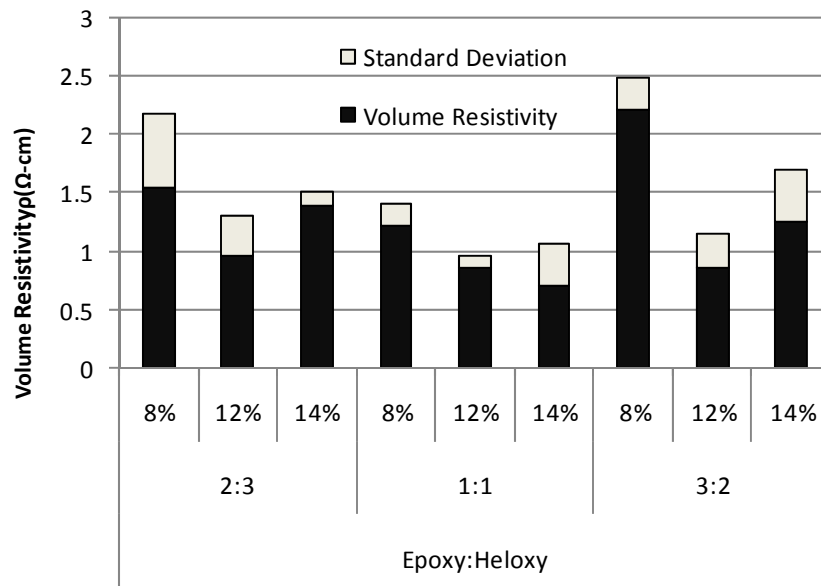


Figure 7: Average volume resistivity versus Epoxy to Heloxy ratio and weight percentage of MWCNT in MWCNT-Epoxy-Heloxymixtures.

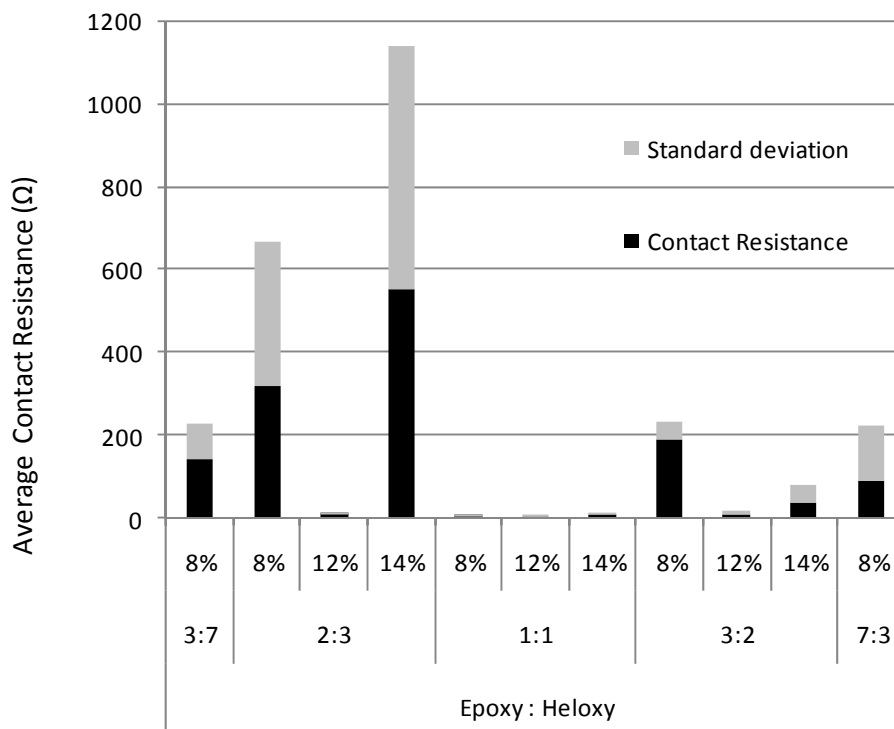


Figure 8: Average contact resistance versus Epoxy to Heloxy ratio and weight percentage MWCNT in MWCNT-Epoxy-Heloxymixtures.

Contact Resistance Results:

Although the contact resistance daisy chains allow us to average 80 contact points per test board, the results are often dominated by a few high resistance joints. The resulting data includes large standard deviations from various sample combinations. All three surface finishes displayed the extreme variance leading us to focus on tin coated boards as the least expensive test circuits. Unlike the volume resistivity graphs, the data presented in Figure 8 for average contact resistance does not show a clear trend as a function of loading or epoxy to Heloxy ratio. Across the epoxy to Heloxy ratios, the 1:1 composition has given minimum contact resistance for 8, 12 and 14 wt % loadings with values of 5-8 Ohms per contact. Among the various loadings, 12 wt% MWCNT has given consistent results across the epoxy to Heloxy ratios in the range 5-12 Ohms per contact.

One explanation for the variability in the contact resistance data may be the absence of flux. Lead-tin and lead free solders contain thermally activated flux compounds to remove native oxides from the circuit board pads and component leads at temperatures below the melting point of the solder. The MWCNT filled adhesives do not contain a fluxing agent and rely primarily on pressure applied during curing to form electrical contacts between the component leads, nanotubes and circuit board pads. Conversely, MWCNT filled adhesives do not produce flux residues and therefore eliminate the need for cleaning and reduce long term corrosion of printed circuit assemblies.

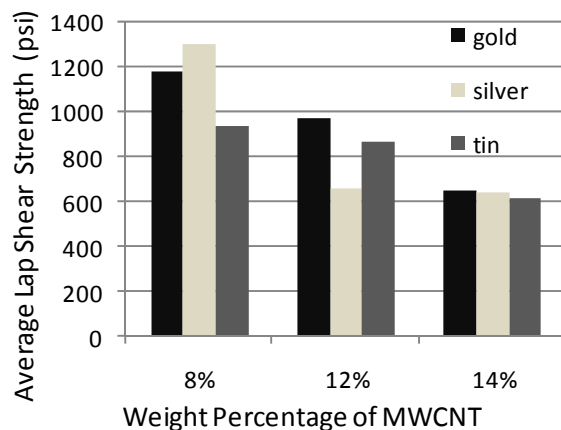


Figure 9: Average lap shear strengths for 1:1 epoxy to Heloxy ratio mixtures with 8, 12 and 14 wt% MWCNT loading on circuit board tabs coated with immersion tin, immersion silver or ENIG .

Lap Shear Strength Results:

All three surface finishes were evaluated in lap shear strength testing. The 1:1 epoxy to Heloxy ratio showed the lowest and most consistent results in volume resistivity and contact resistance experiments. Therefore, the 1:1 composition was used to compare the lap shear strength of various loadings on tin, silver and gold surface finishes. Data from 8, 12 and 14 wt% MWCNT loadings are plotted in Figure 9. Increasing the loading of MWCNT decreases the strength for all three surface finishes. Gold coated tabs exhibited the highest strength for each loading. At 14 wt% loading, the strengths are nearly equal across all surface finishes showing compatibility with tin, silver and gold.

At higher MWCNT loadings, the cured tab samples were extremely brittle and failed during handling prior to lap shear testing. Similarly, mixtures with higher proportions of Heloxy were dry and brittle due to bleed out during curing.

IV. Acknowledgements

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VI. Biographies

Keerthivarma Mantena is a Master's student in Electrical and Computer Engineering. He received the B.E. degree in Electrical and Electronics Engineering from Anna University, Chennai, Tamilnadu, India, in 2005. His research is extending the carbon nanotube filled conductive adhesive work to evaluate lead free surface finishes.

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Poojitha Sirigiri received the Bachelor's degree in 2007 in Electronics and Communication Engineering from Jawaharlal Nehru Technological University, Hyderabad, India. She is pursuing her Master's degree at University of Kentucky in Electrical Engineering Department. She is currently working on electrical properties of carbon nanotube filled electrically conductive adhesives.

Janet K. Lumpp received the B.S. and M.S. degrees in metallurgical engineering from Purdue University, West Lafayette, IN, in 1988 and 1989, and the Ph.D. degree in materials engineering from the University of Iowa, Iowa City, IA, in 1993. She then joined the faculty of the Electrical and Computer Engineering Department at the University of Kentucky where she is now an Associate Professor. Her research areas include application of carbon nanotubes in gas sensors, conductive adhesives, and composites, as well as laser micromachining, electronic packaging, and K-12 math and science education. She is also active in IMAPS and serves as faculty advisor to the UK Student Chapter of IMAPS.

