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Advanced Electrically Conductive Adhesives for High Complexity PCB Assembly

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Abstract. Electronic packaging, or assembly of packed electronic components on printed circuit boards, present challenges that require innovative solder pastes and electrically conductive adhesives to face the increasing complexity of PCB assembly, with denser board occupation and demanding thermal management during assembly. Our aim is to prepare carbon particle based conductive adhesives. The first step to achieve this goal was to prepare composites with epoxy resin and a variety of nano to micron scale carbon particle, produced by mixing on a three roll mill. The percolation threshold for each particle type was determined as well as the conductivity level reached after percolation.

INTRODUCTION

Electronic packaging has become one of the most important sectors in modern electronic industry. In fact, this interest rose from the miniaturization of electronic components, where the interconnection of chips on printed circuit boards (PCBs) is frequently made by soldering [1]. Traditionally, this process is achieved using lead-based or lead-free solders, which provides an electronic conductive pathway between PCB and components [2].

As an alternative to solder, electrically conductive adhesives (ECAs) have been produced, since they can be environmentally friendly, light weight and requiring less processing steps [3, 4]. There are a few commercial ECAs being used, most of them made of epoxy and high amounts of silver microflakes [5]. Despite all the progress with these ECAs, the complete replacement of the traditional solders has not been achieved yet because of unstable contact with nonmetal finished components, silver migration, and poor electrical conductivity, which results from the small contact points formed in the percolated network [5]. To overcome this limitation, different strategies have been employed such as the incorporation of silver nanoparticles (NPs) or the usage of one dimensional materials (1D) like carbon nanotubes and metal nanowires, simultaneously with two dimensional (2D), graphene or graphite flakes, or three dimensional particles (3D) such as microparticles. NPs may present different behaviour, very much depending on their size. An example of that is the effect that NPs above 10 nm have on the electrical resistance above a certain NP content. The increase of NP contact points results in higher electrical resistance. In turn, for NPs smaller than 10 nm, a better contact between flakes is achieved and thus the number of contacts are reduced. This is possible through the sintering process that produces larger particles from its powders, based on atoms diffusion. In the particular case of metallic particles, the surface atoms are less bonded than the bulk atoms and thus may leave the surface when sufficient energy is given. Thus, in the case of the NPs, the large surface area per given volume provides a good source of atoms with weak bonds. Sintering of silver NPs has been reported for temperatures as low as 150 ºC [4, 6].

Carbon materials such as carbon nanotubes (CNTs) and graphene are recognized their high electrical conductivity, nano size and high aspect ratio. These features allow them to easily establish an electrically conductive network for electron transport, achieving a percolation threshold at low nanoparticle contents. Nevertheless, some drawbacks still exist. For 1D materials such as CNTs the main problem is related with their dispersion in the polymeric matrix. After

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composite production, reagglomeration of CNTs is observed in low viscosity resins or melted polymers. Reagglomeration has been prevented through covalent or non-covalent surface functionalization [7]. The former leads to atomic rearrangement of the surface carbon structure, while the latter involves the non-covalent modification of the carbon nanoparticle surface with molecules such as pyrene derivatives, without disrupting the carbon structure of the nanoparticles and maintaining the CNT properties [8]. Another approach consists on the "decoration" of graphene or CNTs with silver nanoparticles [4, 9-11]. Tab. 1 presents a selection of results reported in the literature for carbon hybrid composites.

TABLE 1 Silver and carbon hybrid composites properties.

Silver flakes (wt %)	CNTs (wt %)	Graphene (wt %)	Bulk resistivity (Ω.cm)	Reference
66.5	0.27	-	10^{-3}	12
80	-	0.05	4.3×10^{-5}	13
79.5	1.5	-	4×10^{-6}	14
65	-	15	2.37×10^{-4}	15

In the present work it was intended to use mainly carbon particles to achieve a high electrical conductivity level and at the same time to improve the adhesive and mechanical properties of the materials using, to achieve that goal, the minimum amount of filler.

EXPERIMENTAL

Single wall carbon nanotubes (SWCNT) were Tuball from OCSiAl; multi wall carbon nanotubes (MWCNT) were NC 7000 from Nanocyl; Carbon nanofibers (CNF) were Pyrograf III from Applied Sciences Inc.; Chopped carbon fibers were KRECA Chop from Kureha; Graphite nanoplatelets were XGnP H5, and XGnP C from XGSciences and Micrograf from Nacional de Grafite. The epoxy was Biresin® CR83 and hardener Biresin® CR832, from Sika.

The dispersion of the carbon nanoparticles in the epoxy resin was carried out on a three roll mill equipment EXAKT 80E (EXAKT Advanced Technologies GmbH, Germany). The epoxy and nanoparticles were initially hand mixed and then fed to the rear rolls of the mill and collected from the front collection tray. The mixing process consists of passing the composite mixture through the mill several times, decreasing the gap between the rolls until the minimum gap, 5 μm, is reached, followed by several passages using force mode between the front rolls. The epoxy resin hardener was manually mixed after the dispersion process was carried out. The final mixture was degassed under vacuum and cured at 80 ºC for 60 min.

Surface resistivity was measured on samples prepared by manually impregnating medium porosity filter paper (Prat Dumas 009210 Ø of 90 mm) with the composite, squeezing it with a glass rod onto filter paper over a glass base. "Dog bone" test samples were prepared with standard dimensions for tensile testing on the universal testing machine and were also used for volume electrical characterization. The samples were produced on a silicone mold.

Electrical surface resistivity of the epoxy composite-impregnated papers was obtained using a Keithley Picoammeter/Voltage Source Model 6487 with Model 8009 Resistivity Test Fixture. A Keithley System Source Meter (SMU) Model 2635B with Model 5809 Kelvin Clip Lead Set was used for volume resistivity measurements.

The measurements of surface resistivity were performed appling a potential of 10V to the sample, and measuring the current intensity. Electrical resistivity was calculated for the electrode geometry of the test fixture. I-V curves were obtained by sweeping the potential from -10 V to 10 V at 0.5 V increments. At each potential step, the corresponding current was measured. Volume resistivity was calculated from the slope of the I-V curve and geometry of the sample.

RESULTS AND DISCUSSION

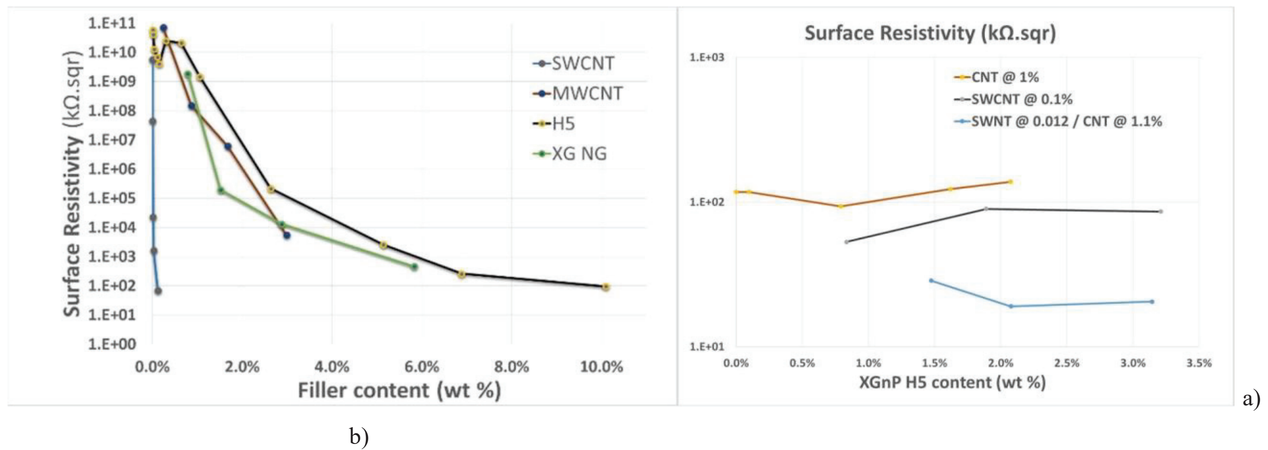
The initial characterization of the electrical properties of the composites prepared was based on the surface resistivity of composite impregnated paper. The lowest surface resistivity measured for each filler combination used, and the filler content, are presented in Tab.2. The compositions tested included the electrical percolation, that is, a large change of the electrical properties within the range of filler contents used. The single filler composites with lower percolation threshold were those based on SWCNT, MWCNT and exfoliated graphite H5, and the corresponding percolation curves are presented in Fig, 1. Notice that in this set of composites those with SWCNT required ten times lower filler weight content to attain the same level of resistivity.

The hybrid composites (containing two types of fillers) also presented noticeable gain in electrical properties, in particular those with SWCNT, MWCNT and graphite XGnP H5.

TABLE 2. Fillers and amount ranges used, for preparation of epoxy composites, and lowest surface resistivity measured in the sample of paper impregnated with composite.

Filler	Filler Amount (wt %)	Filler	Filler Amount (wt %)	Lowest Surface Resistivity (kΩ.sqr)
No filler				$1.36x10^{11}$
SWCNTs	0.001 – 0.12			$7.05x10^{1}$
MWCNTs	– 1.9			$9.56x10^{1}$
Graphite H5	0.001 – 10			$3.07x10^{5}$
Exf. Graphite H5				$9.47x10^{1}$
Graphite C	0.02 – 1			$7.92x10^{8}$
Graphite NG	0.79 – 5.83			$4.66x10^{2}$
Carbon nanofiber (CNF)	0.35 – 13			$1.34x10^{6}$
Carbon fiber (CF)	1.16 – 34			$3.59x10^{3}$
SWCNTs	0.27	MWCNTs	0.2	$2.32x10^{1}$
SWCNTs	0.12	Graphite H5	0.8 – 3.2	$3.90x10^{1}$
SWCNTs	0.12	Graphite C	0.4 - 1	$1.18x10^{2}$
MWCNTs	0.1 – 1.7	Graphite H5	0.1 – 2.5	$1.13x10^{2}$
MWCNTs	0.1	Graphite C	0.5 – 3.5	$5.39x10^{5}$
MWCNTs	0.1 – 0.3	CNF	5	$4.44x10^{3}$
MWCNTs	0.1 – 0.3	CF	7 – 28	$2.53x10^{3}$
SWCNTs and MWCNTs	0.005 – 0.26 0.1 – 1	Graphite H5	1.4 – 3.1	$1.60x10^{1}$

All the ternary systems studied present electrical conductivity. The presence of graphite nanomaterials as filler up to 3.5 wt % in combination with carbon nanotubes did not change significantly the surface electrical properties, as shown in Fig. 1 b). The presence of graphite, however, has the advantage of an apparent viscosity reduction of the epoxy composite.



b)

FIGURE 1. Surface resistivity measured on the paper impregnated composite samples a) Percolation curves for selected fillers, and b) Influence of XGnP H5 content on the electrical characteristics of SWCNT and MWCNT composites

Figure 2 presents the I-V curves and percolation curve of SWCNT samples with filler contents of 0.05, 0.1, 0.2 and 1 wt %, where the resistivity values obtained at the higher filler content are in the range of a few Ω.cm with percolation at 0.25 wt% of SWCNT.

Composites with 0.5 and 1 wt % of SWCNT and 5 wt % of graphite H5, were prepared and characterized. They presented a reduction of the electrical resistivity, from 51.5 and 8.45 Ω.cm without graphite, to 11.1 and 4,82 Ω.cm with 5 wt % of graphite.

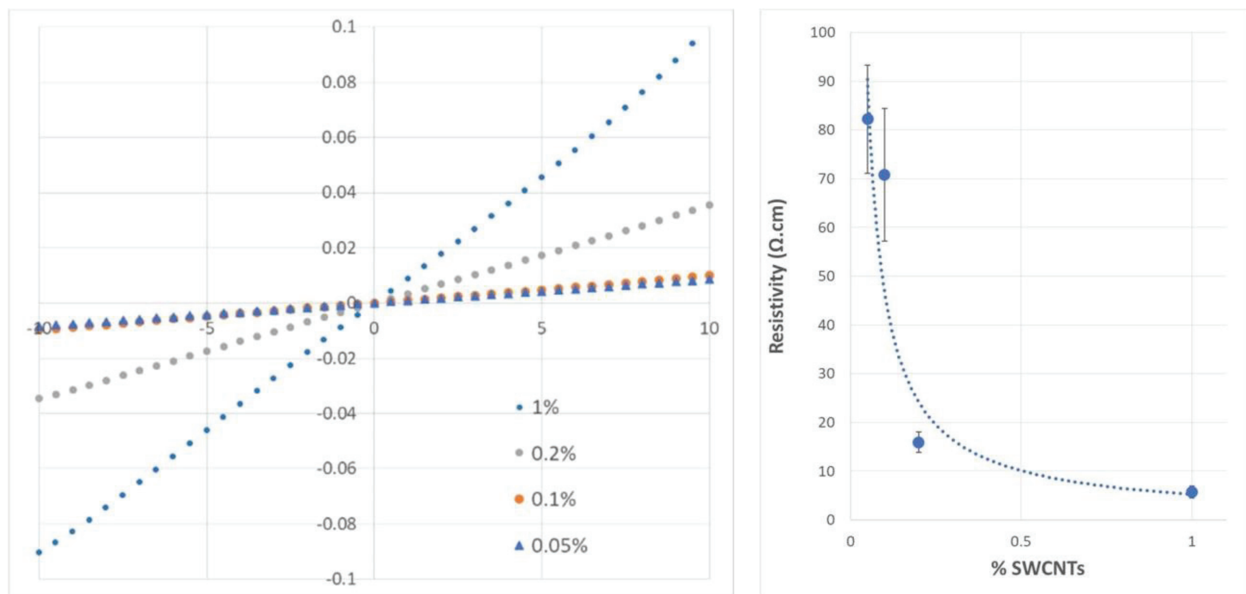


FIGURE 2. I-V curves (left) obtained with SWCNT composites using the dog bone samples and volume resistivity (right) determined from the slope of the I–V curves, accounting for the geometry of the samples.

CONCLUSIONS

Dispersion of the carbon nanoparticles in epoxy resin was achieved using a three roll mill, and percolation was observed in four composite materials with filler loads below 5 wt %. Also, hybrid composites with two nanomaterials with total loadings around 5 wt %, presented electrical conductivity.

Addition of graphite up to 3.5 wt % to SWCNT and/or MWCNT epoxy composites had no impact on the electrical properties, and at 5 wt % with SWCNT an increase of the bulk electrical conductivity was observed. Conductivity values achieved are still insufficient for the wide application on electronic soldering. Different materials combinations and carbon surface modifications will be tested in the future, to improve these properties.

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