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Preliminary Investigation on Multi-Walled Carbon Nanotubes Filled Epoxy Composite as Electrically Conductive Adhesive

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ABSTRACT: Carbon nanotubes filled epoxy resin is one type of electrically conductive adhesives (ECAs) that is used as interconnect materials in electronic application. Carbon based conductive adhesive usually have lower electrical performance in term of conductivity, compared to silver, which is the most popular filler in metal-filled ECA. The carbon based ECA is however better than silver filled ECA in terms of bonding integrity. The objective of this study is to improve electrical properties of the composite adhesive in terms of sheet resistance without compromising its bonding strength by using different size of multi-walled carbon nanotubes (MWCNTs). The aspect ratio of the two types of MWCNT fillers are of 55.5 and 1666.5, for the large diameter and small diameter, respectively. The filler loading for both MWCNTs varies from 5 wt.% to 12.7 wt.%. From the preliminary study, it has been observed that ECAs of higher MWCNTs' aspect ratio has better sheet resistance; 4.42kΩ/□ compared to 44.86 kΩ/□ at 10 wt.%. Such observation is supported by morphological analysis of the ECA showing distribution of the MWCNT in the ECA with different diameter size. Further investigation will consider the effect of different aspect ratio of the MWCNT on the mechanical properties of the ECA material, focusing on the interlayer properties of such materials.

KEYWORDS: ECA, MWCNT, aspect ratio, electrical conductivity

1. INTRODUCTION

Interconnect materials are one of the crucial part in microelectronics industry since it is where electronic components are electrically connected onto circuit board to make an electronic system functioning.

At the early stage of this industry, lead solder alloys (Sn/Pb) were used as interconnect materials without realizing the dangerous of the materials toward environment and human health as the materials are very high in toxic [1]. It is well known that the high toxicity of leads would be detrimental to human's brain development. Based on World Health Organization, lead poisoning alone renders about 9.8% of global population languishing from the idiopathic intellectual disability [2].

With better awareness of environmental protection, two alternatives are introduced to replace the lead solder alloys which are lead-free solder alloys and electrically conductive adhesive (ECA). In terms of material toxicity, lead-free solder alloys or solder paste (Sn/Ag and Sn/Ag/Cu) are working very well in eliminating the issue. Despite that, high processing temperature of the paste especially during reflow temperature (~220 ˚C) is the new challenge and have become a major drawback in surface mount component especially in plastic assembly. The processing temperatures are even higher than lead solder, that is only of 183 ˚C [3]. Moreover, such higher processing temperature could further affect the functionality and reliability performance of electronic components. Besides, higher power consumption which will further increase the manufacturing cost and companies' liability [4].

Therefore, it is crucial to have low processing temperature of interconnect materials especially during the assembly of heat-sensitive electronic component. There is a growing body of literature that recognizes the ability of ECA to be processed in a low temperature (<150 ˚C) [4] where its thermal properties are basically influenced by their polymer matrix [5]. In this study, multi-walled carbon nanotubes (MWCNTs) have been promoted as the conductive fillers in order to produce low processing temperature of electrically conductive adhesives.

Due to the intrinsic material resistivity, carbon based filler can never match the electrical performance of metallic materials such as gold, silver or even

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copper. MWCNTs have resistivity in the order of 1 x 10-3 Ω.cm [6] meanwhile 1.59 x 10-6 Ω.cm is the resistivity for silver [7]. However, better enhancement in mechanical properties are the added value of using carbon nanotubes as the fillers compared to those metallic materials. Filler content greatly influence the mechanical properties of an ECA. In conventional metal filled ECA, up to 60-80 wt.% of metal is used to achieve percolation threshold and ensuring electrical conductivity [8-12]. Since mechanical properties of an ECA is influenced by its polymer matrix, this high filler content will be affecting the mechanical integrity of the ECA and limits its usage as interconnect materials.

Nonetheless, this obstacle can be overcome by using higher aspect ratio of conductive fillers. Based on a previous study by Balberg et al. on randomly distributed stick-shaped object, critical volume fraction of percolation is inversely proportional to the aspect ratio [13]. Therefore, utilizing higher aspect ratio of filler such as MWCNT could give much lower percolation threshold whilst enhancing the mechanical properties of an ECA. To-date, the electrical properties of MWCNTs filled epoxy is yet to reach the same level as metal filled epoxy such as silver. Therefore, in this study, the effect of using different aspect ratio of MWCNT on electrical and mechanical properties of the ECA is considered.

2. MATERIALS AND METHODS

2.1 Material Selection

The polymer matrix used in Araldite 506 Epoxy Resin (Bisphenol A-epichlorohydrin) with a density of1.168 g/ml and viscosity range from 500-750 mPa.s at 25 °C. For the lower aspect ratio, MWCNTs used have an outer diameter and length ranging from 110-170 nm and 5-9 µm respectively, with a density of 1.7 g/ml at 25 °C. The carbon purity is approximately 90% as claimed by the manufacturer and labelled as A-MWCNT. Both materials above are supplied by Sigma Aldrich. Meanwhile, the bigger aspect ratio, labelled as B-MWCNT are acquired from Nanostructured & Amorphous Materials, Inc. with an outer diameter and length from 10-30 nm and 10-30 µm. Aspect ratio for both MWCNTs are tabulated in Table 1. The curing agent used is D230 of poly ether amine with density of 0.948 g/ml and 97% purity, purchased from Huntsman.

Table1: Conductive Filler Properties

MWCNT	Outer Diameter, OD (nm)		Length, L (µm)		Aspect Ratio (L/OD)		
	Min.	Max.	Min.	Max.	Min.	Max.	Avg.
A-MWCNT	110	170	5	9	29	82	55.5
B-MWCNT	10	30	10	30	333	3000	1666.5

2.2 Material Selection

First, epoxy is mixed manually with the hardener with a ratio of 100;30 by weightfor about 1 minute. MWCNT is then mixed with the suspension for another 5 minutes. The loading of MWCNTs filler in the epoxy resin for both aspect ratios varied from 5 wt.% and 12.7 wt.%. The ECA is then cured at 100 ˚C for 30 minutes in a curing oven.

2.3 Electrical Characterizations

The fabrication of the adhesives for electrical characterization is basically using printing technique, with reference to ASTM F390 [14]. First, 3M Scotch tape is used to make small gap that is rectangular, with dimensions of 12.7 mm x 2 mm on a polycarbonate sheet. Small amount of adhesive is applied in the between the gap. The adhesive is squeezed and small metal sheet is used as a squeezer. In total, six number of rectangular printed adhesives for each filler loading. See Figure 1. The adhesive is then cured under stated condition in Section 2.2. The sheet resistance of the ECAs are determined using JANDEL In-Line Four Point Probes with 1 mm distance between each probe. Input current is set to 10 µA throughout the test. Based on the ASTM standard, value of sheet resistance depends on the geometric shape of the sample. According to a previous study by Smits, in which a correction factor should be applied during measurement of sheet resistance on two-dimensional rectangular and circular samples by using four-point probe [15]. The calculation for the sheet resistance is shown in Eq. (1) below

$$R_s = G\frac{V}{I} \quad (1)$$

R_s = Sheet Resistance (Ω/□)

G = Correction Factor = 1.9475

V = Voltage (V)

I = Input Current (A)

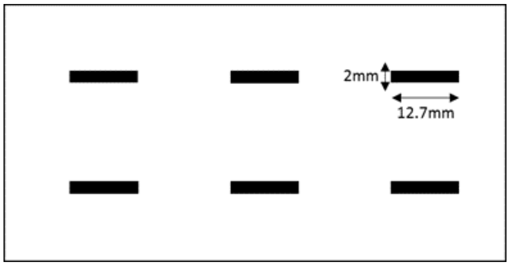


Figure 1: Schematic diagram of printed ECAs on a substrate

3. RESULT AND DISCUSSION

Based on the experimental result in Figure 2, regardless of the diameter of the MWCNT, which results in different value of the aspect ratio, in general, the sheet resistance of an ECA decrease with an increase in the filler loading, from 5 wt% to 12.7 wt%. In other words, better electrical conductivity is achieved with respect to increment of filler content. In addition, the increment of electrical conductivity with filler loading can be explained by percolation theory. This theory states that filler content in conductive polymer composite will reach its critical volume which varies based on the filler's physical properties such as shape and size. After reaching the critical volume, the filler forms a three-dimensional conductive network [16] within the polymer matrix and result in dramatically decrease in sheet resistance.

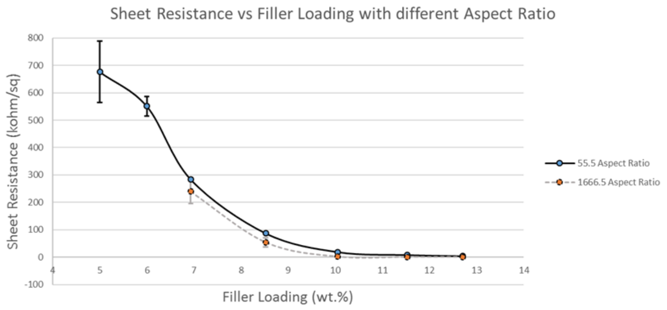
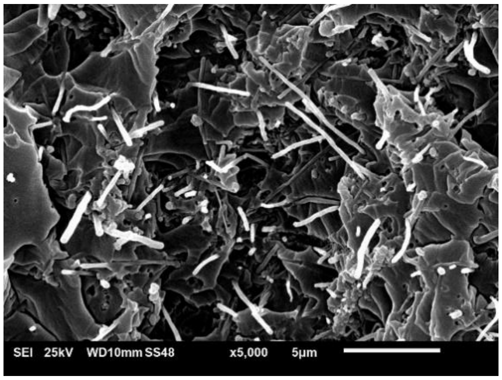


Figure 2: Sheet Resistance of A-MWCNT and B-MWCNT filled epoxy with varies range of filler loading

Referring to Figure 2, for the case of A-MWCNT/Epoxy adhesive, there is a significant difference in the graph gradient before and after 6 wt.% of filler loading, which is 125.43 kΩ/□wt.% and 286.69 kΩ/□wt.% respectively, that is more than two fold. However, when the loading reached approximately 10 wt.%, it can be clearly seen that the sheet resistance is reaching a plateau. This trend suggest that the adhesive have transformed from bulk insulator to bulk electrical conductor by percolated network. Furthermore, during this state, the electrical conductivity of an ECA is determined by intrinsic filler material properties [17]. Such phenomenon also supports the converging trend between graph A-MWCNT/Epoxy and B-MWCNT/Epoxy at 8.5 wt.% MWCNT filler loading and higher. The sheet resistance for both ECAs eventually end up at closer values because both of the filler materials are made up of carbon based material and show similar electrical properties.

The aspect ratio also shows apparent effect on the electrical properties of an ECA and can be used to improvised the electrical conductivity. From Figure 2, the use of higher aspect ratio in the B-MWCNT adhesive give better electrical conductivity by having lower sheet resistance compared to A-MWCNT. As an example, at 10 wt.%, sheet resistance for B-MWCNT/Epoxy is 1.90 kΩ/□ while sheet resistance for A-MWCNT/Epoxy is 19.28 kΩ/□. MWCNT with smaller diameter size and higher aspect ratio can form more contacts than bigger diameter size and lower aspect ratio of the tube, of the same filler loading [17]. The SEM micrographs in Figure 3 shows evidence of MWCNTs distribution at magnifications of 5000 x and 10000 x magnification level for both ECA with different aspect ratio [18]. This contact will eventually form electrical conductive pathaway within the ECA which then improve the electrical conductivity [19,20].

(a)



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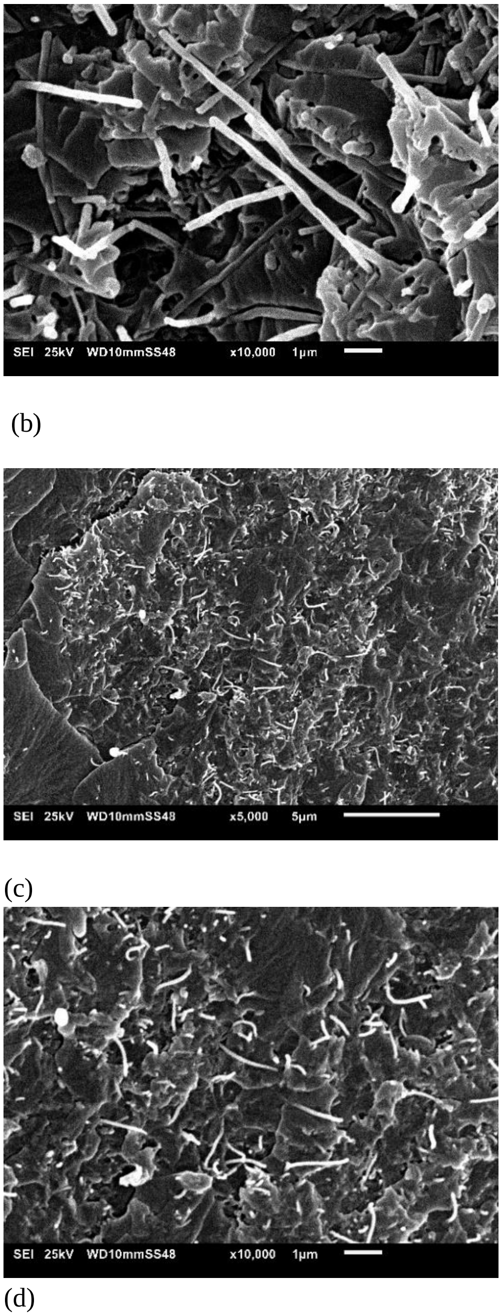

Figure 3: SEM micrographs showing the cross-sectional view of ECA with 10 wt.% filler loading for (a) & (b) A-MWCNT/Epoxy and (c) & (d) B-MWCNT/Epoxy in, at 5000x and 10000 x magnification respectively.

Although that higher aspect ratio of MWCNT give better electrical conductivity, there were no electrical conductivity at 5 and 6 wt.%. This phenomena is due to the agglomeration effect of the MWCNT itself in the ECA. Due to the high aspect ratio and flexibility of MWCNT, it tend to agglomerate with itself or another carbon nanotube. Therefore, tendency to agglomerate will increase as the aspect ratio is increase. This agglomeration will then disturbed the conductive pathaway which then hinder the movement of electron whithin the ECA. However, as the filler loading is increased and the filler concentration is higher, the MWCNT agglomeration became closer and in contact with each other hence allowing the movement of electrons.

4. CONCLUSION

The experimental results of this preliminary study suggest that using higher aspect ratio of MWCNT as a conductive filler for the ECA results in much lower critical volume of the percolation, which occurred at approximately 7 wt.%. Furthermore, better electrical conductivity of MWCNT/Epoxy is achieved by using MWCNT with higher aspect ratio. Further work will investigate the effect of using MWCNT/Epoxy ECA with different aspect ratio on the mechanical performance of an ECA and reveal the functional and reliability performance of such material in comparison to those of metal-filled ECA.

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