SYNERGISTIC EFFECT OF HYBRIDIZATION ON THE FUNCTIONAL PROPERTIES OF AGMF-MWCNT FILLED HYBRID ELECTRICALLY CONDUCTIVE ADHESIVE

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ABSTRACT: This article investigates the functional properties of the hybrid electrically conductive adhesive (ECA) with various filler loadings. Based on the literature, one of the main issues with silver-based ECA is that it typically consumes a large filler amount. Therefore, the objective of this study is to minimize the quantity of filler used by hybridizing multiwalled carbon nanotube (MWCNT) with silver micro-flakes within an epoxy binder. The experimental results suggest that there is a decreasing value in the volume resistivity of the hybrid ECA with increasing silver (Ag) filler loading, up to 6 wt.% (11 wt.% in total). However, increasing Ag flakes beyond this limit did not further reduce the volume resistivity, which could be attributed to the indication of critical filler concentration (percolation threshold) has been reached. Meanwhile, a similar trend was observed in the mechanical property of the hybrid ECA, in which there is a significant reduction in the lap shear strength, after the highest value at 12 wt.% has been reached. Such observation suggests that there is a large formation of conductive channels between micro and nano-sized hybrid fillers, simultaneously minimizing the percentage of polymer binder connections. Overall, it can be concluded that the optimum formulation of the hybrid ECA in this study is a combination of 5 wt.% MWCNT with 6 wt.% of Ag flakes, which exhibit acceptable functional properties.

KEYWORDS: *Electrically Conductive Adhesives (ECAs); Hybridization; Epoxy Resin; Conductive Fillers; Adhesion Strength*

1.0 INTRODUCTION

Electrically Conductive Adhesive (ECA) is an advancement from soldering techniques used for electronic parts assembly on circuitry components such as Printed Circuit Board (PCB), that offers lower processing temperature and eco-friendly. However, some of the main challenges for such materials to play a similar role to solder, are, in terms of the relatively poor performance of specific functions and high material consumption, which affects cost-effectiveness, proving that the ECA system is in dire need of an upgrade. Applying the new material method for solder replacement, besides the isotropic conductive adhesive (ICA), the anisotropic conductive adhesives are primarily related to its low temperature and high interconnect density capabilities in the case of touch panels. However, assembly cost and speed may also be considerations [1]. Plus, a polymer binder and conductive filler are used for chip-to-die connections in the semiconductor industry and are considered environmentally friendly [2].

To ensure excellent performance, the electrical function on Surface-Mount Technology (SMT) must be adequately monitored first to transport a sufficient amount of electricity from electronic devices to the PCB. High and stable electrical conductivity is the primary properties of these adhesives [3]. Secondly, the mechanical strength established must be strong enough to hold the mounted device from detached under certain circumstances. Thus, this article aims to address the limitations of conventional ECA by combining a carbon-based filler, i.e., multiwalled carbon nanotube (MWCNT), which is known as the stiffest material with a highly conductive adhesive, i.e., silver (Ag), to produce highly functional hybrid ECA with the optimum formulation. Some of the limitations could be overcome by the addition of silver and carbon nanotubes (CNT) as the metal filler in ECAs. The structure factors of CNTs, such as dispersion, morphology, and size have effects on the conductivity of compositions [4].

To the best of our knowledge, there have been very few studies focusing on the formulation of the hybrid ECA, particularly examining the effects of varying ranges of relative weight percentages of the conductive fillers. In this study, correlation is made with the previous research in which the hybrid ECA is formulated using a similar filler material, but with different relative weight percent. The objective is to evaluate the effect of hybridization on electrical and mechanical properties of the hybrid ECA The electrical property of the hybrid ECA was characterized using a four-point probe technique, while the mechanical property was evaluated using a Universal Testing Machine under lap shear testing mode. This research highlights the synergistic effect of hybridization of the AgMF-MWCNT fillers at relatively much lower weight percent on the electrical and mechanical properties of the hybrid ECA. The electrical property attained is reported in terms of sheet resistance while the mechanical strength of the hybrid ECA is published based on its lap shear strength values, as a function of the filler loading.

2.0 METHODOLOGY

This section explains in detail, the formulation of the hybrid ECA, which is the novelty of this research work, in which a specific ratio between the AgMF and MWCNT are considered to establish an optimum formulation for the HECA.

2.1 Formulation and Preparation

The polymer used in this research, Araldite 506 epoxy resin and the silver, which was in flakes form, were both supplied by Sigma-Aldrich, with 1.168 g/cm^3 and 10.49 g/cm^3 densities, respectively. The multi-walled carbon nanotubes were supplied by Nanostructure & Amorphous Material Inc. (NanoArmor), USA, stated with ~2.1 g/cm^3 at 20 °C. The MWCNT used had a large aspect ratio with a length of over 100 times the diameter, with high chemical stability. Finally, polyether amine (JEFFAMINE D-230) with a density of 9.466 g/cm^3 was supplied by Hunstman Singapore Pte Ltd. and used as the hardener at 30% of that weight of epoxy, as suggested in the previous works [5].

Table 1: Hybrid filler composition of the hybrid ECA

MWCNT		Silver Flakes		Total Filler Loading (wt.%)
(wt.%)	(g)	(wt.%)	(g)	
5	0.25	3	0.15	8
		4	0.20	9
		5	0.25	10
		6	0.30	11
		7	0.35	12
		8	0.40	13

The weight fraction and amount of hybrid fillers used for the present hybrid ECA are shown in Table 1. The filler loading range of both micro-nano (AgMF: MWCNT) filler was controlled in a way to study the effect of lower (3:5), equivalent (5:5), and higher (8:5) amount of micro-filler (AgMF) towards a constant amount of nano-filler (MWCNT). The materials were weighed using Mettle Toledo analytical balance, poured onto a container, and then mixed inside a centrifugal mixer (Thinky Mixer Model ARE 310). The mixing was done at 2000 rpm for 5 minutes. Lastly, the sample was applied or printed onto the substrate, inserted into a preheated Memmert oven at 100 °C for half an hour for curing process, and let cool at room temperature.

2.2 Electrical Test

The 3 mm thick acrylic substrate used for an electrical test was cut using a laser cutter machine. The laser cutter machine was used since the machine offers a sharp cutting edge and uniform size of the substrate needed, providing appropriate space for the sample strips to be printed. The hybrid ECA suspension was spread onto the pre-cleaned substrate by using a razor blade. As shown in Figure 1, the length and width of the printed strip were controlled at 12.7 mm and 2 mm, respectively.

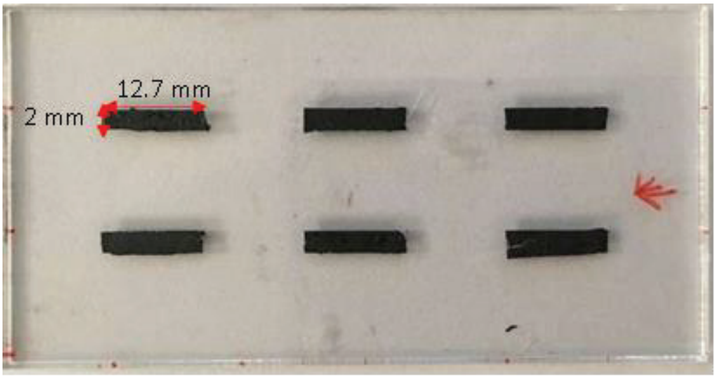

Figure 1: Printed sample strips on the acrylic sheet substrate for electrical test

A JANDEL RM3000+ 4-point probe was used to measure the resistivity of the printed hybrid ECA. The standard used for this electrical conductivity test is by referring to ASTM F390 as the standard guideline. There are six strips printed for each type of specimen, as demonstrated by Figure 1. A minimum of six readings was taken for each of the strips, with a total of 36 readings taken for each specimen. The average sheet resistance reading for each specimen was then calculated as in Equation (1) to determine the conductivity of the specimen.

$$\mathrm{R} = G\frac{V}{I} \tag{1}$$

where R is the 'sheet resistance (Ω/sq.)', G is the 'correction factor' set constant at 1.9475, V is the 'voltage (V)', and I is the 'input current (A)'.

2.3 Mechanical Test

The mechanical research was performed according to the ASTM D1002-10 standard. The procedure involves cutting of substrates using a shearing machine; substrates surface cleaning using acetone; application of hybrid ECA, and specimen calibration. An aluminium sheet with a thickness of 1.5 mm was used for the lap shear mechanical test. The formulated hybrid ECA was applied to attach the coupling substrate with an overlapping area of 322.58 mm^2, using a specially designed jig as shown in Figure 2 to control the thickness of the adhesive and the overlap parameter.

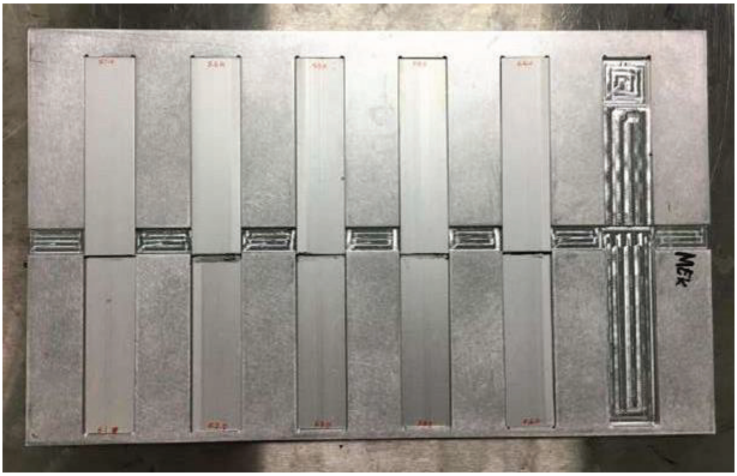

Figure 2: Sample preparation on a designed jig for lap shear test

The maximum shear strength was quantified using an Instron 8872 Universal Testing Machine (UTM) machine under the tensile loading mode, at a constant speed of 1.3 mm/min in the room temperature condition. Five samples were measured for each hybrid ECA formulation, which then converted to one average reading. The stress-strain curve was extracted from this experiment, and the shear strength of the hybrid ECA was determined using an expression as given in Equation (2) as follows:

$$\tau = \frac{F}{A} \tag{2}$$

where τ is the 'shear strength (MPa)', F is the 'maximum tensile force (N)', and A is 'overlapping area (m^2)'.

3.0 RESULTS AND DISCUSSION

3.1 Sheet Resistance

Figure 3 depicts that it is apparent that the average sheet resistance decreases from 63.97 ± 3.19 kΩ/sq. for the hybrid ECA with 8 wt.% of total filler loading, to the lowest value of 16.09 ± 0.80 kΩ/sq. at 11 wt.%. This trend is in good agreement with the previous hybrid ECA study, where increasing filler loading promotes the formation of electrons conductive channels [6 ,7]. Moreover, the percolation threshold is expected at 11 wt.% of the filler loading as the addition of Ag to 7 wt.% in the hybrid ECA with a total filler loading of 12 wt.%, results in increasing resistivity value to 39.88 ± 1.99 kΩ/sq. It is possibly due to the surface contacts among fillers beyond the percolation limit that have been ineffective in producing more electron paths, which did not further improve the electrical conductivity [5].

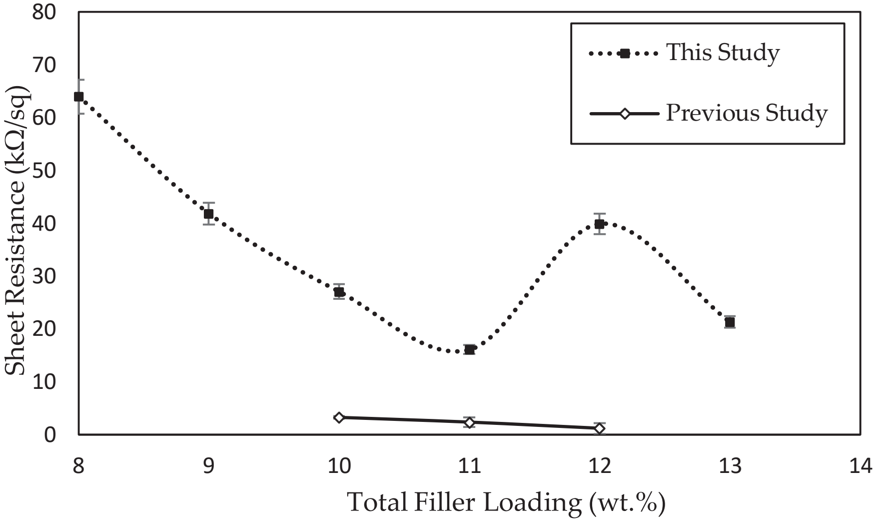

Figure 3: Plot of sheet resistance upon varying total filler loading [5]

Such findings could be attributed to the size of the MWCNT that is in the nano range, which features an outside diameter of 10-20 nm as compared to the silver flakes that are in the micron-size, with an average size of 10 µm. Therefore, the efficiency is more significant when using a higher loading of nano-sized fillers as compared to those of micron-sized filler, although Ag, on its own, has a conductivity of 6.3×10^7 S/m as compared to MWCNT, with conductivity in the range of 10^6 to 10^7 S/m for pure CNT. Thus, it can be suggested that overall, for the hybrid ECA within ranged filler loading, the synergistic improvement in the conductivity of the hybrid ECA is limited at increasing Ag filler loading limited to 6 wt.% only, with 5 wt.% of MWCNT.

Nonetheless, the electrical performance of hybrid ECA in this study is inferior to previous work that increased the MWCNT loadings higher than AgMF. Such observation could be correlated with the relative amount of micro and nanofillers, where it is proven that more MWCNT loadings over AgMF in hybrid filler ratio enhanced the electrical conductivity of the HECA [8, 9]. Another study also found that using a higher amount of micron-sized than nano-sized filler exhibit increased electrical resistance [10]. Plus, an enhanced formation of conducting channels has been achieved with the formation of nano-sized branches among Ag micro-flakes at an optimum ratio between hybridized fillers [11]. Hence, although the AgMF filler contributes to the electrical conductivity, the appropriate amount of each involving micro-nano fillers play an important role that may bring both superior and inferior conductivity performance [12].

3.2 Shear Strength

Based on Figure 4, the overall trend shows a gradual increase in the average lap shear strength of the hybrid ECA, from 8 to 11 wt.% of total filler loading, followed by a large increase from 16.09 ± 3.35 MPa at 11 wt.% to the highest value of 39.88 ± 5.05 MPa at 12 wt.%. Following this, with the addition of 1 wt.% Ag in the hybrid ECA system (13 wt.% total filler loading), there is a marginal reduction in the hybrid ECA average lap shear strength, with a value of 21.32 ± 4.45 MPa. Such observation is possible because, beyond a saturation limit or threshold of the filler loading in the ECA system, the filler is unable to carry the external load efficiently and results in decreasing shear strength of the composite [13], in which the strength of the composite is lower than the strength of the neat polymer matrix [14]. Moreover, it was found that beyond a specific limit of filler loading content, the adhesion bond between the epoxy resin and filler loading would decrease, resulting in the strength reduction of the composite [15]. In other words, it suggests that the composition of filler loading will increase the mechanical properties of the composite until it reaches a specific level or percolation and result in a decrease in the mechanical properties of the composite when exceeding the limit or threshold [16].

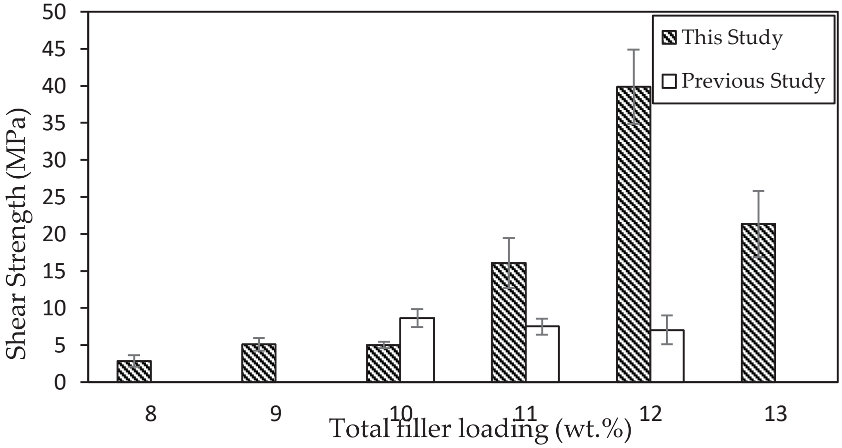

Figure 4: Plot of shear strength upon varying total filler loading against previous study [17]

On the contrary, the previous study reported a decreasing trend in the average lap shear strength with increasing filler loading [17] because the density of the composite is decrease compared to the polymer itself [16]. Higher filler loading will lead to poor wetting and a reduction in the stress transfer efficiency across the filler resin interface [14].

However, at a total filler loading of 11 and 12 wt.%, the correlation between the hybrid ECA shows that the lap shear strength of the current study is superior.

Moreover, with an increasing amount of metal filler Ag up to 7 wt.%, greater lap shear strength is achieved, which is in strong agreement with Luo et al. [17], who stated that an optimum amount of metal filler loading would promote a higher tensile strength due to maximized contact surfaces among chains of polymer and metal fillers [18]. It was argued that by controlling of the filler loading could improve mechanical performance while enhancing the composite's electrical properties [19,20].

Therefore, considering both electrical and mechanical performance, the optimum amount of filler in this hybridization is established at 5 wt.% MWCNT and 6 wt.% Ag flakes (11 wt.% total filler loading), with the lowest sheet resistance and a moderate shear strength value. A better adhesion strength could be achieved through appropriate chemical treatment on the substrate surface [20].

4.0 CONCLUSION

Based on the findings, the objective of this paper has been achieved in which a relatively small amount of the conductive fillers is sufficient to produce a synergistic effect on the functional properties of the hybrid electrically conductive adhesive, that is in terms of electrical and mechanical properties of the hybrid ECA. Based on the experimental results, in terms of electrical property, the formulation range limit that is practical in increasing the electrical conductivity is up to 11 wt.% only, as too much amount of Ag flakes will deteriorate the performance. Furthermore, a higher amount of micro-filler over nano-filler exhibits lower performance in electrical conductivity, as found by comparison in the current and previous studies. In terms of mechanical property, the results from the lap shear test revealed that increasing the total filler loading up to 12 wt.% obtained a gradual increase in the maximum shear strength. However, beyond this filler loading, there is a gradual decrease, suggesting a saturation state for the hybrid ECA system; therefore, adding more filler does not further enhance the mechanical strength of the hybrid ECA. Additionally, the presence of increasing metal filler (AgMF) has improved the adhesion strength multiple times from the previous study, despite the lower performance in electrical conductivity. More specifically, overall, it has been found that an optimum hybrid ECA formulation is established at a combination of 5 wt.% MWCNT with 6 wt.% Ag flakes is the optimum formulation in which the hybrid ECA exhibit acceptable functional properties in terms of electrical and mechanical properties.

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AUTHOR CONTRIBUTIONS

The main contributions of the authors for this research article are as follow:

S.H.S.M. Fadzullah: Supervision, Validation, Writing- Reviewing and Final Editing; Z. Adnan: Methodology, Writing- Original Draft Preparation; G. Omar: Co-Supervision and Validation; Z. Mustafa: Formulation, Validation; I. Ismail: Reviewing; S.D. Malingam: Methodology and Reviewing.

CONFLICTS OF INTEREST

The manuscript has not been published elsewhere and is not under consideration by other journals. All authors have approved the review, agree with its submission, and declare no conflict of interest on the manuscript.

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