THE EFFECT OF ASPECT RATIO ON MULTI-WALLED CARBON NANOTUBES FILLED EPOXY COMPOSITE AS ELECTRICALLY CONDUCTIVE ADHESIVE

M.M. Nasaruddin[1], S.H. Sheikh Md Fadzullah[1], G. Omar[1], Z. Mustafa[2], M. Ramli[1], M.Z. Akop[1], I.S. Mohamad[1] and B. Çoşut[3]

[1]Centre for Advaced Research on Energy, Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

[2]Advanced Manufacturing Centre, Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

[3]Department of Chemistry, Gebze Institute of Technology, 41400 Kocaeli, Turkey.

Corresponding Author's Email: [1]hajar@utem.edu.my

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ABSTRACT: Multi-walled carbon nanotubes (MWCNTs) filled epoxy resin is a type of Electrically Conductive Adhesive (ECA) that is used as interconnect materials in electronics application. Carbon-based conductive adhesive usually has inferior electrical conductivity to silver but mechanically superior in terms of its bonding integrity. The aim of this paper is to study the effect of aspect ratio on the electrical and mechanical properties of the composite adhesive. The aspect ratio of the two types of MWCNT fillers are of 55.5 and 1666.5. The filler loading for both MWCNTs varies from 5wt.% to 12.7wt.%. From the experimental study, the sheet resistance for the ECA with higher aspect ratio is approximately 4.42kΩ/□ in comparison to only 44.86kΩ/□ for the ECA with lower MWCNT aspect ratio. Morphological analysis of the ECA showed evidence of MWCNT distribution in the ECA with different diameter size. Nonetheless, the MWCNTs filled epoxy with lower aspect ratio exhibit higher shear strength with a maximum value of 8.08MPa, in comparison to only 4.68MPa to that of the ECA with higher MWCNTs aspect ratio, possibly due to the tendency in forming agglomeration of the MWCNT with smaller tube diameter, resulting in weaker interfacial strength.

KEYWORDS: *ECA; MWCNT; Aspect Ratio; Electrical Conductivity; Lap Shear Strength*

1.0 INTRODUCTION

Electrically Conductive Adhesive (ECA) is regarded as an alternative for interconnect material replacing the conventional material such as lead solder and lead-free solder due its low processing temperature. ECA is made up of polymer matrix that acts as a binder to the conductive fillers. In conventional ECA, metallic materials such as silver are used as the conductive fillers due to better electrical conductivity. However, compared to metal-filled conductive adhesives, multi-walled carbon nanotube (MWCNT)- filled adhesives are corrosion and metal migration resistant, high in strength, and lightweight. Due to the intrinsic material resistivity, carbon- based filler can never match the electrical performance of metallic materials such as gold, silver or even copper. MWCNTs have resistivity in the order of 1 x 10-4Ω.cm [1] meanwhile 6 x 10-6Ω.cm is the resistivity for silver [2]. However, better enhancement in mechanical properties is the added value of using carbon nanotube as a filler compared to those of metallic materials. Filler content greatly influences 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 ensure electrical conductivity [3-5]. Since mechanical properties of an ECA are influenced by their polymer matrix, this high filler content will affect the mechanical integrity of the ECA and limit its usage as interconnect materials.

Nonetheless, this obstacle can be overcome by using higher aspect ratio of conductive fillers. Based on an early study on randomly distributed stick-shaped object, critical volume fraction of percolation is inversely proportional to the aspect ratio [6-8]. Therefore, utilizing higher aspect ratio of filler such as MWCNT could give much lower percolation threshold whilst enhancing the mechanical properties of an ECA. However, the main concern in choosing MWCNT as a filler material is that it has difficulty to be disentangled, leading to formation of agglomerates that is expected to affect the performance of ECA. To-date, the electrical properties of MWCNT- filled epoxy is yet to reach the same level as metal- filled epoxy such as silver. Therefore, the objective of this work is to study the effect of different MWCNT aspect ratio on electrical and mechanical properties of the ECA.

2.0 MATERIALS AND METHODOLOGY

2.1 Material Selection

Araldite 506 Epoxy Resin (Bisphenol A-epichlorohydrin) with a density of 1.168g/ml was used as a polymer binder for the ECA fabricated in this study, having a viscosity in the range of 500-750 mPa.s at 25°C. Meanwhile, two types of MWCNT were used, termed either the low aspect ratio (A-MWCNT), having an outer diameter and length ranging from 110-170nm and 5-9µm respectively, with a density of 1.7g/ml at 25°C and carbon purity of approximately 90%. Besides, the MWCNT with relatively high aspect ratio (B-MWCNT) is was purchased from Nanostructured & Amorphous Materials, Inc., with an outer diameter and length from 10-30nm and 10-30µm. Detailed dimension and specific aspect ratio for both MWCNTs are tabulated in Table I. The curing agent used in this study was purchased from Huntsman, that is the D230 poly ether amine with a density of 0.948g/ml and 97% purity.

Table 1: Floating-poin operations necessary to classify a sample

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 Adhesive Preparation

Epoxy resin was manually mixed with the hardener with a ratio of 100:30 by weight for about 1 minute. MWCNT was then added in the mixture and mixed for another 5 minutes. The loading of MWCNTs filler in the epoxy resin for both aspect ratio varied from 5, 6, 6.93, 8.52, 10.05, 11.53 and 12.7 wt.%. The ECA was then cured at 100 ˚C for 30 minutes in a curing oven.

2.3 Electrical Characterisations

The fabrication of the adhesives for electrical characterization included the use of printing technique, with reference to ASTM F390 [9]. Here, a 3M Scotch tape was used to make small rectangular gap, with dimension of 12.7 mm x 2 mm on a polycarbonate sheet. Small amount of adhesive was applied in the gap between. The adhesive was then squeezed and small metal sheet was used as a squeezer. In total, a minimum of six rectangular- printed adhesives were prepared for each filler loading (Figure 1). The adhesive was then cured under the condition described in Section 2.2. The sheet resistance of the ECAs was determined using JANDEL In-Line Four Point Probes with 1-mm distance between each probe.

Based on the ASTM standard, the value of sheet resistance depends on the geometric shape of the sample. Therefore, correction factor was considered during the measurement of sheet resistance on two-dimensional rectangular and circular samples by using four-point probe. The sheet resistance was calculated using an expression as given in Equation (1):

$$R_S = G\frac{V}{I} \tag{1}$$

where R_S is sheet resistance (Ω/□), G is correction factor with the value of 1.9475, V is voltage (V) and I is input current (A).

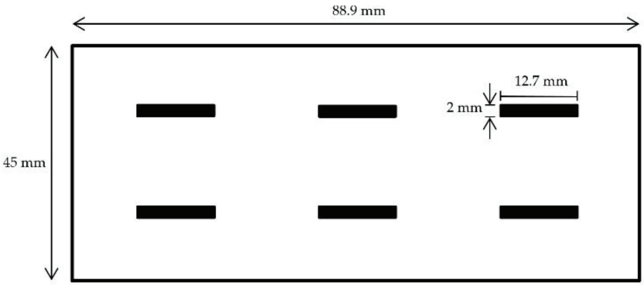


Figure 1: Schematic diagram of printed ECAs on a substrate

2.4 Mechanical Characterisations

This test was conducted to evaluate the adhesion strength in terms of lap shear strength of the ECA under tensile loading, with reference to the ASTM D1002 [10]. Aluminium sheets with dimension of 25.4 mm (width) x 101.6 mm (length) x 1.6 mm (thickness) was used as a substrate. The length for gripping area was set to be at 30 mm and 25.4 mm for adhesive overlap area. Figure 2 shows the schematic diagram of the lap shear test set up.

In this test, it is crucial to have double layer of substrate at the gripped area with the direction being parallel during tensile loading. Another important factor is the bonding line thickness which needs to be controlled throughout the test. Bonding line thickness used in this test is of 0.1 mm, as shown in Figure 2. During testing, the crosshead displacement rate used was at 1.3 mm/min, in accordance with the ASTM D1002 standard with a minimum of 5 readings for each sample tested.

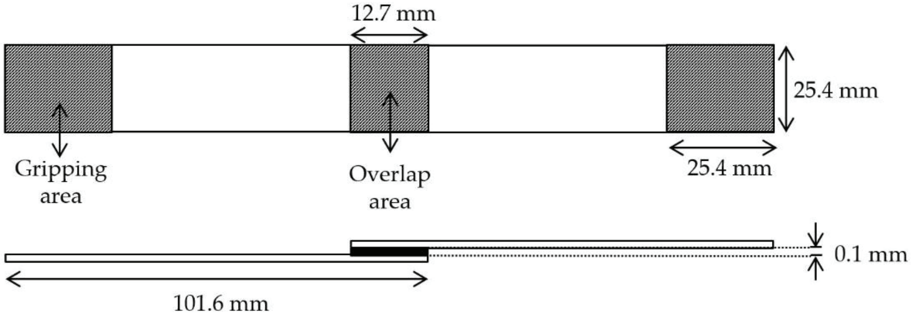


Figure 2: Schematic diagram of sample assembly for lap shear test

The result obtained from this test, which is lap shear strength was calculated by dividing maximum tensile force with the adhesive overlap area. The expression used to determine the lap shear strength is given in the expression written in Equation (2) as follows:

$$\tau_{Lap} = \frac{F_{Max}}{A} \tag{2}$$

whereby τ_{Lap} is lap shear strength (MPa), F_{Max} is the maximum tensile force (N) and A is the adhesive overlap area (m^2).

3.0 RESULTS AND DISCUSSION

3.1 Sheet Resistance

Based on the sheet resistance plot vs. filler loading for both types of ECA with high (A-MWCNT/Epoxy) and low aspect ratio (B-MWCNT/Epoxy) shown in Figure 3, in general, regardless of the MWCNT aspect ratio,sheet resistance of the ECA decreases 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 increase in the filler loading. Such observation is supported by the percolation theory, which states that filler content in conductive polymer composite reaches its critical volume that varies, based on the filler's physical properties such as shape and size. Upon reaching the critical volume, the filler forms a three-dimensional conductive network [11] within the polymer matrix and results in dramatic decrease in the sheet resistance.

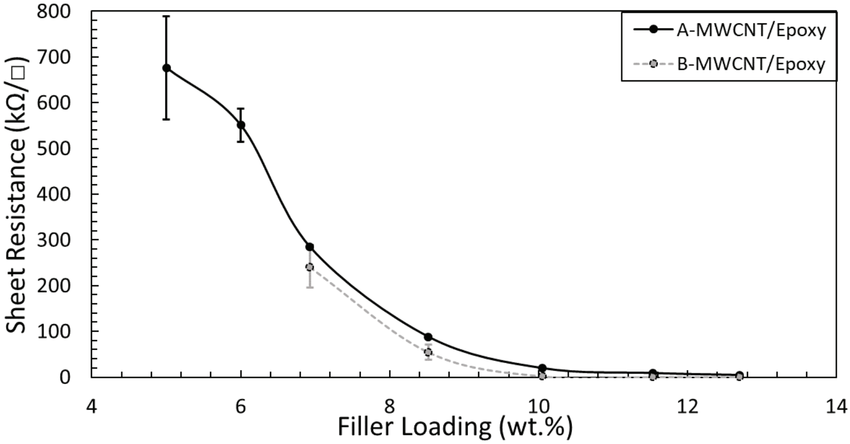
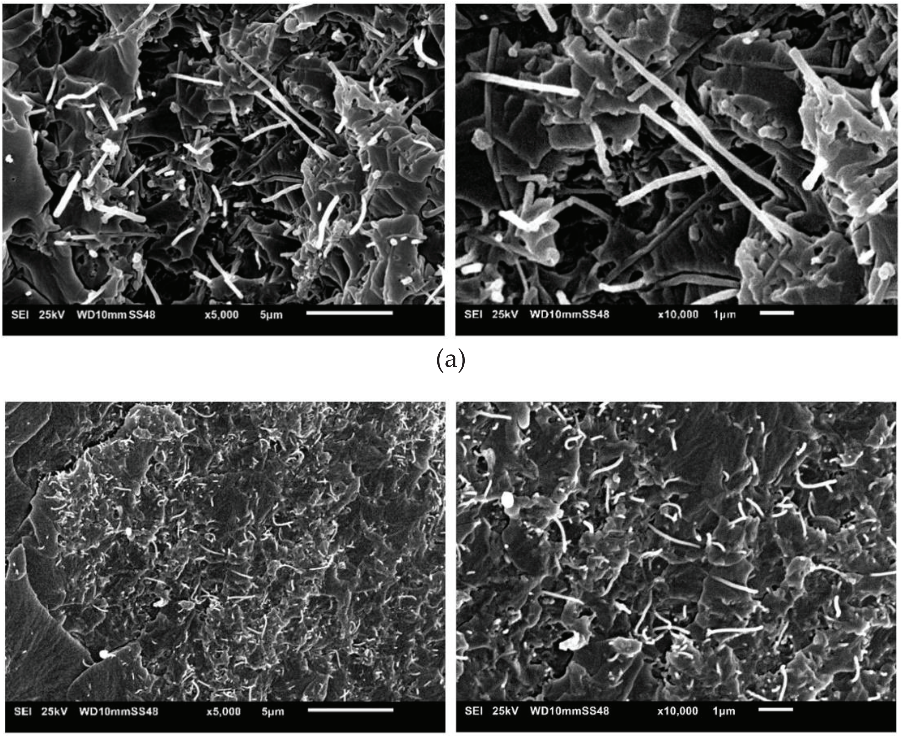


Figure 3: Sheet resistance of A-MWCNT and B-MWCNT as epoxy filler with varies range of loading

Moreover, for the case of high aspect ratio ECA (A-MWCNT/Epoxy), 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 could be clearly seen that the sheet resistance has reached a plateau. This trend suggests that the adhesive has transformed from bulk insulator to bulk electrical conductor by percolated network. Furthermore, during this state, the electrical performance of an ECA is determined by intrinsic filler material properties [12]. Such phenomenon is also supported by the converging trend between graph A-MWCNT/Epoxy and B-MWCNT/Epoxy at 8.5 wt.% MWCNT filler loading and higher which end up at closer values.

The aspect ratio also shows apparent effect on the electrical properties of an ECA and can be used to improvise the electical conductivity. From Figure 3, the use of higher aspect ratio in the B-MWCNT/Epoxy adhesive gives better electrical conductivity by having lower sheet resistance compared to A-MWCNT/Epoxy. As an example, at 10 wt.%, the 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 (high aspect ratio) can form more contacts than bigger diameter size (low aspect ratio), at the same filler loading [12]. The SEM micrographs in Figure 4 shows the evidence of MWCNTs distribution at magnification of 5000 x and 10000 x level for both ECA with different aspect ratio. This contact eventually forms electrical conductive pathaway within the ECA which then improves the electrical conductivity.



(a)

(b)

Figure 4: SEM cross-sectional micrographs of ECA with 10.05 wt.% filler loading for (a) A-MWCNT/Epoxy and (b) B-MWCNT/Epoxy

Although higher aspect ratio of MWCNT exhibits better electrical conductivity, there is no electrical conductivity at 5 and 6 wt.%. This phenomenon is possibly due to the agglomeration effect of the MWCNT itself in the ECA. Due to the high aspect ratio and flexibility of MWCNT, there is a tendency for agglomeration within itself or another carbon nanotube [13]. Moreover, the tendency to agglomerate will increase as the aspect ratio is increased. This agglomeration will also disrupt the conductive pathway which then hinders the movement of electron whithin the ECA. However, as the filler loading is increased and the filler concentration is heightened, the MWCNT agglomeration becomes closer and in contact with each other hence allowing the movement of electrons.

3.2 Lap Shear Test

Figure 5 displays the experimental results following lap shear test using three different filler loadings following the electrical conductivity test. The chosen filler loadings are 7 wt.%, 8.52 wt.% and

10.05 wt.%, besides neat epoxy as a benchmark. From Figure 5, the plots show a similar trend for the results using both aspect ratios of MWCNTs, in which the lap shear strength increases with an increase in the MWCNT filler loading, up to a maximum point. Beyond this point, the lap shear strength showed a decrease despite the increasing content of the MWCNT filler.

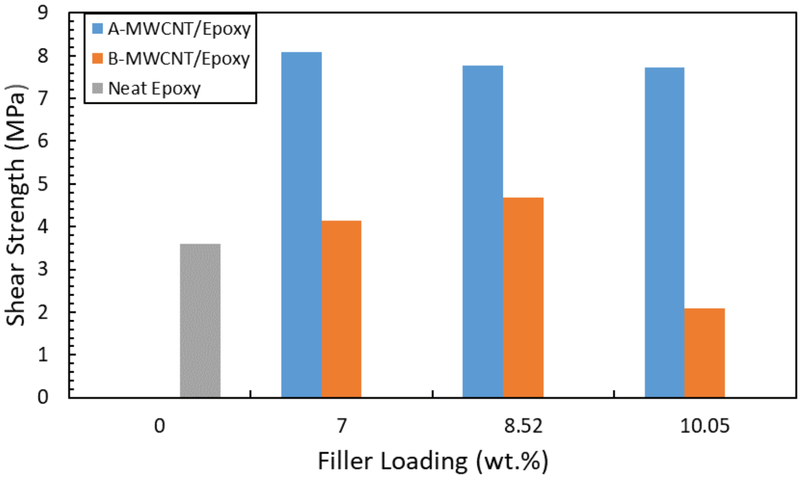
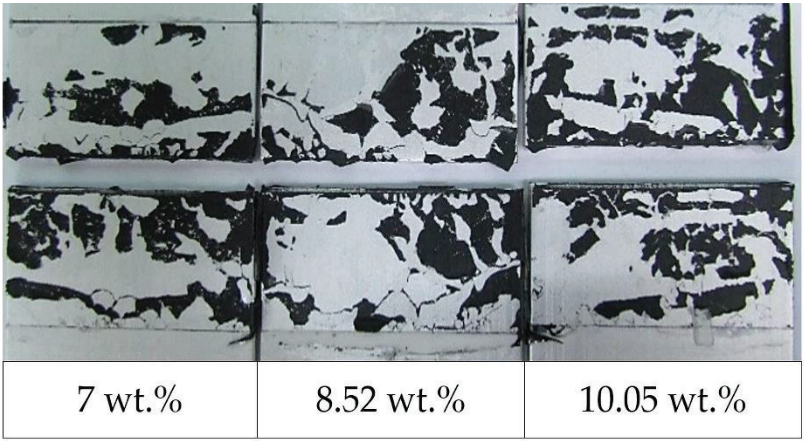


Figure 5: Shear strength for neat epoxy, A-MWCNT/Epoxy and B-MWCNT/Epoxy

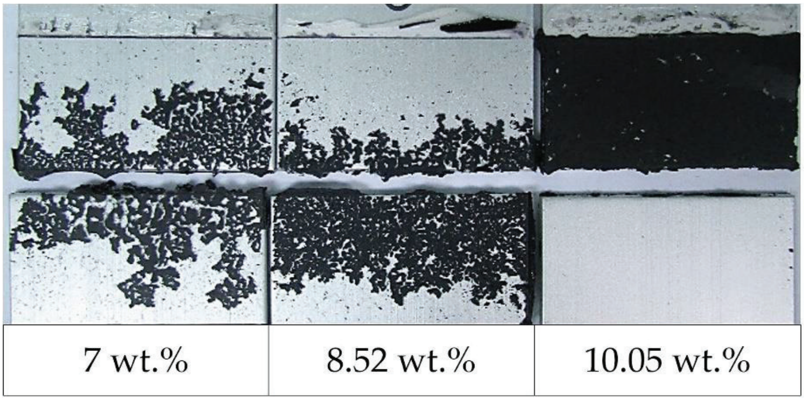
There is a significant enhancement in the lap shear strength for A-MWCNT/Epoxy at 7 wt.% which is 8.08 MPa while 3.59 MPa for neat epoxy, which is double the difference. This value however starts to decrease when filler loading is higher. Despite that, there is no significant decrease since the percentage differences are only 3.96% and 4.33% at filler loadings of 8.52 wt.% and 10.05 wt.% respectively. The trend nevertheless is almost the same for higher aspect ratio of MWCNTs. Based on Figure 5 above, as filler loading is higher, the lap shear strength is also elevated up until 4.68 MPa at 8.52 wt.%. The trend from these experimental results are in good agreement with the findings reported in the literature. Hsiao et al. [14] reported on an increase in the lap shear strength of the adhesive by 31.2% and 45.6% for 1 wt.% and 5 wt.% respectively. Furthermore, they argued that such occurrence is due to the transferred mechanical stress from the adhesive system to the MWCNTs fibre system which is the strongest component in the composite. These observations are supported by visual observations on the failure area of the test samples, where it was found that the failure was in the MWCNTs fibre system meanwhile failure occurred at the epoxy along the bonding interface for neat epoxy.

Additionally, the shear strength for B-MWCNT/Epoxy significantly decreased to 2.09 MPa which is more than two-fold, at filler loading of 10.05 wt.%. In addition, the shear strength recorded at the highest filler loading is the lowest among all the readings, that is even lower than the shear strength for neat epoxy. The shear strength at this filler loading gradually declined for 41.78% relative to the neat epoxy. This occurrence suggests that lap shear strength of ECA for both types of MWCNT aspect ratio show a critical filler loading where the shear strength has eventually declined. Hence, adding up more MWCNTs in the composite adhesive beyond the critical filler loading does not enhance the ECAs' mechanical properties. The mechanical integrity of the matrix materials (epoxy resin) that acts as a binder will be reduced with respect to the abundant presence of fillers (MWCNTs) in the system [15].

Moreover, such observation could be due tosome portion of the epoxy resin clinging onto the MWCNT surface, thus leaving less amount of epoxy to be bonded with the substrate. In this aspect, two failure modes can be categorized from the adhesive bond failure; these being the cohesive failure and adhesive failure [16] in which the adhesive failure exhibits the weakest strength.Thus, the conductive adhesive will have better cohesive strength rather than adhesive strength, which could have affected the adhesive bond failure modes towards adhesive failure. The MWCNT filler contact area to the epoxy resin increases with increasing aspect ratio, thus aids in an improvement in the cohesive strength of the composite adhesive. However, it must be noted that ECA should essentially exhibit good adhesive strength since the application is to bond two materials together (electric component and PCB).



(a)



(b)

Figure 6: Visual observation of each sample following lap shear test for (a) A- MWCNT/Epoxy and (b) B-MWCNT/Epoxy

Visual observation on the test samples surface area is captured in Figure 6, showing evidence of different failure modes of the adhesive bond. Based on Figure 6 (b), it is apparent that the failure modes shift from mix modes adhesive-cohesive failure to pure adhesive failure with increasing filler concentration. Such observation supports the reason for the inferior lap shear strength for B-MWCNT/Epoxy at 10.05 wt.%. However, the shifting failure modes can be barely seen at lower aspect ratio of MWCNTs; A-MWCNT which are displayed in Figure 6 (a). Another factor that affects the performance of lap shear strength is the formation of agglomerates within the MWCNTs which is expected to form a weak interface with the epoxy resin [17]. Since the tendency to agglomerate is higher with higher aspect ratio [13], A-MWCNT is less likely to form agglomerates thus shows insignificant difference in the failure modes as well as lap shear strength at various filler loading.

4.0 CONCLUSION

In summary, the effect of different MWCNT aspect ratio on electrical and mechanical properties of ECA has been presented. It can be concluded that the ECA with higher MWCNT aspect ratio (B-MWCNT/Epoxy) exhibits better electrical conductivity as compared to those with low MWCNT aspect ratio (A-MWCNT/Epoxy). Such observation is possibly due to more contacts formed between the fillers of the epoxy, which results in an increased number of conductive pathways, thus yields in an enhanced electrons mobility. Nonetheless, B-MWCNT/Epoxy showed no electrical conductivity at 5 and 6 wt.% filler loading, possibly mainly due to the occurrence of agglomeration. On the other hand, A-MWCNT/Epoxy displayed a greater shear strength in contrast to B-MWCNT/Epoxy. This event can be explained by the fact that at lower MWCNT aspect ratio, the number of fillers in-contact with the epoxy yields in a superior interfacial strength. Moreover, the agglomeration issue which exists in B-MWCNT/Epoxy has further weaken the bond within the former components (fillers and epoxy). Herein, higher MWCNT aspect ratio is verified to encompass a weaker shear strength. The findings of this study would profoundly enhance the information on the effect of different MWCNT aspect ratio of the ECA. This study also emphasizes the importance of MWCNT's aspect ratio for specific ECA applications.

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