INFLUENCE OF MULTI-WALLED CARBON NANOTUBE ASPECT RATIO ON THE ELECTRICAL AND MECHANICAL RELIABILITY OF EPOXY-BASED ELECTRICALLY CONDUCTIVE ADHESIVES UNDER HYGROTHERMAL AGING

S.H.S. Md Fadzullah[1*], M.M. Nasaruddin[1], Z. Mustafa[2], B. Çoşut[3] and I. Ismail[4]

[1]Fakulti Teknologi dan Kejuruteraan Mekanikal,
Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

[2]Fakulti Teknologi dan Kejuruteraan Industri dan Pembuatan,
Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

[3]Department of Chemistry,
Gebze Technical University (GTU),
41400, Gebze,Kocaeli,Türkiye.

[4]Department of Physics, Faculty of Mathematics and Natural Science,
Universitas Syiah Kuala, Banda Aceh 23111, Indonesia

*Corresponding Author's Email: hajar@utem.edu.my

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ABSTRACT: Electrically conductive adhesives (ECAs) are gaining attention as promising alternatives to traditional solder in electronic packaging, particularly for applications requiring low processing temperatures and compatibility with heat-sensitive components. This study investigates the effect of multi-walled carbon nanotube (MWCNT) aspect ratio on the electrical and mechanical performance of epoxy-based ECAs under hygrothermal ageing (85 °C/85 % RH). Low-aspect ratio (L-MWCNT) and high-aspect ratio (H-MWCNT) fillers were incorporated at different loadings, and the resulting adhesives were characterised in terms of volume resistivity and lap shear strength (LSS) before and after up to three weeks of hygrothermal ageing. The results show that H-MWCNT adhesives exhibited markedly lower initial resistivity and higher LSS compared to L-MWCNT adhesives. Under hygrothermal ageing, the H-MWCNT ECAs retained up to 87 % of their initial LSS and showed only a marginal increase in resistivity, while L-MWCNT ECAs degraded more significantly. Optimising filler aspect ratio is thus essential for enhancing the performance and long-term reliability of ECAs in harsh service environments.

KEYWORDS: *Electrically Conductive Adhesives; Multi-Walled Carbon Nanotubes; Aspect Ratio; Hygrothermal Ageing; Epoxy Composites*

1.0 INTRODUCTION

Electrically conductive adhesives (ECAs) have increasingly become a viable alternative to traditional solder interconnects in microelectronics, owing to their low curing temperatures, environmental compliance, and compatibility with flexible substrates [1], [2], [3]. With advancements in polymer formulations and filler dispersion techniques, modern ECAs are engineered to deliver multifunctionality—offering tailored electrical, thermal, and mechanical properties for demanding applications [4]. A key enabler in this evolution has been the integration of multi-walled carbon nanotubes (MWCNTs), which bring high electrical conductivity, mechanical strength, and exceptional aspect ratios to the composite matrix [5]. The aspect ratio of MWCNTs significantly influences the formation of conductive networks, percolation thresholds, and mechanical reinforcement, enabling enhanced performance even at low filler loadings [6], [7]. Furthermore, innovations in interfacial chemistry—such as tailored binder formulations [8] and post-processing methods like water vapor treatments [9]; have improved interparticle contact, filler-matrix adhesion, and thermal transport in epoxy-based ECAs. Nevertheless, challenges remain regarding how these enhancements impact processing complexity, viscosity, and long-term performance [10].

Despite substantial progress, relatively few studies have systematically examined hygrothermal reliability—specifically how ECAs sustain their electrical and mechanical integrity under prolonged high-temperature and high-humidity conditions (~85 °C/85 % RH). Earlier investigations into silver- or nanofiller-based adhesives report degradation mechanisms such as oxidation, plasticization, and interfacial failure [11], [12], [13], but a clear understanding of how filler geometry, especially MWCNT aspect ratio, governs long-term durability is still lacking. Foundational works on conductive adhesives [14] and recent efforts to optimize stability in hybrid formulations [15] provide valuable insights, yet stop short of delivering a comprehensive, geometry-centered ageing analysis under controlled humidity and temperature. The present study addresses this gap by evaluating how the aspect ratio of MWCNTs affects the performance of epoxy-based ECAs under hygrothermal ageing. Specifically, we compare low-aspect ratio (L-MWCNT) and high-aspect ratio (H-MWCNT) systems in terms of volume resistivity and lap shear strength, both before and after controlled environmental exposure. Our findings aim to illuminate the critical balance between filler geometry and adhesive resilience, with important implications for the design of robust ECAs in harsh service environments.

2.0 METHODOLOGY

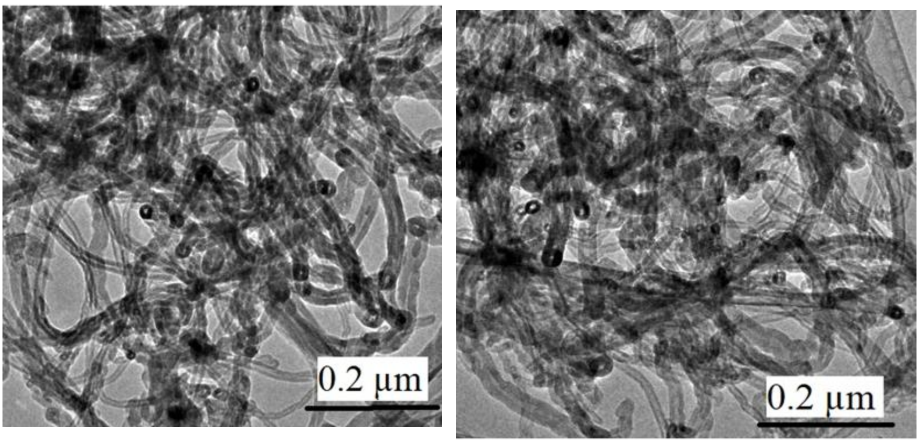
2.1 Materials

The epoxy matrix used in this study was a commercially available bisphenol-A-based thermosetting resin (Araldite LY 5052, Huntsman Advanced Materials, Switzerland), cured with a cycloaliphatic amine hardener (Aradur 5052). Multi-walled carbon nanotubes (MWCNTs) of two different aspect ratios were employed as conductive fillers: low-aspect ratio MWCNTs (L-MWCNT) with average length 5–15 μm and diameter 10–20 nm, and high-aspect ratio MWCNTs (H-MWCNT) with average length 10–30 μm and diameter 8–15 nm. The aspect ratio values were selected to study their influence on electrical network formation and mechanical reinforcement, in line with earlier work demonstrating the strong dependence of percolation and conductivity on filler geometry [6], [7], [8]. All materials were used as received without further purification.

Two adhesive formulations were prepared using low-aspect ratio (L-MWCNT) and high-aspect ratio (H-MWCNT) multi-walled carbon nanotubes, as detailed in Table 1. The difference in nanotube geometry is illustrated in the TEM micrograph images in Figure 1, showing that H-MWCNTs possess a significantly greater length-to-diameter ratio, enabling more efficient conductive network formation.

Table 1: Physical and morphological characteristics of L-MWCNT and H-MWCNT fillers

MWCNT	Outer Diameter, OD (nm)		Length, L (µm)		Aspect Ratio (L/OD)		
	Min.	Max.	Min.	Max.	Min.	Max.	Avg.
L-MWCNT	10.0	20.0	0.5	2.0	25.0	200.0	112.5
H-MWCNT	10.0	20.0	10.0	30.0	500.0	3000.0	1750.0



(a) (b)

Figure 1: TEM micrographs of MWCNT arrangement for (a) low aspect ratio (L-MWCNT); (b) high aspect ratio (H-MWCNT)

2.2 Preparation of Electrically Conductive Adhesives

The overall preparation process is shown in Figure 2, with the corresponding formulation details presented in Table 2. The epoxy resin and MWCNTs were mixed in predetermined weight ratios using a mechanical stirrer at 2000 rpm for 10 minutes, followed by three cycles of ultrasonication at 40 kHz to ensure homogeneous filler dispersion and minimize agglomeration. Previous studies have shown that insufficient dispersion can significantly increase resistivity due to poor conductive network formation [5], [6]. The curing agent was then added at a resin-to-hardener ratio of 100:40 by weight, and the mixture was mechanically stirred for a further 5 minutes. To remove entrapped air bubbles, the mixture was degassed under vacuum at 25 mbar for 10 minutes before application to the substrates.

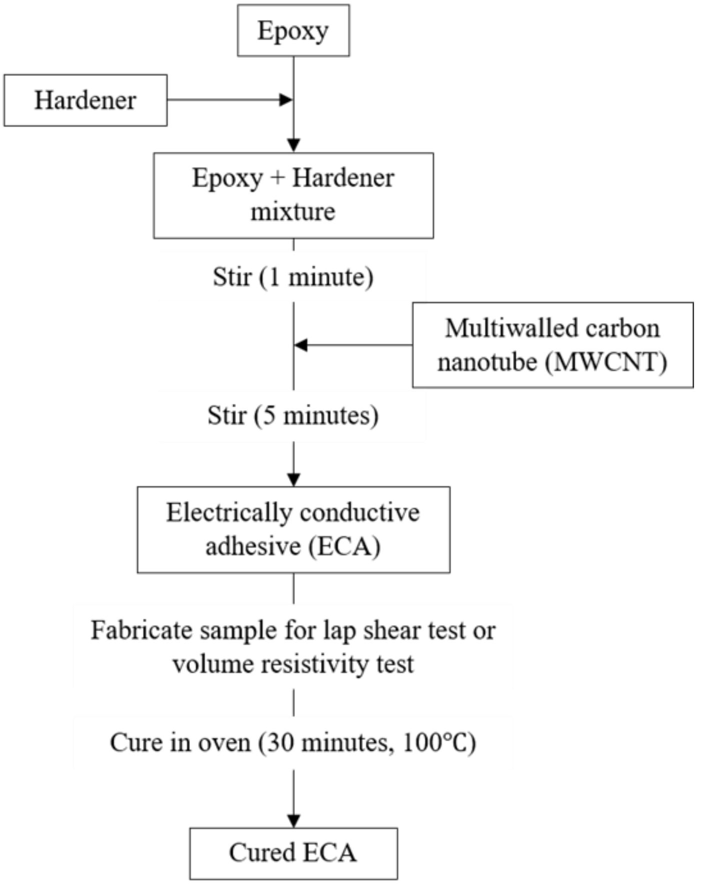


Figure 2: Fabrication process flow of epoxy-based ECA specimens

Table 2: Formulation and mixing parameters for adhesive preparation

Filler loading (wt.%)	MWCNT (g)	Epoxy (g)	Hardener (g)	ECA (g)
3	0.15	3.395	1.455	5
4	0.20	3.360	1.440	5
5	0.25	3.325	1.425	5
6	0.30	3.290	1.410	5
7	0.35	3.255	1.395	5
8	0.40	3.220	1.380	5

2.3 Specimen Fabrication

Volume resistivity was determined using the four-point probe method, which minimizes the influence of contact resistance and is widely recognized for thin-film and composite measurements [17]. A collinear probe head with 1 mm spacing was used, and the resistivity was calculated according to ASTM F390 [18] and the Smits equation [17]. The measurement protocol followed the guidelines of the IEC TS 62788-8-1:2024 standard for electrically conductive adhesives [19].

2.4 Electrical Resistivity Measurement

Volume resistivity was determined using the four-point probe method, which minimizes the influence of contact resistance and is widely recognized for thin-film and composite measurements [19]. A collinear probe head with 1 mm spacing was used, and the resistivity was calculated according to ASTM F390 [18] and the Smits equation [19] as given in Equation (1) as follows: -

$$\rho = \frac{V}{I} G t_s \tag{1}$$

where ρ is the volume resistivity (Ω·cm), V is the measured voltage, I is the applied current, G is a correction factor and t_s is the specimen thickness. To ensure consistency, each specimen was measured at five random positions, and the average value was reported. The measurement protocol followed the guidelines of the IEC TS 62788-8-1:2024 standard for electrically conductive adhesives.

2.5 Lap Shear Strength Testing

Lap shear strength (LSS) was evaluated according to ASTM D1002 [16] using a universal testing machine (Instron 5569) at a crosshead speed of 1.3 mm/min. The LSS test provides an important measure of adhesive mechanical integrity, particularly under environmental exposure [13], [10].

2.6 Hygrothermal Ageing Protocol

Hygrothermal ageing was conducted in a controlled environmental chamber set at 85 °C and 85 % RH, conditions widely used to accelerate moisture ingress and simulate harsh service environments [11], [12]. Exposure durations were set at 168 h, 336 h, and 504 h to evaluate time-dependent degradation trends. Previous studies have reported that such conditioning is necessary to ensure reproducible results after hygrothermal exposure [11], [15].

3.0 RESULTS AND DISCUSSION

3.1 Effect of MWCNT Aspect Ratio on Initial Electrical Resistivity

Initial volume resistivity results are presented in Figure 3. The H-MWCNT adhesive exhibited a significantly lower resistivity (2.1×10^{-3} Ω·cm) compared to the L-MWCNT system (5.8×10^{-3} Ω·cm). This reduction is attributed to the higher aspect ratio of the H-MWCNTs, which promotes earlier percolation and facilitates the formation of continuous conductive pathways at lower filler loadings [6], [7], [8]. This trend aligns with recent reports showing that increasing CNT aspect ratio improves network connectivity and reduces tunneling resistance between particles [2], [4]. Similar observations were made by Fukushima and Inoue [8], who demonstrated that binder chemistry tailored for CNT alignment further enhances conduction pathways.

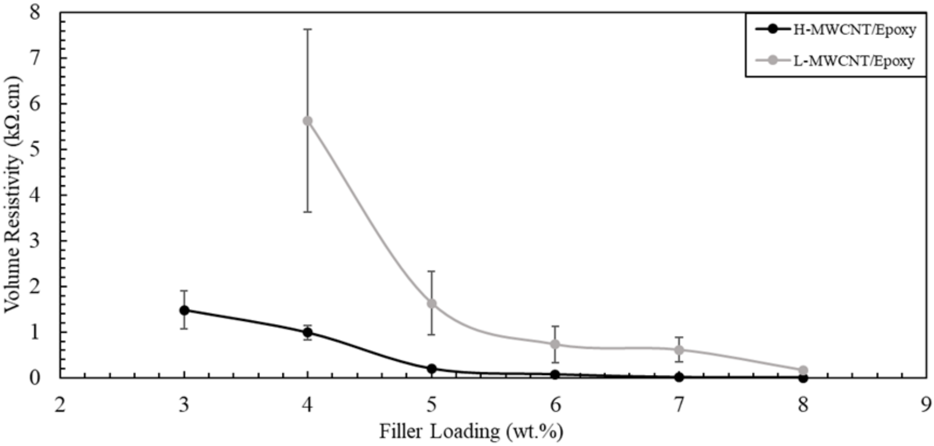


Figure 3. Initial volume resistivity of L-MWCNT and H-MWCNT epoxy-

based electrically conductive adhesives (ECAs) before environmental exposure.

3.2 Influence of Aspect Ratio on Lap Shear Strength (LSS)

Initial lap shear strength values are shown in Figure 4. The H-MWCNT adhesive demonstrated slightly higher shear strength (14.2 MPa) compared to the L-MWCNT adhesive (13.4 MPa). This improvement can be linked to the higher load transfer efficiency provided by the elongated nanotubes, which interact more extensively with the epoxy matrix [5], [7].

Recent work by Yang et al. [4] confirms that well-dispersed, high-aspect ratio fillers improve not only conductivity but also adhesive toughness by acting as crack-bridging reinforcements. However, excessive aspect ratio may lead to increased viscosity during processing, potentially limiting wetting on the substrate [10].

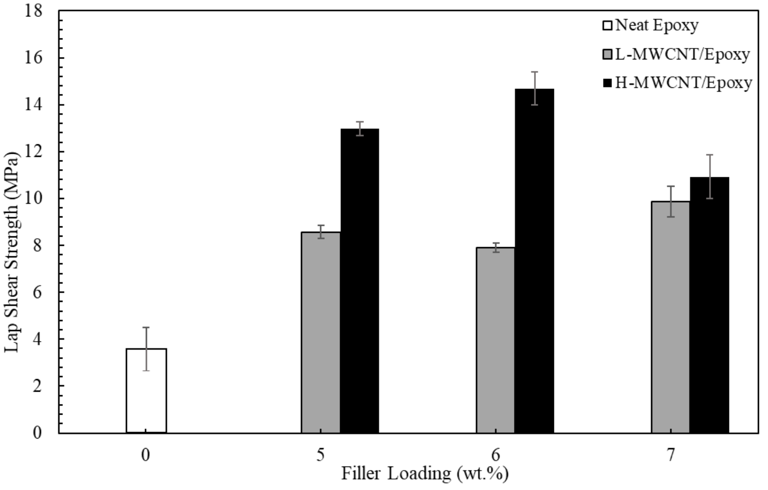


Figure 4: Initial lap shear strength of L-MWCNT and H-MWCNT adhesive

3.3 Electrical Performance under Hygrothermal Ageing

Changes in volume resistivity over three weeks of hygrothermal ageing are shown in Figure 5. Both adhesives showed a gradual increase in resistivity with ageing time. The superior performance of the H-MWCNT, as shown in Figure 5 (b) adhesive is likely due to its denser, more continuous conductive network, which is less susceptible to moisture-induced disruption [11], [12], [15]. Comparable trends have been reported by Ma et al. [20], who found that conductive polymer composites with higher filler connectivity resist moisture ingress more effectively. Furthermore, the reduced interfacial debonding in high-aspect ratio systems can delay the formation of high-resistance pathways, as noted by Cui et al. [11].

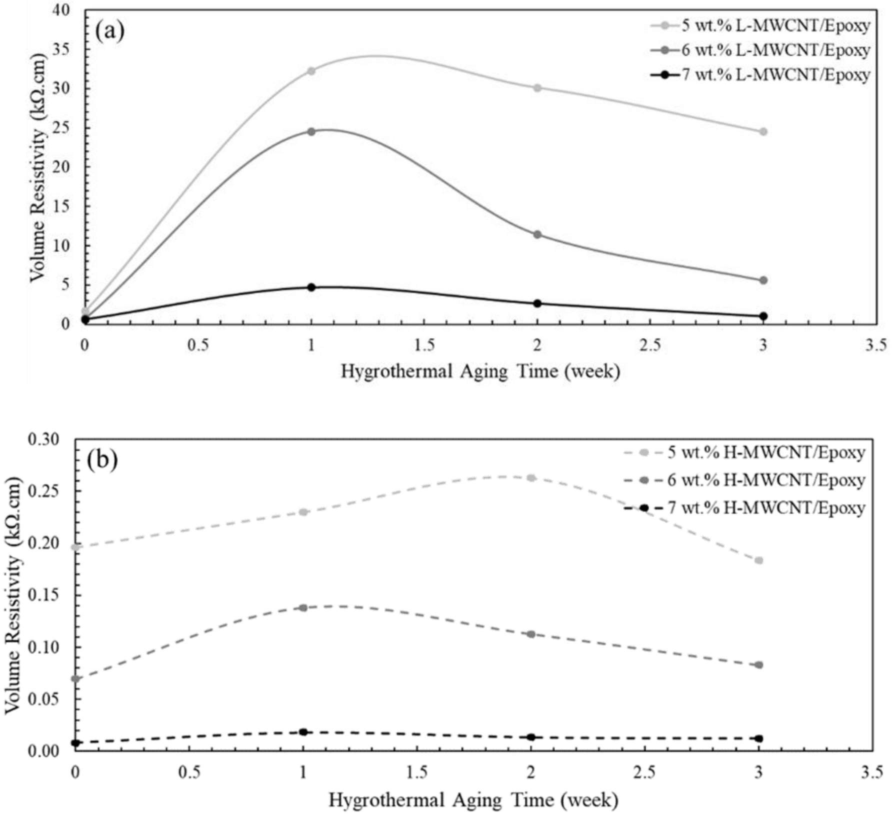


Figure 5: Volume resistivity change with hygrothermal ageing time for (a) L-MWCNT and in (b) H-MWCNT respectively

3.4 Mechanical Performance under Hygrothermal Ageing

Lap shear strength retention results are shown in Figure 6. Both adhesives exhibited a decrease in shear strength over time, but the decline was less severe in the H-MWCNT adhesive, which retained

87 % of its initial strength after 504 h. This difference can be attributed to better stress transfer and crack deflection mechanisms afforded by the high-aspect ratio fillers [5], [4].

Jagatap et al. [13] and Sugiman and Salman [12] have reported that moisture uptake can plasticize the epoxy matrix. In this work, the enhanced retention of strength in the H-MWCNT system suggests that its filler geometry improved interfacial resistance to moisture-induced damage, consistent with trends in similar nanofilled adhesive systems [15], [9].

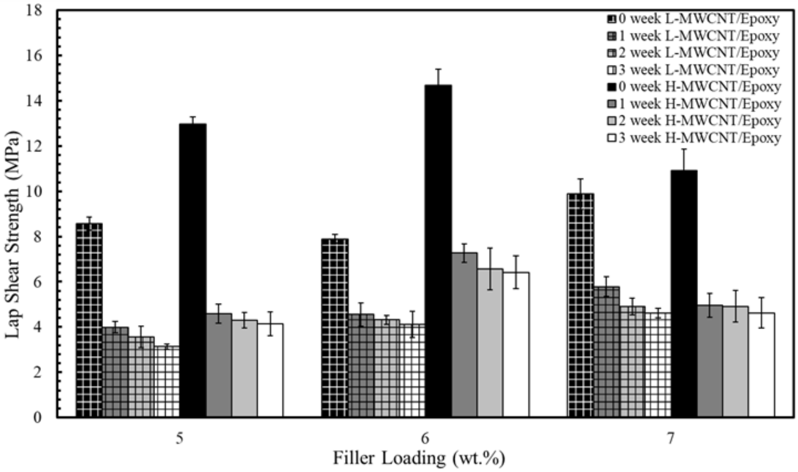


Figure 6: Lap shear strength retention after hygrothermal ageing

3.5 Comparative Performance and Practical Implications

The combined electrical and mechanical performance results are summarised in Table 3. Overall, the H-MWCNT adhesive outperformed the L-MWCNT adhesive in both electrical and mechanical stability under hygrothermal ageing. The results underscore the importance of optimizing filler aspect ratio to improve not only initial performance but also long-term durability. These findings agree with recent literature on hybrid and modified nanofillers, which emphasise the role of network robustness in sustaining functional properties over time [2], [8], [4]. From a manufacturing perspective, the trade-off between viscosity and performance must still be carefully managed [10].

Table 3: Summary of electrical and mechanical results before and after ageing

Aspect ratio / Filler type	Filler loading (wt.%)	Volume resistivity (kΩ·cm)				Lap shear strength (MPa)			
		0 week	1 week	2 weeks	3 weeks	0 week	1 week	2 weeks	3 weeks
L-MWCNT/Epoxy	5	1.634 ± 0.699	32.246 ± 15.387	30.111 ± 15.156	24.493 ± 9.605	8.57 ± 0.29	3.99 ± 0.25	3.56 ± 0.46	3.13 ± 0.13
	6	0.733 ± 0.397	24.557 ± 10.075	11.450 ± 10.137	5.574 ± 1.305	7.90 ± 0.19	4.56 ± 0.51	4.32 ± 0.20	4.12 ± 0.59
	7	0.613 ± 0.267	4.692 ± 2.670	2.640 ± 0.666	1.011 ± 0.454	9.88 ± 0.66	5.79 ± 0.44	4.90 ± 0.36	4.61 ± 0.21
H-MWCNT/Epoxy	5	0.196 ± 0.043	0.230 ± 0.063	0.263 ± 0.089	0.184 ± 0.049	12.98 ± 0.30	4.59 ± 0.43	4.30 ± 0.33	4.14 ± 0.53
	6	0.070 ± 0.017	0.138 ± 0.043	0.113 ± 0.048	0.083 ± 0.016	14.68 ± 0.71	7.27 ± 0.40	6.57 ± 0.93	6.41 ± 0.72
	7	0.008 ± 0.002	0.018 ± 0.005	0.013 ± 0.002	0.012 ± 0.003	10.92 ± 0.94	4.96 ± 0.53	4.91 ± 0.69	4.63 ± 0.68

4.0 CONCLUSION

This study demonstrates that the aspect ratio of MWCNT fillers has a significant influence on both the initial and long-term performance of epoxy-based electrically conductive adhesives. High-aspect ratio H-MWCNTs achieved lower initial volume resistivity and higher lap shear strength compared to low-aspect ratio L-MWCNTs. Under hygrothermal ageing, the H-MWCNT adhesives exhibited superior retention of both electrical and mechanical properties, particularly at 6 wt.% loading, where 87 % of the initial lap shear strength was preserved after three weeks. These findings confirm that optimising nanotube aspect ratio can significantly improve the durability and reliability of ECAs in harsh service environments. The insights from this work provide a foundation for developing next-generation ECAs with tailored nanofiller geometries for high-reliability electronics packaging.

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AUTHOR CONTRIBUTIONS

Muhamad Muaz Nasaruddin: Conducted experimental work, performed data analysis, and prepared the draft manuscript.

Siti Hajar Sheikh Md Fadzullah: Conceived the research idea, supervised the work, developed methodology and validated results and contributed to writing, reviewing, and editing the manuscript.

Zaleha Mustafa, Ismail Ismail and Bunyemin Cosut: Assisted with data curation and contributed to manuscript review.

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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