Hygrothermal Effect on MWCNT-Filled Epoxy Electrically Conductive Adhesives

S. H. S. M. Fadzullah[1*], M. M. Nasaruddin[2], G. Omar[3], Z. Mustafa[4], M. B. Ramli[5], M. Z. Akop[6] and I. S. Mohamad[7]

[1,2,3,5,6,7] Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia

[1,2,3,5,6,7] Centre for Advanced Research on Energy, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia

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

ABSTRACT

To-date, limited studies are found in the literature on the reliability performance of electrically conductive adhesive (ECA) using multiwalled carbon nanotube (MWCNT) fillers. Hence, this study aims to provide an understanding on the performance of the ECA with the objectives (i) to study the electrical conductivity and (ii) joint strength of ECA with varying conductive filler's aspect ratio and environmental conditions. Here, epoxy with MWCNT aspect ratio of 55.5 and 1666.5 were subjected to 85°C and 85% RH for up to 96 hours. The test specimens were prepared in accordance with ASTM F390-11 using a four-point probe for electrical conductivity measurement while the lap shear test was conducted with reference to ASTM D1002-10 using a universal testing machine. For the thermal aging study, the ECA samples were conditioned in a humidity chamber at 85 °C and 85 % of relative humidity to assess the reliability performance of the ECA. Overall, it was found that ECA filled with higher aspect ratio of MWCNT exhibit better electrical and mechanical stability when subjected to hygrothermal aging. Moreover, the presence of moisture attack has yield in an increase in the electrical conductivity of the ECA with thermal aging period. Meanwhile, lap shear test results revealed a contradicting trend. Regardless of the amount of MWCNT filler loading, voids are created in the epoxy matrix of the ECA, which results in a decrease in the shear strength of the ECA, when the samples were subjected to thermal aging.

KEYWORDS: *ECA; MWCNT; Aspect Ratio; Hygrothermal Aging; Mechanical strength*

1.0 INTRODUCTION

Electrically Conductive Adhesives (ECAs) are the alternative for conventional interconnect materials (Pb/Sn and Sn/Ag/Cu) in electronic packaging due to it toxic-free material and also low in processing temperature (Lee et al., 2005; Tan et al., 2006). ECA is predominantly made up of two main materials; a matrix and a filler. The polymer matrix material function is to provide the mechanical properties of the ECA. Meanwhile, the role of a conductive filler is to enable the adhesive to inherit its ability in conducting electricity. In addition, properties of the filler such as types, shapes and sizes will remarkably affect the performance of the ECA (Lu et al., 2002). Besides, the

*Corresponding author. Email: hajar@utem.edu.my

ECA’s performance is also affected by environmental conditions (Cui et al., 2013). Therefore, it is essentially important to study the effect of environmental condition on the ECA since interconnect materials are often exposed to various surrounding setting during its actual applications. Hence, the focus of this study is to investigate the effect of hygrothermal aging on the electrical performance of ECA filled with different aspect ratio (size) of MWCNT (in terms of the MWCNT length).

2.0 EXPERIMENTAL PROCEDURE

ECA was prepared by mixing the epoxy with hardener by 30% to the weight of the epoxy and manually blended until the solutions are homogenized within one minute of manual mixing time. The conductive filler, that is the MWCNT is then inserted into the suspension and further mixed for an additional 5 minutes. The filler loading used for this present study are 7.0 wt.%, 8.5 wt.% and 10.0 wt.% for both aspect ratios of MWCNT; low aspect ratio (L-MWCNT) and high aspect ratio (H-MWCNT). Description of the aspect ratios are displayed in Table 1.

Table 1. Details Dimension of MWCNT

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

By referring to ASTM F390 as a guideline for the electrical resistivity measurement, the mixed adhesive was printed on 3 mm-thick acrylic substrates, as shown in Figure 1. The adhesive was cured at temperature of 100 °C for 30 minutes in a readily heated curing oven. The cured sample was cooled for 24 hours and further measured in terms of its electrical resistivity by using a JANDEL four-point probe. The samples were then subjected to hygrothermal aging for up to 96 hours at 85 °C and 85 % RH in a Memmert Humidity Chamber model HCP 108

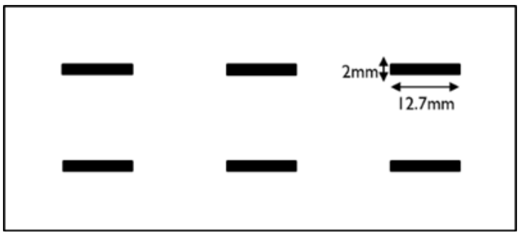


Figure 1. Schematic diagram of printed ECA arrangement

Furthermore, ASTM D1002 is reffered as the guidlines to conduct the single-lap bonded joint test for the adhesive in order to clarify the joint strength of the ECA. The sample for this kind of test is assembled as presented in Figure 2 and conducted by using universal testing machine model Hengzhun HZ-1003. According to the standard, the test speed is fixed at 1.3 mm/min and with five times repitition for each of test parameter.

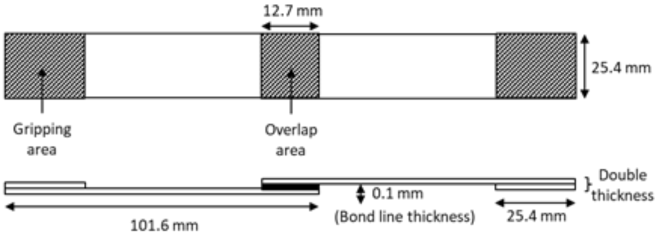


Figure 2. Sample assembly for single-lap bonded joint test

3.0 RESULTS AND DISCUSSION

Figure 3 illustrates the experimental results following electrical resistivity measurements, with respect to different filler loading, at room temperature condition, for each aspect ratio used in this study. It is apparent that the electrical resistivity for both types of ECA exhibit the same trend, that is a decreased in electrical resistivity with an increasing filler loading. Such observation suggests that by increasing the amount of MWCNT filler loading will lead in an improved electrical conductivity of the adhesive. Furthermore, with higher amount of the MWCNT, the tendency of the MWCNT to be in contact with each other will also increase. This can improve the conductive path away of the electron in between the adhesive as well as providing better electrical conductivity for the ECA. Nonetheless, visual observation during the experiment showed that at much higher filler loading, the rheological characteristic of the adhesive is disturbed since the adhesive would become too viscous (Potschke et al., 2002) and lead to some difficulties during the printing process. In addition, Figure 3 also depicts that ECA with higher MWCNT aspect ratio yield in better electrical conductivity by having lower electrical resistivity of the ECA, which is 0.54 Ω.cm compared to 0.88 Ω.cm at 8.5 wt.% filler loading. This is because MWCNT with higher aspect ratio (longer in length) could more easily form contact with other MWCNT, due to its flexibility plus high aspect ratio of the filler itself (Geng et al., 2008). This occurrence will build the conductive path away and allow high percentage of electron to flow through the adhesive. The arrangement of the MWCNT in the ECA are captured by using SEM and the micrographs are as displayed in Figure 4.

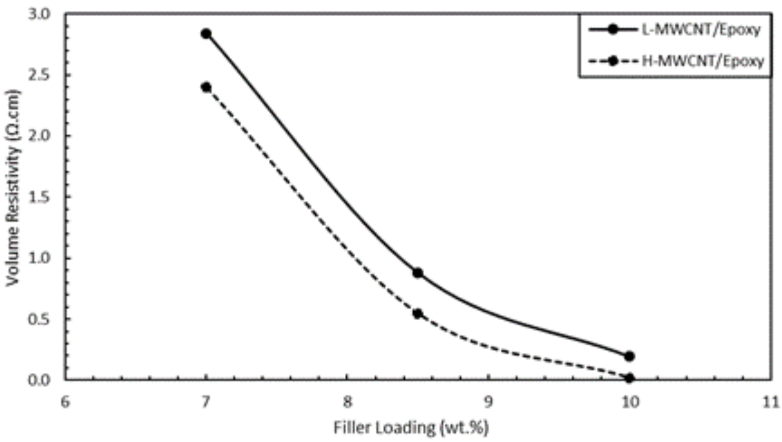
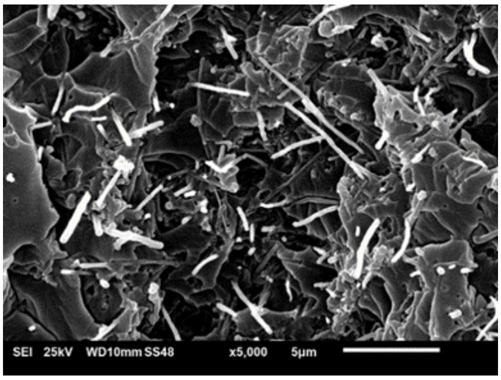
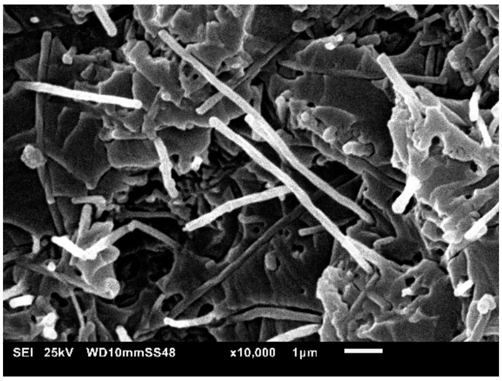


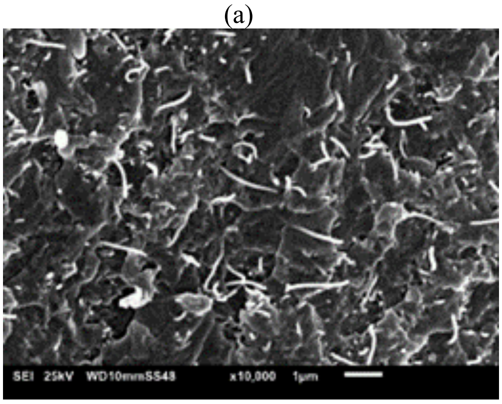
Figure 3. Volume resistivity against filler loading for L-MWCNT/Epoxy and H-MWCNT/Epoxy



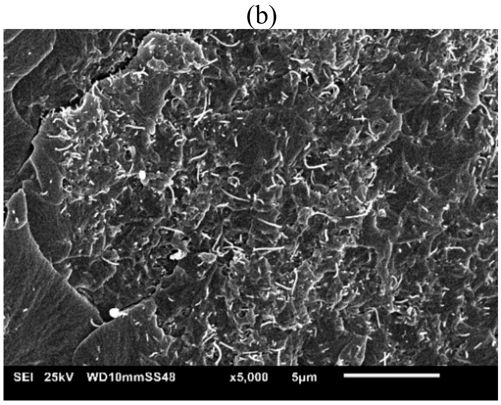
(a)



(b)



(c)



(d)

Figure 4. SEM micrographs showing the cross-sectional view of ECA with 10.05 wt.% filler loading for (a) & (b) A-MWCNT/Epoxy andd (c) & (d) B-MWCNT/Epoxy, at 5000x and 10000x magnification respectively.

Followed by hygrothermal aging, the results in Figure 5 show that the volume resistivity shift of the ECA decrease with higher MWCNT filler loading. This signifies that the destruction of the ECA's electrical conductivity can be delimited by adding up the volume of MWCNT inside the ECA. This occurrence could possibly be due to the barrier effect provided by the MWCNT itself (Sima, 2015). As its amount is increase, the gap between each of the MWCNT become smaller, hence hinder the movement of water molecule inside the conductive adhesive. Another important finding to note from this experiment is that, in order to make the barrier effect become prominently effective, high aspect ratio of MWCNTs can be used as the conductive filler for the ECA. Figure 5 shows that the volume resistivity shift for low aspect ratio of MWCNT/Epoxy is 2.23 Ω.cm while the resistivity shift value recorded for the ECA with high aspect ratio is only 0.04 Ω.cm, at 10 wt.%. Due to the flexibility and high aspect ratio of the MWCNT, it has a tendency to agglomerate with each other (Geng et al., 2008) which provide the closer gap consequently enhance the barrier effect towards the water movement.

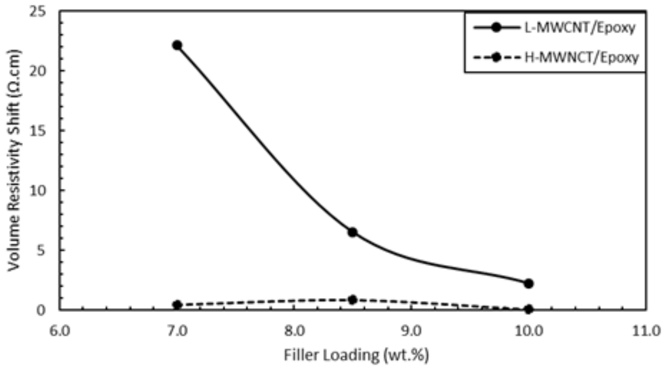


Figure 5. Volume resistivity shift after aged in 85 °C and 85 %RH for 96 hours

Figure 6 suggest that in normal condition, lower aspect ratio of MWCNT (A-MWCNT/Epoxy) filled ECA exhibit better shear strength compared to ECA filled with higher aspect of MWCNT (B-MWCNT/Epoxy). The results are also supported by surface failure of the ECA as displayed in Figure 7. In ECA failure analysis, there are two types of failure mode that can be obtain which are adhesive and cohesive failure modes, (Subramaniam et al., 2016) and adhesive failure is the type of failure that need to be avoided in conductive adhesive field since it indicates the weak performance of the ECA. As shown in Figure 7(b), the failure type for B-MWCNT/Epoxy are adhesive-cohesive failure and significantly shifted to adhesive failure at 10.0 wt.%. In comparison with A-MWCNT/Epoxy, the failure types shown are constant at cohesive-adhesive failure. This is because, higher aspect ratio of MWCNT (B-MWCNT) have larger surface area which will causing more contact to the epoxy resin in the adhesive system. Therefore, there will be less amount of epoxy resin left to make contact or adhere with the surface of the substrate hence resulting weak adhesion between them. This problem will become more severe as the filler loading is increase which means more MWCNT surface are exposed to be clinged with the epoxy resin. This explain the significantly shifted failure mode from adhesive-cohesive failure to adhesive failure of B-MWCNT/Epoxy.

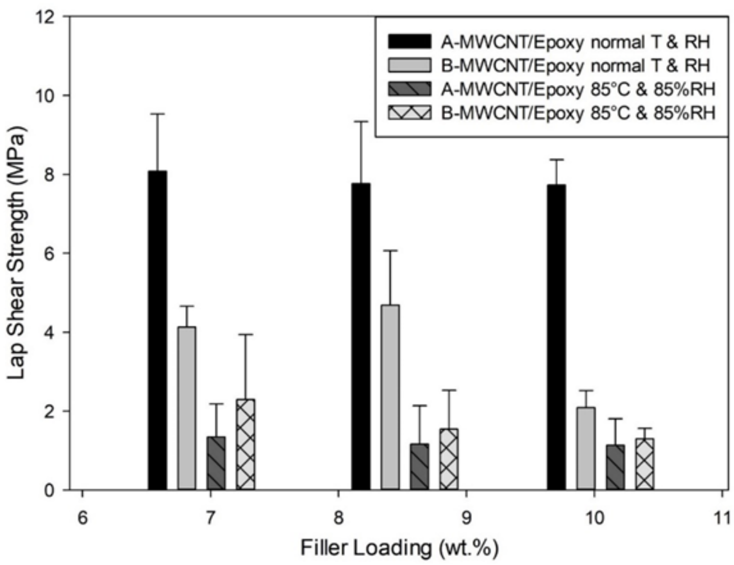


Figure 6. Shear strength of ECA at normal and elevated temperature and humidity

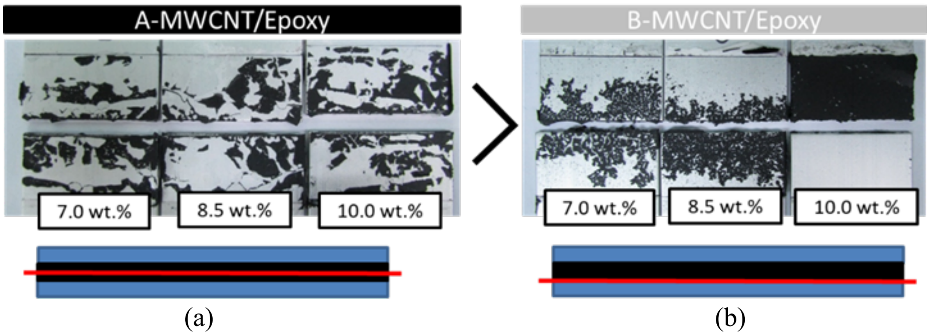


Figure 7. Surface failure of the ECA subjected to normal temperature and relative humidity, showing (a) adhesive-cohesive failure and in (b) adhesive failure

However, following hygrothermal aging at temperature and humidity of 85 °C/85 % RH for 96 hours, the ECA filled with both type of MWCNT aspect ratio showed a similar mode of failure, that is the adhesive failure, as shown in Figure 8 (a) and (b). This indicates that the moisture attack is prominently affecting the adhesive strength. What can be highlighted from this outcome is that, although B-MWCNT/Epoxy produce relatively poorer shear strength following hygrothermal aging, the strength shift is much lower than the case for A/MWCNT/Epoxy as displayed in Figure 9. This outcome suggests that higher aspect ratio of MWCNT is effective as barrier effect to hinder the movement of water molecule from diffused inside the ECA system. Due to high flexibility characteristic from high aspect ratio of MWCNT, it leads to higher tortuosity in the diffusion path of the ECA system. This event will intensely resist the penetrating of moisture from getting inside the ECA.

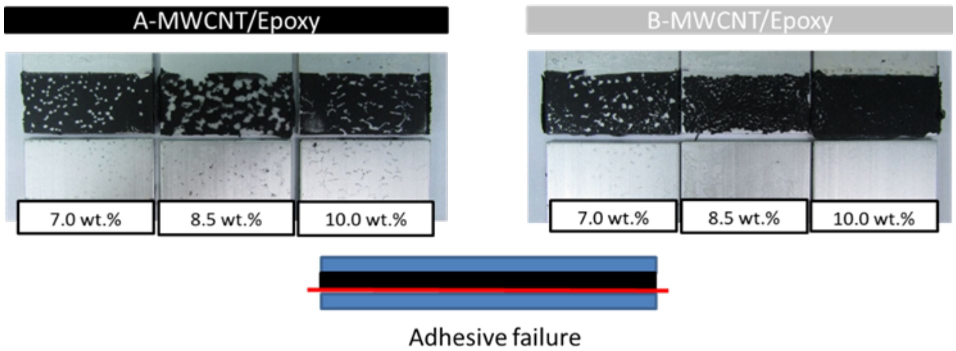


Figure 8. Surface failure for ECAs at 85 °C temperature and 85 % relative humidity

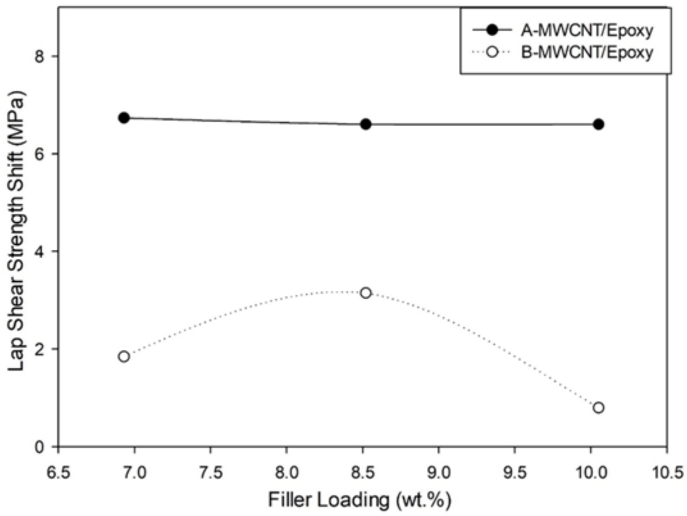


Figure 9. Shear strength shift for A-MWCNT/Epoxy and B-MWCNT/Epoxy ECAs

Apart from the aspect ratio of MWCNT, another factor that is helping the sustainability performance of an ECA under hygrothermal aging is the amount of filler loading used in the system. Based on Figure 9 above, it can be concluded that as the filler loading is increase the shear strength shift will also decrease. This occurrence flashes that MWCNT can be used to improve the stability performance of the ECA under high humidity and temperature surrounding conditions. This is because, by having higher crowd of MWCNT, it will fill up the empty spaces inside the ECA and between the filler itself. There will be less distance between the MWCNT which consequently become a wholesome blockade towards water molecule. As a result, the water will be having difficulties in diffusing into the ECA systems. However, too much filler loading in an ECA system will degrade the adhesion performance of ECA as exhibited in Figure 6 where the shear strength is the lowest at the highest filler loading for both cases of aspect ratio. Therefore, right amount of filler loading need to be used in order to produce good balance between mechanical bonding and durability under high temperature and humidity condition.

4.0 CONCLUSION

The experimental result shows that ECA with high MWCNT filler loading and aspect ratio exhibit greater stability in resisting the hygrothermal aging with relatively lower electrical resistivity degradation shift in comparison to those of lower aspect ratio. Besides that, the same result also displayed in term of mechanical aspect where the higher aspect ratio of MWCNT gives lower lap shear strength shift compared to ECA filled with lower aspect ratio of MWCNT. Beside aspect ratio of the filler, amount of the filler also plays an important role in order to improve the durability performance of ECA under extreme condition. However, too high amount of MWCNT will not also going to produce a good overall performance of an ECA. Therefore, right amount of filler loading need to be used in order to produce good balance between mechanical bonding and durability under high temperature and humidity condition.

5.0 ACKNOWLEDGEMENT

The authors are grateful to the Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka (UTeM), Ministry of Higher Education Malaysia (MOHE) and Jabil Circuit Sdn Bhd. for the technical and financial supports under PJP/2016/FKM/HI1/S01464 and GLUAR/JABIL/2016/FKM-CARE/I00016 grants. Special thanks to Zamalah Scheme under UTeM for funding the MSc research degree for one of the authors.

6.0 REFERENCES

Cui, H., Li, D., Fan, Q. & Lai, H. (2013). Electrical and mechanical properties of electrically conductive adhesives from epoxy, micro-silver flakes, and nano-hexagonal boron nitride particles after humid and thermal aging. *International Journal of Adhesive and Adhesion,* 44, 232–236.

Geng, Y., Liu, M. Y., Li, J., Shi, X. M. & Kim, J. K. (2008). Effects of surfactant treatment on mechanical and electrical properties of CNT/epoxy nanocomposites, *Composite Part A: Applied Science and Manufacturing,* 39(12), 1876–1883.

Lee, H. H., Sen Chou, K., & Shih, Z.W. (2011). Effect of nano-sized silver particles on the resistivity of polymeric conductive adhesives. *International Journal of Adhesive and Adhesion*, 25(5), 437–441.

Lu, D., Luo, S. & Wong, C. P. (2002). Conductive Polymer Composites. *Encyclopedia of Polymer Science and Technology*. Georgia Institute of Technology, 652–697.

Potschke, P., Fornes, T. D. & Paul, D. R. (2002). Rheological behavior of multiwalled carbon nanotube/polycarbonate composites. *Polymer*, 43(11), 3247–3255.

Sima Nabavizadeh, R. (2015). *The Effect of Moisture on Electrical Resistivity of MWCNT Reinforced Epoxy Nanocomposites*. (Unpublished master's thesis). Concordia University, Montreal, Quebec, Canada.

Subramaniam, A. S., Tey, J. N., Zhang, L., Ng, B. H., Roy, S., Wei, J. & Hu, X. M., (2016). Synergistic Bond Strengthening in Epoxy Adhesives using Polydopamine/MWCNT Hybrids. *Polymer,* 82, 285-294.

Tan, F., Qiao, X., Chen, J. & Wang, H. (2006). Effects of coupling agents on the properties of epoxy-based electrically conductive adhesives. *International Journal of Adhesive and Adhesion,* 26(6), 406–413.