Effect of Boron Nitride Nano Filler Filled Epoxy Composites for Underfill Application

Muhammad Firdaus Shafee and Mariatti Jaafar*

School of Materials and Mineral Resources Engineering,
Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal,
Seberang Perai Selatan, Pulau Pinang, Malaysia

*Corresponding author: mariatti@eng.usm.my

Abstract: *The research aims to fabricate and characterise epoxy nano composites for underfill applications. Deglycidyl ether of bisphenol-A (DGEBA) and epoxide novolac resin were used in this study and they are referred as EPON 8281 and DEN 431, respectively. Flow ability, thermal conductivity and flexural properties of boron nitride (BN) filled EPON 8281 and DEN 431 epoxy composites were investigated. BN fillers in epoxies were varied from 1 to 4 vol%. The results showed that EPON 8281 had a good flow ability with higher flow rates than DEN 431. The thermal conductivity of the composites increased with the addition of filler. Higher thermal conductivity value was observed in DEN 431. At maximum loading of BN filler (4 vol%), the thermal conductivity of DEN 431 is 3.2% higher than EPON 8281. Generally, EPON 8281 showed higher flexural strength but lower flexural modulus compared to DEN 431.*

Keywords: Boron nitride, epoxy nano characterisation, epoxy composite properties, nano filler epoxy, underfill applications

1. INTRODUCTION

Wire bonding is the oldest method used for first-level interconnection, particularly for integrated circuit (IC) chips with a moderate number of inputs/outputs (I/O). Continuous improvement of microprocessor performance created high demands for smaller, cheaper, faster and lighter assemblies for high-volume productions. Among the methods for interconnecting semiconductors with external circuitry, flip-chip technology is receiving an increased attention.

Flip-chip technology provides higher packaging density, shorter interconnection length, better electrical performance, improved reliability, higher I/O and better manufacturability.[1] In this method, the contact area between the chip and substrate is much smaller than in wire bonding. A small contact area gives rise to many reliability issues such as decreased thermal performance and mechanical reliability. To address these issues, an underfill that fills the gap between the I/C chip and substrate after joining is introduced. The underfill is

usually dispensed along the periphery of the chip, and flows into the gap between the chip and substrate via the capillary force.[2,3]

Underfill material used to distribute the shear stresses at the solder interconnections caused by coefficient of thermal expansion (CTE) mismatched.[4,5] High filler loadings can decrease the CTE problem but result in a highly viscous mixture, which increases the time of the underfill to flow between IC chip/substrate.[6–9] Fast-flow underfills for flip-chips are currently being studied because a fast flow can reduce the processing time required for the underfill to flow. There are many factors that influence the flow rate of the underfill in the gap, such as filler particles (dispersion, density, distribution, loading, material, size, surface area, surface morphology and shape), underfill material (density, rheology, surface tension, temperature and viscosity), IC chip/substrate surfaces (roughness, surface structure and temperature), as well as obstructions (bump pattern, bump size, contamination and particle size-to-gap height ratio).[6] Figure 1 shows a schematic diagram of an epoxy underfill encapsulant.

Advancements in nanotechnology have resulted in heightened interest in the application of nanofillers for underfill application. Previous studies have demonstrated the use of micron-size filler for underfill application.[2–9] In the present study, nano particle of boron nitride (BN) was used as filler in epoxy for the underfill application. This BN filler can be loaded to epoxy resin at lower percentages (1–4 vol%) if compared to micron-sized filler which normally been loaded up to 60 vol%. Low filler loadings can decrease the cost of producing underfills for electronic applications. Deglycidyl ether of bisphenol-A (DGEBA) and epoxide novolac resin were used in this study and they are referred as EPON 8281 and DEN 431, respectively. The flow rates of the underfill materials were measured using parallel plates. Thermal and mechanical tests were also conducted to characterise the properties of the materials.

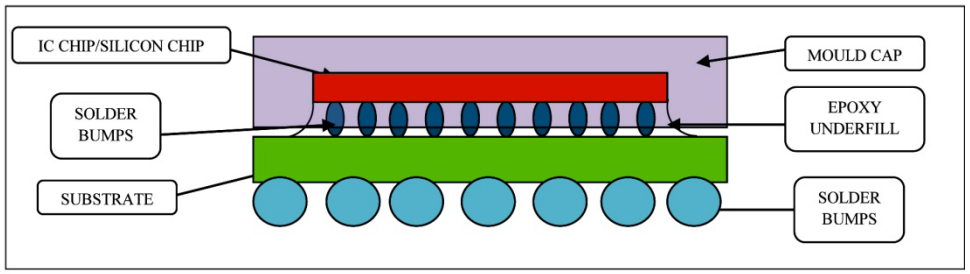

Figure 1: The schematic diagram of epoxy underfill.

2. EXPERIMENTAL

2.1 Materials

DGEBA and epoxide novolac resin were used in this study. They are referred as EPON 8281 (supplied by Hexion Specialty Chemicals) and DEN 431 (Penchem), respectively. Same curing agent was used, i.e., Polyetheramine D230 (BASF Corporation), in the study. The mixing ratio of EPON 8281 and DEN431 to Polyetheramine D230 was set at 100:32. BN nano filler was used in the epoxy matrix. The properties of epoxy resin and BN particles are listed in Table 1 below.

Table 1: Properties of epoxy resin and BN filler used in the study.

Properties	EPON 8281	DEN 431	Boron nitride
Density (g cm^{-3})	1.15	1.19	2.3
Thermal conductivity (W mK^{-1})	0.23	0.25	300
Mean particle size (nm)	–	–	60
Viscosity at 25°C (P)	110–140	600–800	–

2.2 Sample Preparation

Nano BN filler was added to the resin at filler loadings of 1, 2, 3 and 4 vol%. Each resulting mixture of epoxy and filler was stirred for approximately 10 min with a sonicater to facilitate filler dispersion. The mixture was vacuumed for approximately 0.5 h at 35°C to remove bubbles. Then the curing agent was added and the mixture was sonicated for another 10 min. The mixture was kept in a vacuum oven for 1 h at room temperature to remove remaining bubbles. Finally, the mixture was cured in the same oven at 100°C for 1 h followed by post-curing at 125°C for 3 h.

2.3 Characterisation

The flow rates of the underfills were measured using a parallel translucent polypropylene (PP) thermoplastic polymer plate based on the method proposed by Wong et al.[6] The parallel polymer plate had a chip size of 30 × 30 mm^2 and a substrate size of 35 × 35 mm^2, in accordance with the previous work of Shih and Young.[10] The two parallel polymer plates were separated by a 200 μm gap. The plates were pre-cleaned with acetone for characterisation purpose. Thermal conductivity was tested using a Hot-Disk™ Thermal Constant Analyser. Round specimens of 4 mm thick and 30 mm in diameter were prepared. The potential power was fixed at 0.02 W mK^{-1}, and the time was 40 s. A flexural test was performed based on the standard test method

ASTM D790. The specimens used were 70 mm long, 12.7 mm wide and 2 mm thick. An Instron 3366 instrument with a crosshead speed of 5 mm min^{-1} was used to measure the flexural properties of the underfill materials at room temperature. The span length-to-specimen thickness ratio was maintained at 16:1.

3. RESULTS AND DISCUSSION

3.1 Flow Rates

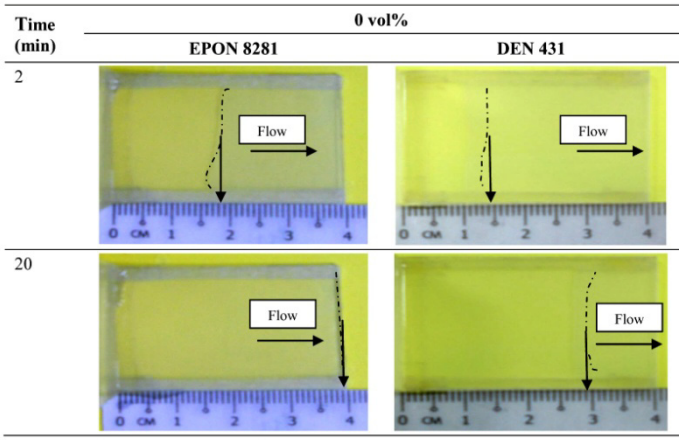

Figure 2: Flow ability for 0 vol% filler (as a control) for EPON 8281 and DEN 431. Arrow shows the position of underfill.

Figure 2 shows the flow ability for control sample (0 vol%). Figure 3 illustrates the flow for 1 and 4 vol% of BN at 2 and 20 min. Flow rates between epoxy resin EPON 8281 and DEN 431 were measured using parallel polymer plate. Apparently, low filler loadings showed higher flow rates compared to high filler loading. EPON 8281 showed higher flow rates compared to DEN 431 because EPON 8281 has lower viscosity as shown in Table 1. As known, viscosity plays a major role in the flow rates of the underfills. An underfill with a high viscosity was indicated by a slow-flow ability. The velocity and acceleration values of the underfills flowing with the parallel polymer plate are summarised in Table 2. As indicated in the table, EPON 8281 epoxy composites underfill had a higher acceleration compared with DEN 431. At neat epoxy (0 vol%), the acceleration of EPON 8281 is 34% higher than DEN 431.

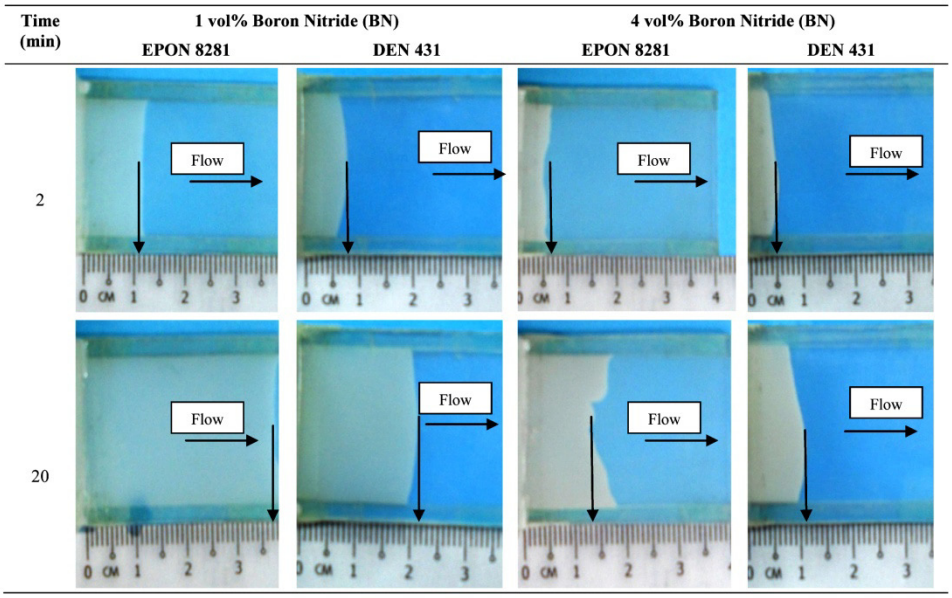

Figure 3: Flow ability of 1 vol% and 4 vol% of BN filled EPON 8281 and DEN 431 resin. Arrow shows the position of underfill.

Table 2: Velocity and acceleration values of the underfill.

Specimen	Start velocity (mm min^{-1}) (at 2 min)	End velocity (mm min^{-1}) (at 20 min)	Acceleration (mm min^{-2})
0 vol% EPON 8281	9.0	2.0	0.35
0 vol% DEN 431	6.0	1.4	0.23
1 vol% BN EPON 8281	6.0	1.9	0.21
1 vol% BN DEN 431	4.0	1.1	0.15
4 vol% BN EPON 8281	3.0	0.7	0.12
4 vol% BN DEN 431	2.5	0.6	0.10

3.2 Thermal Conductivity

For underfill applications, good thermal conductivities are important to dissipate heat faster from the IC chip and substrate. In addition, it is reported that the smaller and faster the microchip, the higher the heat produced.[9] Good thermal conductivity for underfill is required to prevent the microchip from failure. Generally, the thermal conductiviies of the nano BN filler-containing epoxy composites increased with increased filler loadings, as shown in Figure 4. DEN 431 showed slightly higher thermal conductivity compared with EPON 8281. As the filler content increase, lumps of filler particles easily cohered with one

another in DEN 431 due to higher viscosity compared to EPON 8281. This subsequently provides heat conduction paths, thereby raising thermal conductivity by conduction between fillers.[2] Conduction is the flow of heat from high temperature region to low temperature region and occurs as a result of direct energy exchange among molecules.

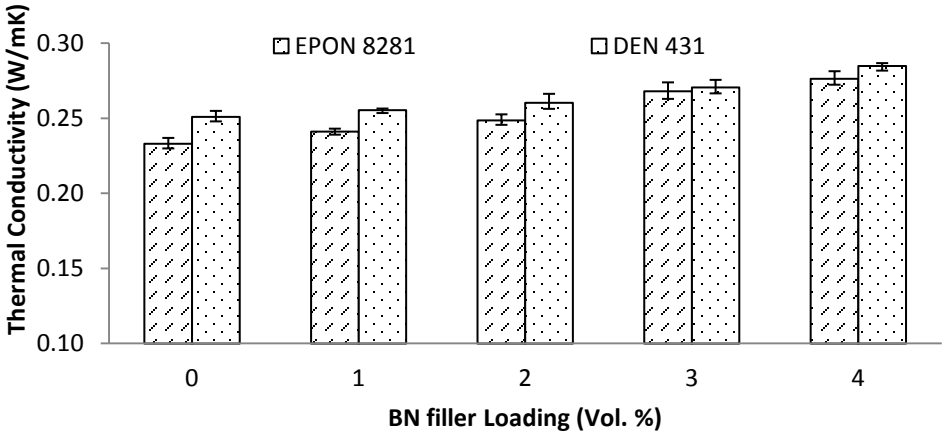

Figure 4: Thermal conductivity versus filler loading of nano BN filler filled EPON 8281 (dashed) and DEN 431 (dotted) epoxy composites.

3.3 Flexural Properties

Figure 5 shows the flexural strengths of nano BN filler filled EPON 8281 and DEN 431 epoxy composites. It is found that the trend decreased with increasing amount of filler loadings. Higher filler loading, i.e., at 4 vol% results in reduction of 29% and 36% flexural strength of EPON 8281 and DEN 431 systems respectively, compared to the control sample (0 vol%). According to the previous work,[11] at high filler loading, the insufficiency of epoxy resin to coat the filler resulted in low filler-matrix interaction which lowered the flexural strength if compared to the control sample (0 vol%). In addition, high filler loading also leads to an increase in viscosity, which in turn reduces the ease of processing. This subsequently increased void content and reduced the strength of the composites. DEN 431 showed higher flexural strength at 0 vol% if compared to EPON 8281 but the strength reduced when the filler is added, this might be due to the filler agglomeration and voids cause by higher viscosity of DEN 431 as shown in Table 1. When the filler is added into the DEN 431 the viscosity will further increase which in turn lowered the flexural strength. The agglomeration and voids in the DEN 431 composites can be observed in the scanning electron microscopy (SEM) images (Figure 6).

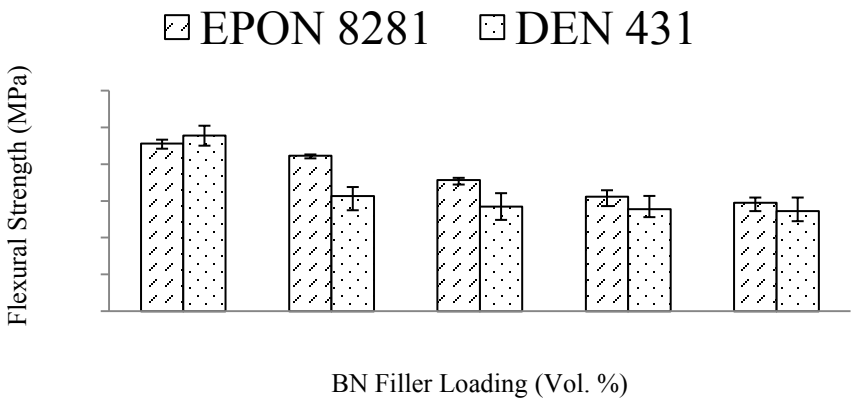

Figure 5: Flexural strength versus filler loading of nano BN filler filled EPON 8281 and DEN 431 epoxy composites.

Flexural modulus of the nano filler filled epoxy composite showed an increasing trend with increasing amount of filler loading. The addition of fillers, which were usually stiffer than the matrix, generally led to an increased in flexural modulus (Figure 7). A previous work indicated that high filler loadings can reduce the ultimate elongation of the matrix and increase Young's modulus.[11] The increment in flexural modulus as filler loading increased was also in good agreement with the rule of mixture.

Theoretically, the rule of mixture suggested increments in the modulus of the composite materials with increasing filler loading. EPON 8281 showed slightly lower flexural modulus compared to DEN 431. This might be due to low viscosity of the matrix, which leads to filler settling. According to another previous work,[8] a decrease in underfill viscosity has a negative impact on filler settling, since there is less buoyancy to overcome the gravitational force of the fillers and they are unable to suspend. Filler is usually stiffer than the matrix as the filler settling is not dispersed very well in the matrix, which contributed to lower flexural modulus.

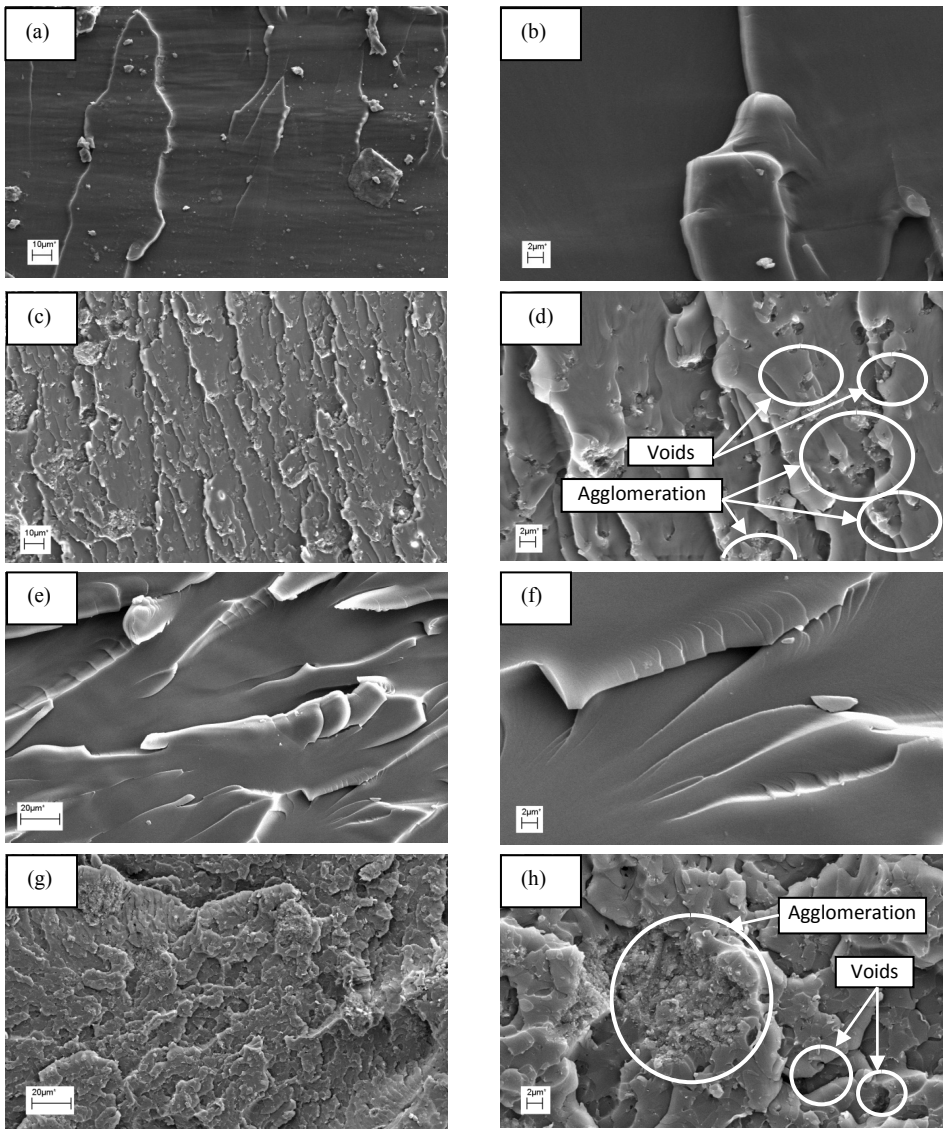

Figure 6: Fracture surfaces of (a, b) neat epoxy, (c, d) 4 vol% BN-filled EPON 8281, as well as (e, f) neat epoxy, and (g, h) 4 vol% BN-filled DEN 431. The left micrographs (a, c, e, g) refer to 500× magnification and the right micrographs (b, d, f, h) refer to 2000× magnification.

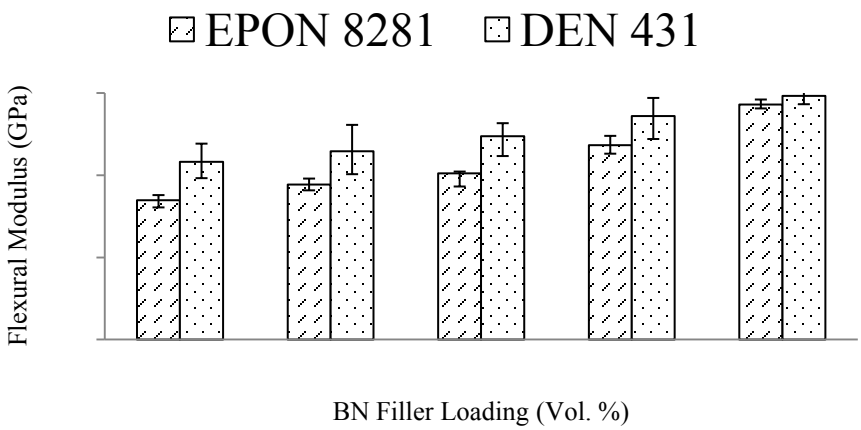

Figure 7: Flexural modulus versus filler loading of nano BN filler filled EPON 8281 and DEN 431 epoxy composites.

4. CONCLUSION

From the findings, it can be concluded that the flow rates of filled epoxy decreased with increasing filler loadings. It was noted that EPON 8281 showed good flow rates compared to DEN 431. In general, thermal conductivity increased with increasing filler loading and DEN 431 showed higher thermal conductivity. As expected, the high filler loading will reduce the flexural strength but increase the flexural modulus. EPON 8281 showed higher flexural strength but lower flexural modulus compared to DEN 431. The trend of flexural properties has been supported by the SEM images, which indicate that agglomeration of filler and voids reduce the flexural strength at high filler loading of epoxy composites.

5. ACKNOWLEDGEMENTS

This work was supported by the research university grant 0110/PBAHAN/814853 from Universiti Sains Malaysia, and Malaysia Government for MyBrain15 in MyMaster financing program under the Tenth Malaysia plan.

6. REFERENCES

1. Yi, H. et al. (2000). Thermal characterization of an epoxy-based underfill material for flip chip packaging. *Thermochim. Acta*, 357–358.
2. Woong, S. L. & Jin, Y. (2005). Comparative study of thermally conductive filler in underfill for the electronic component. *Diamond Relate. Mater.*, 14 1647–1653.
3. Wan, J. W., Zhang, W. J. & Bergstrom, D. J. (2007). Recent advances in modelling the underfill process in flip-chip packaging. *Microelectron. J.*, 38, 67–75.
4. Noor, F. (2006). Studies on various shapes of mineral silica fillers on the properties of epoxy for underfill applications. MSc. diss., Universiti Sains Malaysia, Malaysia.
5. Teh, P. L. (2008). Development of core layer materials using particulate filled epoxy composites. PhD diss., Universiti Sains Malaysia, Malaysia.
6. Wong, C. P., Vincent, M. B. & Shi, S. (1998). Fast-flow underfill encapsulant: Flow rate and coefficient of thermal expansion. *IEEE Trans. Compon. Packag. Manuf. Technol. Conf. Part A*, 21(2), 360–364.
7. Vo, H. T. et al. (2001). Towards model-based engineering of underfill materials: CTE modeling. *Microelectron. J.*, 32, 331–338.
8. Wang, J. (2007). The effects of rheological and wetting properties on underfill filler settling and flow voids in flip chip packages. *Microelectron. Reliab.*, 47, 1958–1966.
9. Lee, W. S. et al. (2007). Thermal characterization of thermally conductive underfill for flip-chip package using novel temperature sensing technique. *Thermochim. Acta*, 455, 148–155.
10. Shih, M-F. & Young, W-B. (2009). Experimental study of filling behaviors in the underfill encapsulation of a flip-chip. *Microelectron. Reliab.*, 49, 1555–1562.
11. Suriati, G., Mariatti, M. & Azizan, A. (2011). Effects of filler shape and size on the properties of silver filled epoxy composites for electronic applications. *J. Mater. Sci.: Mater. Electron*., 22(1), 56–63.