Sheet resistivity and morphological analysis of silver nanoparticles-filled epoxy conductive ink

R. Hamidi[1], M.A. Salim[1,2,*] and G. Omar[1,2]

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

[*]Corresponding e-mail: azli@utem.edu.my

Keywords: Silver nanoparticles; conductive ink; sheet resistivity

ABSTRACT – This paper presents measurement of sheet resistivity of silver nanoparticles-filled conductive ink with Four-Point probe. The Four-Point probe was used to measure the sheet resistance value of the silver nanoparticle-filled epoxy conductive ink sample in ohms-per-square, then the resistivity volume is in ohms-cm, and finally the thickness of sample also be measured too. Based on the results, some percentage of conductive ink was detected the presence of the resistivity value. The highest resistivity value was detected in low percentage of conductive ink loading, while the lowest resistivity was founded in high percentage of conductive ink loading, respectively. On the other hand, the dispersion of silver nanoparticles-filled epoxy also been investigated in morphological study through light microscopy analysis. The dark spot was presumed as a silver nanoparticles, and the rest were presumed the filled epoxy

1. INTRODUCTION

Conductive ink, which is an ink printed to conduct electricity have been in some talk for a few years for their applications in printed electronics (PE) and flexible electronics (FE), respectively. It has the ability to print circuits on paper or some form of flexible surface through the inkjet printing technology. Although the early growth of the printed electronics industry is not as drastic as expected, there are some great demands to use these products (conductive inks) in daily activities such as cell phones, displays, smart wearable, lighting, small packaging, labels, shipping, storage or any else.

Choosing the right ink loading is a crucial successful factor for quick, simple and affordable production of PE prototypes and electronically functional prints. It is mainly based on the electrical properties of the conductive ink itself. In this experiment, the investigation in the characterization of conductive ink is related to the formulation of ink loading and preparation method of the ink samples.

The objective of this study is to investigate the sheet resistivity measurement of silver nanoparticles-filled epoxy conductive ink with Four-Point probe, and evaluate the morphological study of the conductive ink through the light microscopy analysis.

2. RESEARCH METHODOLOGY

2.1 Samples preparation

Firstly, samples of silver nanoparticles-filled epoxy conductive ink was fabricated. The silver nanoparticles acted as the filler element, epoxy as the binder and hardener were used. The materials were weighed based on the values of weight in Table 2.1. The loading of hardener was 30% of amount of binder loading while the total value in the table only included the total sum of amount of filler loading and binder loading. The total value was set at the beginning of experiment.

Table 2.1 Composition of Ink Loading

Sample	Filler		Binder		Hardener (g)	Total (g)
	(%)	(g)	(%)	(g)		
1	10	0.2	90	1.8	0.54	2
2	20	0.4	80	1.6	0.48	2
3	30	0.6	70	1.4	0.42	2
4	40	0.8	60	1.2	0.36	2
5	50	1.0	50	1.0	0.30	2
6	60	1.2	40	0.8	0.24	2
7	70	1.4	30	0.6	0.18	2
8	80	1.6	20	0.4	0.12	2
9	90	1.8	10	0.2	0.06	2

After they were weighed, all three materials were mixed in a beaker and stirred for 10 minutes by using glass rod in the same direction and consistent speed. After stirring process completed, the mixture was deposited onto the glass slide by applying doctor-blading method with 0.5 cm of width gap. Then, the sample was placed in an oven with the setup of 160 °C for 60 minutes in order to preserve the adhesion between ink and the substrate. The sample was put aside until it fully dried.

2.2 Sheet resistivity measurement

The study of resistivity was carried on by using Four-Point probe after the ink was fully dried. For the purpose of this study, three readings of sheet resistance were taken at each constructed points of the ink track. The average values of resistivity were recorded.

2.3 Morphological study

This study was conducted using light microscope with 100 μm and the magnification 5X, 10X and 20X, while the magnifications were 5x, 10x and 20x. All the results have been recorded to predict the silver nanoparticles and filled epoxy dispersion.

3. RESULTS AND DISCUSSION

3.1 Results of sheet resistivity

The Four-Point probe was been used to evaluate the sheet resistivity of the silver nanoparticles-filled epoxy conductive ink. Table 3.1 shows the values of sheet resistivity of conductive ink for sample A and sample B. These two samples basically have same filler loading and same binder. At 60% of filler, the resistivity were recorded at 150.54 Ω/sq and 369.63 Ω/sq, but by increasing the filler value, the sheet resistivity were decreased to 0.06 Ω/sq and 0.10 Ω/sq for sample A and sample B, respectively. Based on this results, the value of sheet resistivity is inverse proportional with filler loading.

Table 3.1 Total Average Sheet Resistivity based on Filler Loading Percentage

Filler (%)	Average Resistivity (Ω/sq)	
	Sample A	Sample B
60	150.54	369.63
70	37.37	36.52
80	7.77	4.29
90	0.06	0.10

At 60 % of filler loading, the average of sheet resistivity was identified. By increasing the filler loading at 70%, the sheet resistivity was recorded lower compared the previous one. The value is too different by comparing 60 % of filler. For filler loading at 80 % and 90 %, their average values of resistivity were rapidly decreased; being linked to the high amount of conducting materials composition in the ink. For the filler with highest percentage of 90 % filler loading, it was produced the highest conductivity among all the filler percentages.

Figure 3.1 indicated the percentage of filler loading from 60 % until 90 % of filler loading, the average resistivity alternately decreased as the amount of conducting materials in the sample increased. In addition, the graph illustrate the formulation of ink in term of filler loading was used in sample A and sample B which are the composition of filler and binder are same, but the sheet resistivity value is slightly different. These differences was caused by two reasons, which are printing technique and Four-Point probe measurement.

In order to produce fewer flaws of conductive tracks with good resolution, there is a need to alter the silver ink composition and some printing states. It relates to the speed of printing, which is linked to the firing frequency, the temperature of substrate and the inter-spacing interval among the dots [1].

In this case, the difference was due to the printing technique; doctor-blading method. During the printing process, the ink was not well-distributed all over the gap between the Scotch tape on the glass slide when the blade moved across the gap due to the speed or the viscosity of ink. When the speed of blade was high, the ink may lose and not cover all over the gap region. As for the viscosity of ink, it increased as the filler content was getting higher. Ink with high viscosity was hard to print in compliance to the texture of ink; more concentrated texture.

Thus, it affected the thickness of ink tracks printed on the glass slide. Some regions may have different thickness; either thin or thick which led to the different spreads of conducting material. Silver nanoparticles on the substrate where region with high content of silver had low resistivity and vice versa.

Another factor of the difference in resistivity values was the time condition while taking the measurement by using the 4-point probe. The error happened because there was no adequate time in taking the data. Longer time was needed due to RC (resistance-capacitance) delay in the highest resistive samples. It was because, the current required more time to climb up to the value of saturation. Once the data was stable, only then a certain point of measurement can be taken and the average value can be obtained. The inconsistency of measurement time caused the resistivity values to be unstable too.

For the filler composition of 10 % until 50 %, Four-Point probe did not detect any presence of resistivity value of the printed ink as it may lack of conducting materials in the ink. It proved that by lowering the percentage of conductor filler, it reduced the conductivity and increased the resistivity as can be seen in the same figure. Therefore, they were not included in data tabulating for this analysis.

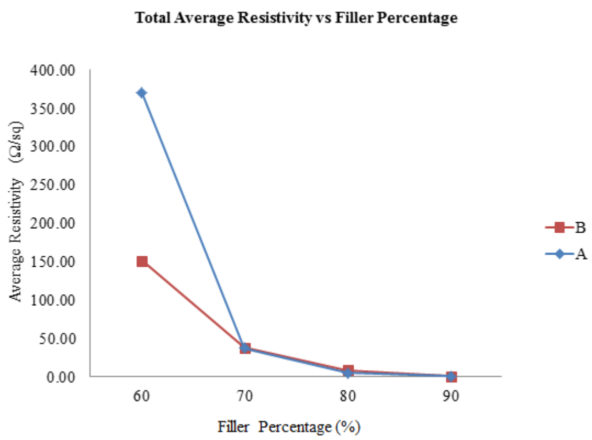


Figure 3.1 Total Average Resistivity versus Filler Percentage

3.2 Comparison of standard deviation between filler percentage

There is no standard benchmarking in determining the standard deviation, but it can be determined by having the lowest value. It presents how tightly the data is gathered around the mean or average or how far the data is spread out from the mean or average.

From the table above, the data of 60 % of filler has a very large standard deviation. It means that the data is spread out widely from the average, which indicates the highest average resistivity. The high range of values at 60 % is expected to be followed by 70 % of filler but, it shows significant difference. It has one of the lowest values among the other filler loadings. While for filler at 80 % and 90 %, the data has a small standard deviation, which tells that the data is gathered closely around the average. It proves that 80 % and 90 % of filler have the lowest and stable average resistivity

Table 3.2 Standard Deviation between Filler Percentage

Standard Deviation				
Sample	Filler (%)			
	60	70	80	90
A	77.82	2.69	5.29	0.08
B	289.86	7.20	1.04	0.03

3.3 Morphological analysis

In this section, results for morphological study will be discussed in detail. The filler loading in the range of 10 % until 50 % showed no presence of conductivity while for 60 % to 90 % of filler loading exhibited the presence of conductivity. For the first assumption, the dark spot was presumed as a silver nanoparticles while the rest is the filled epoxy.

At 10 % of filler loading, the microstructure showed no appearance of silver nanoparticles element that could be traced due to lack of filler loading compared to the amount of binder and hardener. Binder and hardener conquered all over the ink track and if the conductor materials are in low quantity [2], there is no conductivity at all. Overall, the 10 % filler loading only created the formation of voids as shown in Figure 3.2.

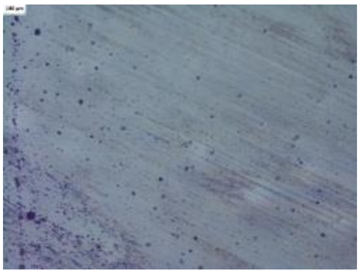
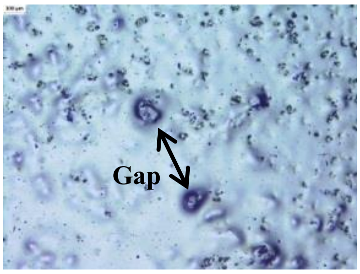
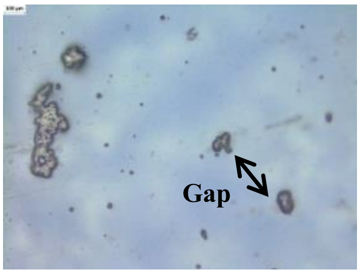


Figure 3.2 Morphological image of 10 % of filler loading on silver nanoparticles-filled epoxy

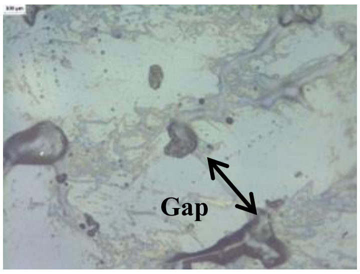
At 20 %, 30 % and 40 % of filler loadings, it showed the existence of gaps between the dark spot. The frequency of gaps was presumed gave an affected the sheet resistivity properties of the conductive ink. By increasing dark spot gap, it caused the higher resistance due to high voltage and it was required to ensure the flowing of current among the filler loading [2]. The percentage of filler loading at 50 % showed the presence of dark spot is a very minimum quantity due to the same amount of filler to binder, respectively. All the results showed in Figure 3.3.



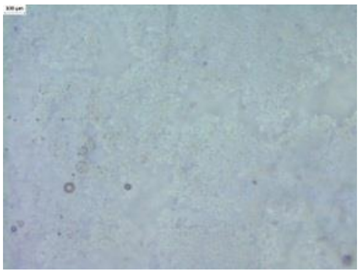
(a)



(b)



(c)

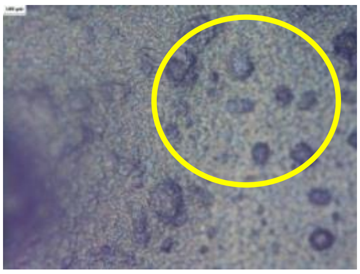


(d)

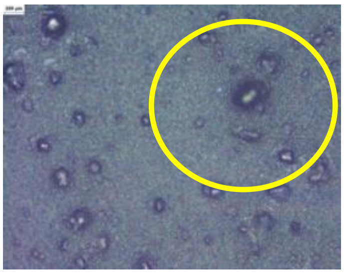
Figure 3.3 Morphological image of
(a) 20%, (b) 30%, (c) 40% and (d) 50% of filler loading

At 60 %, 70 % and 80 % of filler loadings, it were illustrated no outstanding differences between each other either in shape of particle or size of particle compared with the filler loading at 90 %. The ink layer had the presence of granular-like particle. In order become a conductive ink, the granular particle should contain a 3-D connection of conduction that led to the existence of particle necking [3].

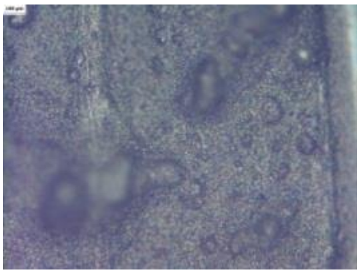
The necking growth provided a continuous connection and once the inter particle neck was produced, the granular-like particle became conductive although it was still porous [3-4]. All the results for 60 % to 80 % showed in Figure 3.4.



(a)



(b)



(c)

Figure 3.4 Granular-like particles in
(a) 60%, (b) 70% and (c) 80% of filler loading

At 90 % of filler loading, the dark spot in the morphological imaging represented the presence of silver nanoparticles while the rest is filled by the epoxy. Major change that could be noticed was the vanished barriers between particles [4-5]. This indicated that the ink layers had a close-packed structure where the particles created a strong bonding between each other. Once the silver nanoparticles were in contact between each other, the particles became more continuous rather than being in the shape of discrete and spherical, thus the contact area between particles became bigger.

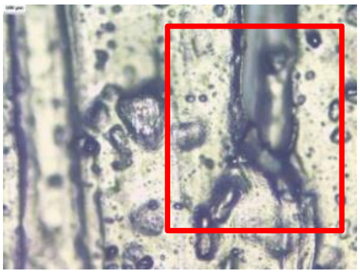


Figure 3.5 Continuous particles in 90% of filler loading

4. SUMMARY

This study was examined the sheet resistivity and morphological study on silver nanoparticles-filled epoxy conductive ink. The Four-Point probe was used to measure the sheet resistance value of the sample in ohms-per-square, the resistivity volume in ohms-cm and the thickness of sample, and light microscope was used in microscopy analysis.

From the results obtained from Four-Point probe measurement, only some percentage of filler loadings detected the presence of resistivity. The highest average resistivity of 369.63 Ω/sq was detected in 60 % of filler loading while the lowest of 0.06 Ω/sq was found in 90 % of filler loading, respectively. The characterization of silver nanoparticles-filled epoxy conductive ink in terms of sheet resistivity can be identified through the results obtained from the Four-Point probe.

Light microscope was used to visualize the morphological study of the silver nanoparticles-filled epoxy conductive. The presented results showed that ink loading with high percentage of silver nanoparticles had conductivity while low percentage had no conductivity. At low percentage, the microstructure image showed no appearance of dark spot element while for high percentage; the image showed the content of dark spot, respectively. The dark spot basically inversely proportional relationship with the sheet resistivity value.

REFERENCES

[1] Kim, D., Jeong, S., Moon, J., & Kang, K. (2006). Ink-jet printing of silver conductive tracks on flexible substrates. *Molecular Crystals and Liquid Crystals*, *459*(1), 45-325.

[2] Nash, C., Spiesschaert, Y., Amarandei, G., Stoeva, Z., Tomov, R. I., Tonchev, D., & Glowacki, B. A. (2015). A comparative study on the conductive properties of coated and printed silver layers on a paper substrate. *Journal of Electronic Materials*, 44(1), 497.

[3] Ghahremani, M., Babaei, M., & Latifi, M. (2016). Evaluating silver tracks conductivity on flexible surfaces. *Journal of Industrial Textiles*, 46(2), 530-548.

[4] Matsuhisa, N., Inoue, D., Zalar, P., Jin, H., Matsuba, Y., Itoh, A., ... & Someya, T. (2017). Printable elastic conductors by in situ formation of silver nanoparticles from silver flakes. *Nature materials*, 16(8), 834.

[5] Zulkarnain, M., Fadzil, M. A., Mariatti, M., & Azid, I. A. (2017). Effects of silver microparticles and nanoparticles on thermal and electrical characteristics of electrically conductive adhesives. *Journal of Electronic Materials*, 46(11), 6727-6735